

Performance of solvent-borne intumescent fire protective coating with Palm oil clinker as novel bio-filler on steel

S. A. S. Mustapa and N. H. Ramli Sulong*

Department of Civil Engineering, Faculty of Engineering, University of Malaya,
Lembah Pantai, 50603 Kuala Lumpur, Malaysia

E-mail: *hafizah_ramli@um.edu.my

Abstract. This research deals with contribution of hybrid fillers with palm oil clinker (POC) as a novel bio-filler in solvent-borne intumescent fire protective coating for steel. The hybrid fillers with POC were mixed in appropriate amount of additives and acrylic binder to produce the intumescent coatings. The intumescent coatings were characterized by using Bunsen burner test, surface spread of flame, thermogravimetric analysis, field emission scanning electron microscopy, static immersion and Instron micro tester equipment. Specimen with POC as a single filler has significantly enhanced the fire protection performances of the intumescent coating due to the high thermal stability of POC, where less than 10% of temperature different when compared to specimens with hybrid fillers. From the flame spread classification, class 1 is the best classification while Class 4 is the worst and considered high risk. All specimens was classified as class 1 since the final spread of flame was less than 165 mm. For hybrid fillers composition, specimen consist of POC/ $\text{Al}(\text{OH})_3/\text{TiO}_2$ has significantly improved the water resistance of the coating due to the low solubility of $\text{Al}(\text{OH})_3$ in water, while specimen contain of $\text{Mg}(\text{OH})_2$ had higher mechanical strength due to the strong bonding between the metal surface and acrylic binder/ $\text{Mg}(\text{OH})_2$ filler. It was found that coating with the incorporation of all hybrid fillers gives excellent fire protection performance with good thermal stability, water resistance and mechanical properties. It can be concluded that, the selection of appropriate composition of fillers and binder in intumescent coating was highly influence the intumescent coating performance.

1. Introduction

Steel starts to lose its strength and stiffness when temperature reached 550°C in fire incident, where collapse of steel structures may occur [1-2]. Intumescent fire retardant coatings was used as passive fire protection materials to protect the steel structures from collapse when exposed to high temperature [3]. It was applied to the steel structure for fire protection, which can save a thousand of precious life and assets if the building can last for longer period and extending time for evacuation. When exposed to a sufficiently high temperature, the intumescent coating forms a porous char that thermally insulates the steel substrate from heat and prevent it from reaching critical temperature [4-5]. Three flame-retardant additives are employed in the formulation of intumescent coatings, i.e. an acid source (ammonium polyphosphate, APP), a carbon source (pentaerythritol, PER) and a blowing agent (melamine, MEL) mixed with flame-retardant fillers and binder. The most commonly used flame retardant fillers are metal hydroxides. As the temperature rises, these inorganic fillers decompose endothermically and therefore absorb energy and release non-flammable molecules such as H_2O and/or CO_2 , which dilute combustible gases, and also promote the char formation of a protective ceramic or vitreous layer [6]. Unfortunately, this inorganic filler is expensive and will increase the production cost of intumescent coatings.



Therefore, there are several attempts in using by-product waste such as chicken eggshells (CES), rice husk and palm oil clinker (POC) as bio-fillers in intumescent coating which was believe can lower the production cost of intumescent coating.

From the previous research Yew et al. 2013, studied the influence of CES as bio-filler in intumescent coating [7]. Before CES can be used as a filler, it has to be cleaned thoroughly and dried at 90°C for 12 h in oven after the membrane was removed. The dried CES were mechanically trituated to a powder form and then milled at a milling speed of 280 rpm for 20 h to 40 h. It takes a lot of effort in processing the CES to obtain appropriate particle size before it can be used as filler compare to by-product waste such as palm oil clinker (POC) which can be used directly from the sources without going through any process and it is available in bulk quantities. Malaysia has to deal with a problem of by-product waste that is generated from palm oil processing as being the second largest country in the world that produce palm oil [8]. POC was produced in large quantities and treated as disposal waste. POC was produced after the burning of oil palm shell and palm oil fibre with 30:70 ratios at high temperature of 850°C in energy generating to run the plants [9]. Using POC as a bio-filler in intumescent coating is another way to lower the production cost as well as protecting the environment from the by-product waste. Many researchers have studied the effectiveness of intumescent coating based on their performance in fire retardancy, mechanical strength and water resistance [10-14]. This research focus on developing the best composition of intumescent fire protective coating using hybrid fillers with POC as a bio-filler on steel structures in the event of fire. The intumescent coatings was characterized based on fire protection performances, mechanical strength and water resistance.

