Fire-Resistant Properties of Modified Epoxy Based Intumescent Fire-Retardant Coating: Hybridizing of Oyster Shell Powder with Glass Frit

Y X Lee\(^*\), F Ahmad\(^1\), S Kakooei\(^1\), Y Azmi\(^1\), and S Kabir\(^1\)

Mechanical Engineering Department, Universiti Teknologi PETRONAS Bandar Seri Iskandar, 32610, Perak, Malaysia.

\(^*\)Corresponding author: yuan_20001965@utp.edu.my

Abstract. Fire retardant coatings play vital role in safety of construction nowadays, to delay the fire propagation and provide more time for evacuation. The current research work aimed to study the use of modified siloxane epoxy binder to develop intumescent coating. Polyamide amine was used as a hardener. Three different sets of formulations were developed by using three different fillers, namely the oyster shell powder (OSP), glass frit (GF) and combination of both oyster shell powder and glass frit (OG). All three set of formulation also includes the basic ingredients of intumescent coating. These samples were used to study the synergistic effects of fillers on thermal performance of the coating as well tested for char expansion, heat shielding, char morphology and composition. Fire resistant testing was conducted by using a Bunsen Burner and GF samples had found to have minimum substrate temperature of 175.3°C. The char morphology was analysed via Scanning Electron Microscope (SEM) which confirmed the adhesion between the matrix with fillers. Furnace test was carried out to investigate the char expansion of OSP/GF/OG with the modified siloxane epoxy composition and the maximum expansion was OSP 1% with intumescent factor of 7.78. XRD was conducted to evaluate the residual compounds in the char and FTIR was utilized to analyse the functional group where O-H, C-N, O=C=O and C=C bonds were found in the degradation compounds in the char residual of the coatings.

1. Introduction

The inclination usage of durable and environmentally friendly materials with wide range of application in global industry boosts the development of composites [1]. Recent development in polymer composites targeted biowaste as reinforcement to be added into polymer to improve the properties of polymer. Researchers believe that some of the biowaste containing high amount of minerals that can be useful as a reinforcement. Utilization of biowaste reduces the pollution caused by waste dumping and it also initiates a new way to enhance the current technology of waste management [2].

Intumescent fire-retardant coating is often being stressed out in the construction industry [3]. Mechanism of fire retardant can be divided into three categories: condensed phase mechanism, gas phase mechanism and combination of both mechanisms. The condensed phase mechanism involves the decreasing rate of degradation of coating material and modification of the mechanism of degradation to produce less flammable volatile products. Meanwhile, the gas phase mechanism involves the releasing...
of non-flammable compounds evolved by additive on heating which dilutes the flammable volatile product feeding the flame [1].

Polymer such as polypropylene, polyurethane and epoxy often become polymer intumescent coating. Polydimethylsiloxane (PDMS) offers heat stability, cold flexibility and chemical resistance which are vital for various applications, especially for cable applications [4]. Pyrolysis of PDMS generates amorphous silica residual, forming a protection barrier which provides a shielding effect from the heat by means of delaying or preventing the heat transfer to the polymer [5]. Besides, researchers believe epoxy are the most versatile thermosetting polymers which offering appropriate properties in terms of chemical, corrosion, adhesion as well mechanical [6]. Modified epoxy resins by mixing PDMS with epoxy believed to offer great dimensional stability, mechanical properties and chemical properties, which are an excellent material for intumescent coating.

Oyster shell powder and glass frit had been targeted to become a filler to be added into epoxy resin. Oyster shell is identified as waste product from mariculture [7]. It has become a major problem in coastal areas, especially in south east Korea. According to Yoon et al. [8], oyster shell comprises up to 95% of calcium carbonate and some other minerals and substances. Calcium carbonate will release a great amount of carbon dioxide upon decomposition. Researches, which compared calcium carbonate extracted from oyster shell powder with commercial calcium carbonate, have shown both material exhibits have similar properties [9]. Rehman Sheh et al. [10] stated that oyster shell powder used for reinforcement as a filler in polypropylene had successfully increased fire retardant of polypropylene. Carbon dioxide is considered a non-flammable gas, which will dilute the temperature of the flame during combustion. Glass frit containing a high amount of silica will form char during combustion. The formation of char will act as a barrier to prevent heat from reaching the coated material [11].

Most of the studies focus on the combination of thermosetting and thermoplastic polymer with other biowaste such as rice husk ash. No study has been reported on combination of epoxy resin with oyster shell powder and glass frit. This project aims to produce an intumescent fire-retarding coating material to synthesize siloxane-based epoxy resin for development of fire-retardant intumescent coating using oyster shell powder and glass frit. The performance of coating for building elements is characterized to impart flame resistance performance.

2. Research Methodology
The materials used in this study were PDMS and epoxy to serve as matrix. Phosphoric acid was used as the catalyst while polyamine act as the hardener. The binding agent used in this study was Bisphenol A. The filler, namely GF obtained from market and processed by utilize facility in university whereby the OSP were obtained from Xi’an Biotechnology. The basic ingredient incorporated in the intumescent coating were melamine, ammonium polyphosphate, boric acid and expandable graphite.

2.1. Glass Frit Powder Preparation
The glass bottles were break into small pieces by using hammer. The smaller pieces of the waste glass were then undergoing grinding process using grinding machine. The process took 1 minutes to acquire powder. The waste glass powder was then sieved using sieving machine and retained at 212 µm sieve.

2.2. Coating Fabrication
Epoxy weighted according to table 1 is heated at 60°C using a hotplate and stirred with 40 rpm for 30 minutes by using a stirrer. The heating and stirring process is continued for 10 minutes after PDMS is added into the epoxy. The bisphenol A is then added into the epoxy resin and stirred for 10 minutes. 6 to 7 drops of phosphoric acid are added in the epoxy resin. The rotational speed of stirrer is increased to 70 rpm for 30 minutes.

All coating formulation is mixed and grind for 1 minute using mixer grinder except for expandable graphite (EG). The EG is then mixed manually with the grinded mixture. The mixture is mixed with epoxy resin by using stirrer for 15 minutes. The hardener is added into the mixture. The rotational speed
of stirrer is then reduced to 40 rpm for 5 minutes. The mixture is then applied to steel plates. It was then left for 2 days for drying.

Table 1: Control weightage of intumescent coating

| Formulation no. | OSP (wt.%) | GF (wt.%) | APP (wt.%) | MEL (wt.%) | Boric Acid (wt.%) | EG (wt.%) | Epoxy (wt.%) | PDMS (wt.%) | Hardener (wt.%) |
|-----------------|------------|-----------|------------|------------|-------------------|----------|-------------|-------------|----------------|
| OSP 1%          | 1          | -         | 11.36      | 5.5        | 11                | 5.5      | 30.63       | 13.13       | 21.88          |
| OSP 2%          | 2          | -         | 11.36      | 5.5        | 11                | 5.5      | 30.17       | 12.93       | 21.55          |
| GF 1%           | -          | 1         | 11.36      | 5.5        | 11                | 5.5      | 30.63       | 13.13       | 21.88          |
| GF 2%           | -          | 2         | 11.36      | 5.5        | 11                | 5.5      | 30.17       | 12.93       | 21.55          |
| OG 1%           | 0.5        | 0.5       | 11.36      | 5.5        | 11                | 5.5      | 30.63       | 13.13       | 21.88          |
| OG 2%           | 1          | 1         | 11.36      | 5.5        | 11                | 5.5      | 30.17       | 12.93       | 21.55          |

3. Characterization

3.1. Fire Test
The fire test will examine the ease of ignition and ability of fire endurance of material under certain temperature according to standard ASTM E119. Flame spread of material also can be examined to investigate burning rate of material across material surface. A portable Bunsen burner was used to burn the coating applied on the steel plate. The distance between the Bunsen burner and the coated steel plate is 7cm. Three thermocouples are attached to the back of steel plate. The thermocouple is then connected to Anarittsu Data logger, Input Channel 6 Model AM 8000K with Anarittsu software. The temperature of the steel plate was recorded for every 30 seconds at an interval of 1 min.

3.2. Furnace Test
Furnace test is also a type of fire resistance test, which is designed to simulate particular fire threats on structures. Furnace test in this project was used box furnace (Carbolite Gero RWF 1100) to examine the char expansion rate, which is a mechanism for increasing the performance of char to serve as a barrier. The heating rate of the furnace was set at 20°C/min for 2 hours. The char was measured by using digital vernier caliper and average values were recorded. The thickness of samples was measured and recorded for before and after. Intumescent factor (IF) was calculated from the thickness obtain.

\[
\text{Intumescent Factor (IF) = } \frac{(d_2 - d_0)}{(d_1 - d_0)} \tag{1}
\]

where \(d_2\) = expanded char thickness; \(d_1\) = coating thickness; and \(d_0\) = steel plate thickness.