2. Materials and methods

The intumescent coating was prepared using three flame retardant additives, i.e. ammonium polyphosphate (APP), pentaerythritol (PER) and melamine (MEL) in ratio of (2:1:1). The flame retardant additives was blended in acrylic binder of 45 wt. %. Then the mixture was added to four different hybrid fillers, i.e. palm oil clinker (POC), magnesium hydroxide [Mg(OH)₂], aluminium hydroxide [Al(OH)₃] and titanium dioxide (TiO₂). POC was taken from the Sri Ulu Langat Palm Oil Mill factory. The POC which looks like a gray porous stone with flaky and irregular shaped was crushed into required size. There are four specimens were prepared; one specimen are having POC as single filler and three specimens with hybrid fillers. The compositions of the intumescent coatings are presented in table 1. The composition of intumescent coatings were blended with a high-speed disperse mixer until completely homogenous. The mixture was coated on one-side of steel plate using brush and this step was repeated until dry film thickness of 1.5±0.2 mm was achieved. The thickness of coating layer was measured using a gauge Elcometer model A456. The coatings were considered ready for characterization when it is fully dried.

Table 1. The composition of intumescent coatings.

Specimen	SBP	SBPM	SBPA	SBPMA
Flame retardant additives:	37 : 45			
Acrylic binder (wt. %)				
POC	/	/	/	/
Fillers TiO ₂		/	/	/
Mg(OH) ₂		/		/
Al(OH) ₃			/	/

2.1. Thermogravimetric analysis (TGA)

TGA was carried out in the temperature range of 30-1000°C at the heating rate of 20°C/min under air flow using a TGA/SDTA851e model. This test was used to measure the weight change of the coating as a function of temperature while being heated at a constant rate.

2.2. Bunsen burner test

Bunsen burner test was carried out to characterize the char formation and determine the temperature development on the single-side coated steel plate of each coating. A coated plate was mounted vertically and exposed to high temperature of Bunsen burner about 1000°C for 1 hour. A thermocouple wire that is connected to a digital thermometer for temperature measurement was attached to the back side of the steel plate during the fire test. The temperature readings were taken every 1 min until the steel reach its critical temperature. Temperature of 400°C has been chosen as the failure temperature for steel structure to ensure higher level of safety and protection [6].

2.3. Surface spread of flame test

The surface spread of flame test was performed according to the procedure specified in the 'BS 476: Part 7' standard. The test involves measuring the lateral spread of flame over the surface of a specimen oriented in a vertical position and classifying the system based on the rate and extent of flame spread. The steel plate (885 mm × 270 mm × 2.3 mm) coated with intumescent coating (thickness: 1.5 ± 0.2 mm) was exposed to specific heating conditions during the test. The test specimen was mounted vertically and placed at a 90° angle from the radiation panel, and was exposed to a radiant panel over a duration of 10 min. Pilot flame was applied to the bottom corner of the specimen during the first minute of the test. The time required for the flame front to reach the reference marks on the specimen and the extent of flame spread were recorded over a period of 1 min 30 s as well as at the end of the test. The burning behaviour of the coating was also observed. The materials were classified according to the test performance, as shown in table 2. Class 1 is the best classification while Class 4 is the worst classification and is considered high risk.

Table 2. Flame spread classification.

Classification	Spread of flame at 1.5 min		Final spread of flame (10 min)	
	Limit (mm)	Tolerance for one specimen in sample (mm)	Limit (mm)	Tolerance for one specimen in sample (mm)
Class 1	165	25	165	25
Class 2	215	25	455	45
Class 3	265	25	710	75
Class 4	Exceeding the limits for class 3			

2.4. Field emission scanning electron microscopy (FESEM)

After the Bunsen burner test, a piece of char was cut from the centre of char layer for FESEM test in order to examine the surface morphology of the char layers. Low beam energy of 1 kV was used to observe the morphology of the char layer using the GEMINI® Based Field Emission SEM launched by ZEISS.

2.5. Static immersion test

Water resistance of thin films was evaluated using static immersion test. The intumescent coating films were immersed in distilled water at 25°C and were dried with a piece of paper towel to remove excess water then weight change was recorded. This step was repeated at a specific time intervals. Weight change was calculated based on equation (1).

$$\Delta W = \frac{W_e - W_o}{W_o} \times 100\% \quad (1)$$

where ΔW is water intake ratio of film (%), W_e is the weight of the film after water immersion (g) and W_o is the weight of the film before water immersion (g).

2.6. Adhesion strength test

The adhesion strength between the intumescent coating layer interfaces with steel substrate was determined by using the pull-off adhesion tester (PosiTest-AT-A Automatic, DeFelsko). The coating was applied on one side of a 50 mm × 50 mm × 2.6 mm steel plate to obtain a film thickness of 0.5 ± 0.05 mm. The flat face of a pull stub (20 mm dolly) is adhered to the coating using epoxy glue (thickness of 0.5 ± 0.05 mm). The force of peeled-off area of the samples were calculated and classified according to ASTM D4541 standard classification. Force was calculated by equation (2).

$$f_b = F/A \quad (2)$$

where f_b is the adhesion strength (MPa), F is the crack charge (N) and A is the sticking area (mm²).

3. Results and discussion

3.1. Thermal analysis of intumescent coatings

The TGA curves of intumescent coatings was presented in figure 1. The curves of the coatings were similar between 100°C to 250°C. After temperature higher than 250°C, the curves became slightly different from each other. The residual weight for specimen SBP, SBPM, SBPA and SBPMA at 750°C was 42.17 wt. %, 46.84 wt. %, 41.98 wt. % and 47.42 wt. %, respectively. The results show that the percentage different between specimen contain POC as single filler and specimens with hybrid fillers is less than 6%, indicate that POC alone significantly enhanced thermal stability of the intumescent coating. It can be explained based on the thermal stability of POC filler. TGA curve of the POC is shown in figure 2. After the temperature reached 500°C, the weight loss for POC is only about 2%. The high thermal stability of POC was attributed to the process of burning of oil palm shell and palm oil fibre at high temperature of 850°C during energy generating. For hybrid fillers composition, specimen SBPM containing POC/Mg(OH)₂ had 5% increase in residual weight which contribute to a better thermal stability compared to specimen SBPA containing POC/Al(OH)₃, which specifies that incorporation of Mg(OH)₂ significantly increased the thermal stability of the intumescent coating than Al(OH)₃. It was found that the incorporation of all hybrid fillers in specimen SBPMA gives the highest thermal stability to the intumescent coating which indicates that the best combination of all hybrid fillers with flame retardant additives and acrylic binder had improved anti-oxidation, thermal stability and fire protection performance of the intumescent coating [15].

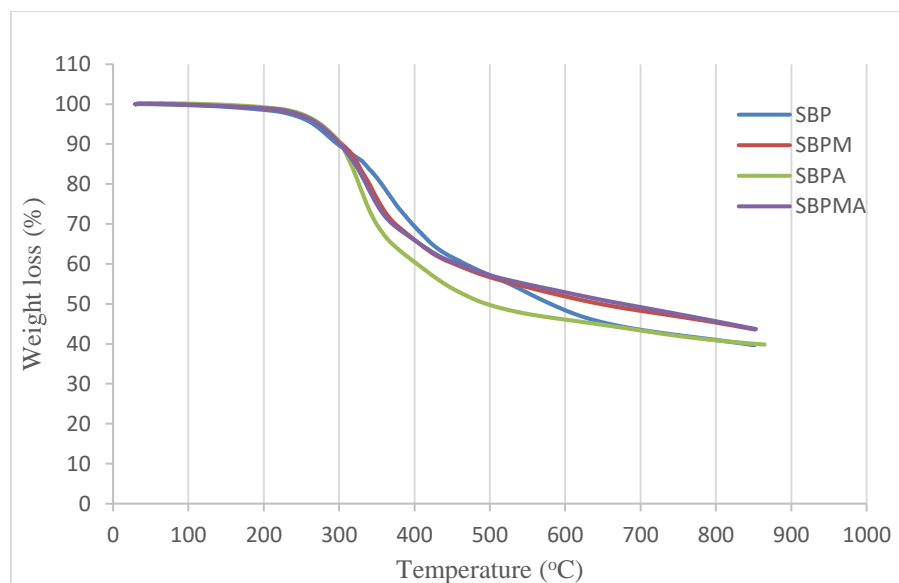


Figure 1. TGA curves of intumescent coatings.