3.3. Scanning Electron Microscope
Scanning electron microscope (SEM) generates a variety of signals on a material’s surface in a sample by using a focused beam of high energy electrons. The signals will reveal information about the sample including external morphology, chemical composition, structure and orientation of sample. SEM is used to evaluate char morphology of the sample after fire test.

3.4. X-Ray Diffraction (XRD)
X-Ray Diffraction is a frequent used non-destructive test to analyze the crystalline materials. In this project the scan range of XRD is set from 10° to 90° with step size 0.01. The results plotted in graphs is interpret using software HighPro Plus.
3.5. *Fourier-Transform Infrared Spectroscopy (FTIR)*
FTIR is an analytical technique used to identify organic, polymeric and inorganic materials. Infrared is used in FTIR to scan test samples to observe the chemical properties of the samples in the range of 4000 cm\(^{-1}\) to 400 cm\(^{-1}\).

4. **Results and Discussion**

4.1. *Heating Shielding*

The substrate temperature for each formulation was plotted after the fire test results were obtained as shown in figure 1. From figure 1, the rapid increase of temperature in first 10 minutes of the fire test due to formation of char was yet to take place. The graphs reach their peak and temperature of substrate gradually decrease due to the formation of char initiated and release of non-flammable gas such as carbon dioxide to dilute the temperature of the flame.

Comparison had been made between 3 fillers; glass frit is found to have the best performance in retarding the heat energy transmission. Sample GF 1% with final temperature 175.3°C has the best performance among other fillers and followed by sample OG 1% and GF 2% with approximately 177°C. This result indicates glass frit performs well in fire retarding properties. We can also observe that oyster shell powder has the least performance among all three fillers. This result may be due to the calcium carbonate which only contribute carbon dioxide where glass frit form silica when decomposed. Silica exists to prevent heat from reaching substrate whereby carbon dioxide dilutes the temperature of the flame while release to surrounding. Other than that, from the plotted graph, we can obtain that combination of oyster shell powder with glass frit able to reduce the peak of temperature due to quick formation of char and release of non-flammable gas.

![Figure 1: Fire test result](image)

4.2. *Char Expansion*

All the samples were sent for furnace test. Table 2 shows the intumescent factor obtained for studied formulations. OG samples showed the least intumescent factor while oyster shell powder shows the best intumescent factor. Among all the sample, modified epoxy resin intumescent coating with 1% of OSP filler showed the highest intumescent factor of 7.78 followed by OSP 2% with 7.06 and GF 2% with 6.84. This result may due to the decomposition of calcium carbonate in OSP samples which contribute carbon dioxide which serve as blowing agent to expand char effectively whereas glass frit only form silica when decompose to serve as physical barrier.
Table 2: Thickness and intumescent coating factor of samples

| Formulation no. | Steel Plate Thickness (mm) | Coating Thickness (mm) | Expanded Char Thickness (mm) | Intumescent Factor |
|-----------------|---------------------------|------------------------|-------------------------------|-------------------|
| OSP 1%          | 1.5                       | 4.52                   | 25.01                         | 7.78              |
| OSP 2%          | 1.5                       | 3.35                   | 14.56                         | 7.06              |
| GF 1%           | 1.5                       | 5.00                   | 25.41                         | 6.83              |
| GF 2%           | 1.5                       | 4.98                   | 25.32                         | 6.84              |
| OG 1%           | 1.5                       | 5.32                   | 25.65                         | 6.32              |
| OG 2%           | 1.5                       | 5.36                   | 24.89                         | 6.06              |

4.3. Char Morphology

Multiple structures consisting of micro- and nano-scale particles were observed in the low-magnified SEM image. Figure 2 showed the char of the samples which the expandable graphite expands after combustion. From figure 2(a) and figure 2(b), there were void gaps between the structure which interfere the fire-retardant properties of the samples [13]. This result also proven the factor that temperature of OSP is higher than other 2 fillers during fire tests. Both GF 1% and GF 2% showed better adhesion compare to OSP as less voids were found [14]. Bubbles were found in figure 2(c) and figure 2(d) due to the emission of N₂, ammonia and CO₂ gases. The bubbles formed improved fire-retardant properties as it increases the difficulty of the heat from reaching the substrate. From figure 2(e) and figure 2(f) we found OG samples showed less adhesion compare to GF but better adhesion than OSP where few voids gaps can be observed on the microstructure of OG.
Figure 2: Microstructure of char (100µm) (a) OSP 1%, (b) OSP 2%, (c) GF 1%, (d) GF 2%, (e) OG 1%, (f) OG 2%