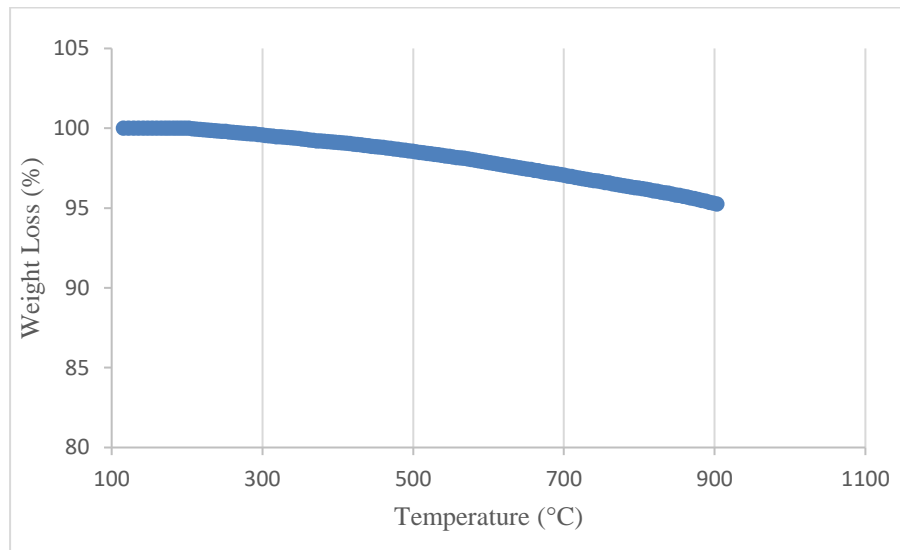


Figure 2. TGA curve of the POC.

3.2. Bunsen burner test

The temperature curves for specimens SBP, SBPM, SBPA and SBPMA are presented in figure 3. The curves for each coating during first 5 to 10 minutes had increased rapidly after exposed to fire. After about 30 minutes, the temperature reached an equilibrium value and almost unchanged. The equilibrium temperature and thickness of char layer was shown in table 3. Specimen SBP having POC as a single filler shows very effective fire protection performance of intumescent coating, where less than 10% of temperature different when compare to other samples with hybrid filler. It proved that, POC as a single filler significantly enhanced the fire protection performance of intumescent coating because of its high thermal stability. The equilibrium temperature of specimen SBPM was 4% lower than specimen SBPA due to the addition of $\text{Mg}(\text{OH})_2$ which indicates that addition of $\text{Mg}(\text{OH})_2$ slightly increase the fire protection performance of intumescent coating. Meanwhile, for specimen SBPMA contain all hybrid fillers was found to be optimum combination as it gives the lowest equilibrium temperature due to its effectives char protection that reduced the heat transfer to the substrate. The thicker the char layer leads to the lower equilibrium temperature which resulted in the better fire protection performance. Figure 4 show the images of intumescent coating specimen before and after Bunsen burner test.

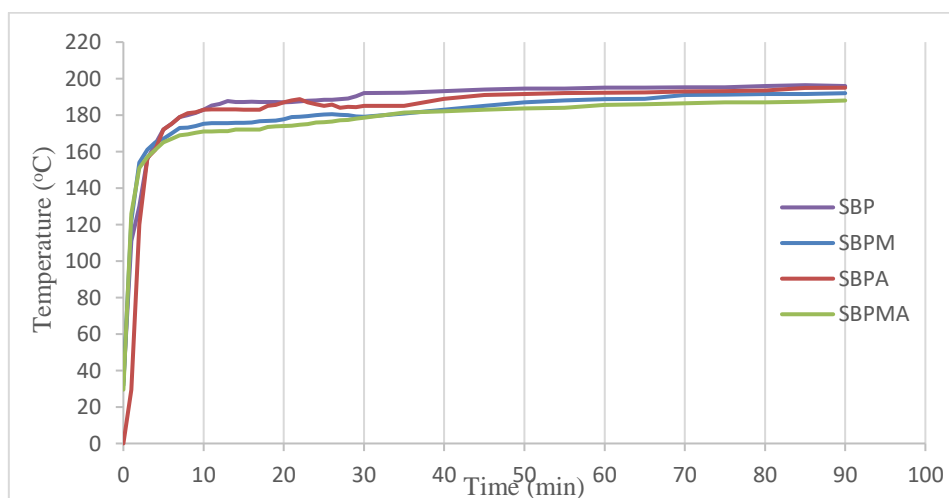
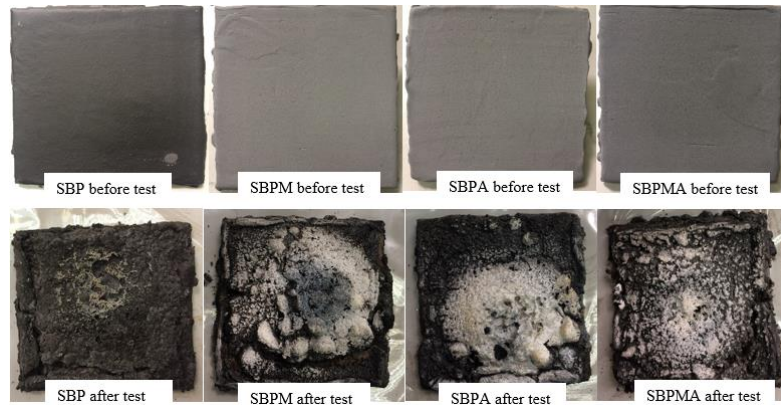


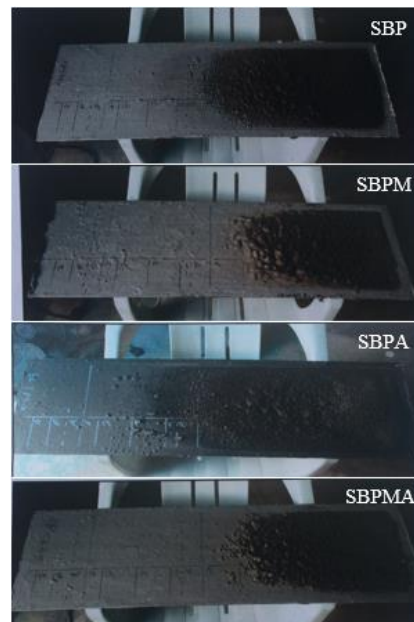
Figure 3. The time-temperature curves of intumescent coatings.

Table 3. Char thickness and equilibrium temperature of intumescent coatings.

Specimen	Equilibrium temperature (°C)	Thickness of char layer (mm)
SBP	187.7	17.21
SBPM	175.3	19.17
SBPA	183.1	17.53
SBPMA	172.0	20.02

**Figure 4.** The image of intumescent coatings before and after Bunsen burner test.

3.3. Surface spread of flame test

**Figure 5.** Specimen SBP, SBPM, SBPA and SBPMA after surface spread of flame test.

The surface spread of flame test was performed according to the procedure specified in the ‘BS 476: Part 7’ standard. The test involves measuring the lateral spread of flame over the surface of a specimen oriented in a vertical position and classifying the system based on the rate and extent of flame spread. The results for the test specimens are shown in table 4. From the flame spread classification, class 1 is

the best classification while Class 4 is the worst classification and is considered high risk. From the results, all specimens was classified as class 1 since the final spread of flame was less than 165 + 25 mm. Specimen SBP and SBPM had 165 mm surface spread of flame at 59 s and 55 s, respectively. Meanwhile, specimen SBPA with addition of $\text{Al}(\text{OH})_3$ had 190 mm surface spread of flame at 1 min. Specimen SBPMA with the best combination of hybrid fillers with POC had 0 mm surface spread of flame compare to other specimen, proved that the best combination of all hybrid fillers with POC resulting in a significant improvement in lowering the rate and extend of flame spread. The char formation after the test are shown in figure 5.

Table 4. Results of surface spread of flame test.