4.4. Analysis of Char Composition

The XRD results were plotted in graphs and interpret using software HighPro Plus. For the formulations for all samples, the major peaks around $2\theta = 24^\circ, 40^\circ, 48.6^\circ$ represent the boron phosphate. The boron phosphate formed due to the reaction between boron acid with phosphoric acid [15]. Based on the Figure 3(a), the highest peak of $2\theta = 27^\circ$ and other major peaks at $2\theta = 44.6^\circ, 54.8^\circ$ represent the carbon element. This result may due to the decomposition of calcium carbonate contain in OSP. Through data interpretation using software, we obtain that for OSP 1% contain 56% of carbon and 44% of boron phosphate whereas OSP 2% contain 61% of carbon and 39% of boron phosphate. From figure 3(b), major peaks at $2\theta = 14.9^\circ, 26.5^\circ, 27.8^\circ$ represent the silicon oxide. This result indicates the presents of silica in glass frit. The data shows the 59% of boron phosphate and 41% of silicon oxide in GF 1% whereas GF 2% contain 33% of boron phosphate and 67% of silicon oxide. Based on the graph 3(c), the major peaks at $2\theta = 14.7^\circ, 26.5^\circ, 27.9^\circ$ shows the presents of silicon oxide. The result of OG is similar to GF as OG is the combination of OSP and GF.
4.5. Analysis of Functional Group of Char

The char of samples is characterized by FTIR. These samples showed similar properties as the same formulation of the intumescent coating was used. Based on the Figure 4 and with the aid of FTIR table, we can analyze that at the wavelength range of 3040 cm\(^{-1}\) to 3300 cm\(^{-1}\), we obtained wide peak absorption of alcoholic groups which the O-H bond stretching [16]. At the range of 2300 cm\(^{-1}\) to 2380 cm\(^{-1}\) wavelength, we obtained the carbon dioxide bond stretching in a small wide peak. We obtained that O-H bond bending which might represent the alcohol at the range of 1320 cm\(^{-1}\) to 1480 cm\(^{-1}\). Whereas at the range of 1000 cm\(^{-1}\) to 1200 cm\(^{-1}\), we confirmed the C-N bond stretching, which indicates the presents of amine. Lastly, at the range of 800 cm\(^{-1}\) to 960 cm\(^{-1}\), we obtained the bending of C=C bond.

Figure 3: XRD spectra of (a) OSP samples, (b) GF samples, (c) OG samples
5. Conclusion
The incorporation of oyster shell powder and glass frit incorporate with modified siloxane-based epoxy, either alone or together, improves fire retardant properties of the modified siloxane-based epoxy. The highest intumescent factor obtained for OSP, GF and OG samples were 7.78, 6.84 and 6.32 respectively, indicating the OSP samples were excellent in expanding the char. Minimum backside temperature of the substrate obtained was 175.3°C for GF samples, 194.6°C for OSP samples and 177.5°C for GF samples from the lab scale jet fire test. Among all three types of samples, GF samples showed the best performance in enhancing fire retardant properties. GF samples were found to decrease the temperature of substrate gradually after the char formation took place. XRD confirmed the presence of boron phosphate in all samples which the main source of char formation. Carbon elements were found in coating with filler of oyster shell powder due to decomposition of calcium carbonate. XRD also confirmed the presence of silicon oxide in the coating with glass frit, which are found to contribute effectively to fire retardant. FTIR data shows the bonds O-H, C-N, O=C=O and C=C bonds presence in the samples indicates the presence of amorphous carbon which comes from amine and graphite functional group, the existence of water and contribution of calcium carbonate and silica towards char formation. The SEM confirmed the good adhesion of the filler with modified siloxane epoxy with GF composition which had least void gaps. OG samples were successful in reducing the peak of the temperature but weakens the adhesion of the coating which confirmed through analysis of char morphology.

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