Specimen No.	SBP	SBPM	SBPA	SBPMA
Spread of flame at 1 1/2 minutes (mm)	165	165	190	0
Distance (mm)	Time of spread of flame to indicated distance (min.s)			
75	0.56	0.34	0.47	
165	0.59	0.55	0.58	
190			1.00	
215				
240				
265				
290				
375				
455				
500				
525				
600				
675				
710				
750				
785				
825				
865				
Time of maximum spread of flame (min.s)	0.59	0.55	1.00	-
Distance of maximum spread of flame (mm)	165	165	190	0
Classification	Class-1	Class-1	Class-1	Class-1

3.4. Morphology of intumescent char layer.

The surface morphologies of char layer for intumescent coatings are shown in figure 6. It was believed that the physical structure of the char layer has significant effect to the fire protection performance of coating [16]. The high porosity surface structure was clearly observed for specimen SBP and SBPA which led to the reduction of fire protection because of the heat may penetrate to steel substrate through the char structure that is high porosity and nonuniform. Meanwhile, the char layer for specimen SBPMA had dense and uniform foam structure which could prevent the heat transfer to the steel substrate and improved fire protection efficiency. Hence, from this result it proved that specimen SBPMA with the best combination of hybrid fillers with POC resulting in homogeneous and dense foam structure had increased the fire protection performance compared to other samples.

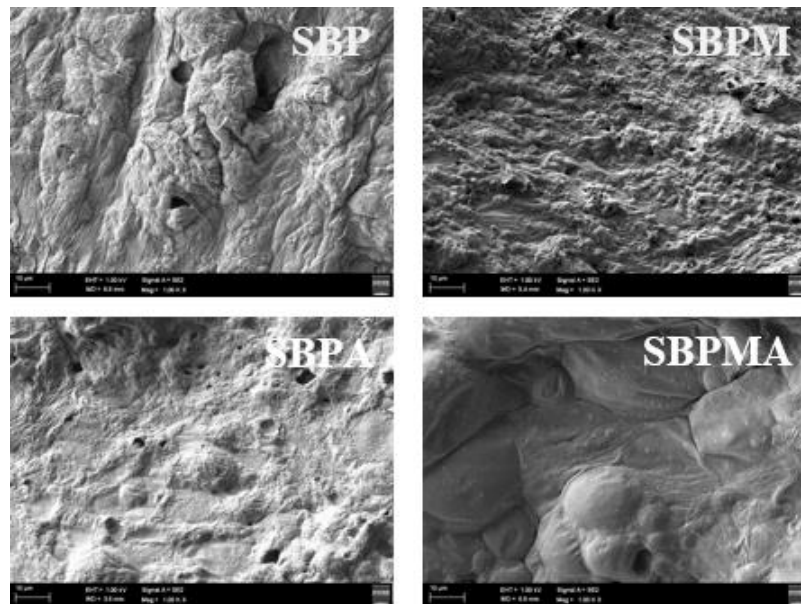


Figure 6. The surface morphologies of char layer of intumescent coatings.

3.5. Static immersion test

The weight change rate curves for specimens SBP, SBPM, SBPA and SBPMA are shown in figure 7. The experimental results show that the weight of specimen SBP was gradually increased due to the permeation process which means water could infiltrate into high porosity structure of the coating which led to the weight gain of the sample. Moreover, this situation has also occurred due to high solubility of POC in water. Moreover, the weight of coatings SBPM and SBPMA was decreased due to the migration process. As reported from previous study, the migration process may occur when some hydrophilic fire retardant additives dissolved in water during the migration process, hence reduce the weight of the coating [17]. For coating SBPA with contribution of $\text{Al}(\text{OH})_3$ as filler, it seems that both migration and permeation process was occurred. The permeation of water and dissolution of fire retardant ingredients could be slow down with the incorporation of $\text{Al}(\text{OH})_3$ in the intumescent coating due to its low solubility in water, which resulting in the improvement of water resistance of the coatings [18].

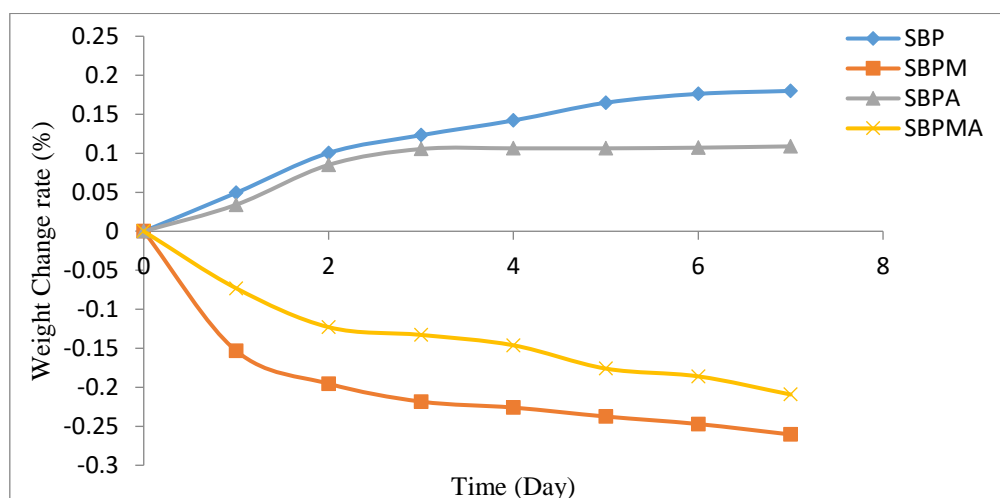


Figure 7. The weight change rate curves of intumescent coatings.

3.6. Adhesion strength test

The bonding strength of intumescent coating was investigated using the Instron microtester. The adhesion strength of specimens SBP, SBPM, SBPA and SBPMA was 4.39, 4.68, 4.03 and 5.21 MPa, respectively as in table 5. Specimen SBP with POC alone, shows better adhesion strength when compared to specimen SBPA which consist of $\text{Al}(\text{OH})_3$ filler. Meanwhile, the addition of $\text{Mg}(\text{OH})_2$ to the specimen SBPM showed improvement compared to other specimens due to the strong bonding strength between the metal surface and acrylic binder/ $\text{Mg}(\text{OH})_2$ filler interface adhesion for effective stress transfer [19]. Meanwhile, the significant improvement in the adhesion strength for specimen SBPMA, proved that this coating contained optimal combination of POC/ $\text{Mg}(\text{OH})_2/\text{Al}(\text{OH})_3$ that led to the highest bonding strength. It can be concluded that the coating with addition of POC and $\text{Mg}(\text{OH})_2$ had improved the adhesion strength of the coating and appropriate combination of hybrid fillers strongly influence the adhesion strength of intumescent coating.

Table 5. Adhesion strength of intumescent coatings.

Specimen	Crack charge, F (N)	Adhesion strength, fb (MPa)
SBP	1378.46	4.39
SBPM	1469.52	4.68
SBPA	1265.42	4.03
SBPMA	1635.94	5.21

4. Conclusion

In this research, different formulation of intumescent coatings was formulated using hybrid fillers POC/ $\text{TiO}_2/\text{Mg}(\text{OH})_2/\text{Al}(\text{OH})_3$. Specimen SBP having POC as a single filler improved the fire protection performance and thermal stability of the intumescent coatings. From the result of Bunsen burner test, the temperature different between specimens contain single POC and hybrid fillers is less than 10%, indicated that the use of POC as a single filler is very effective in fire protection performance of the intumescent coating due to its high thermal stability. From the flame spread classification, all specimens was classified as class 1 as prescribed by the BS 476 part 7, since the final spread of flame was less than 165 mm. The combination of hybrid fillers with $\text{Al}(\text{OH})_3$ to flame-retardant additives and acrylic binder could slow down the permeation of water and dissolution of fire retardant ingredients due to its low solubility in water, which led to an improvement in the water resistance of the coating SBPA. Furthermore, specimen SBPM shows the highest bonding strength due the addition of $\text{Mg}(\text{OH})_2$ in the coating led to its effective interface adhesion between the coating and metal surface. Specimen SBPMA consist of the best combination of POC with all hybrid fillers shows an excellent fire protection, which produced the highest thickness of char layer, good bonding strength and water resistance of intumescent coating. From this research, it can be concluded that the appropriate combination of hybrid fillers with POC has highly influenced the fire protection performance, water resistance and adhesion strength of the intumescent coatings. Moreover, the usage of POC in intumescent coating can contribute in preserving the environment from industrial waste as well as reduced the production cost by minimizing the usage of synthetic fillers in intumescent coatings.

Acknowledgements

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