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THERMAL PERFORMANCE OF GLASS FIBER REINFORCED INTUMESCENT FIRE RETARDANT COATING FOR STRUCTURAL APPLICATIONS

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The results of influence of glass fiber addition into the basic intumescent coating formulation towards the enhancement of its thermal insulation properties are presented. The intumescent coatings were formulated from expandable graphite, ammonium polyphosphate, melamine, boric acid, bisphenol A epoxy resin BE-188, polyamide amine H-2310 hardener and fiberglass (FG) of length 3.0 mm. Eight intumescent formulations were developed and the samples were tested for their fire performance by burning them at 450ºC, 650ºC and 850ºC in the furnace for two hours. The effects of each fire test at different temperatures; low and high temperature were evaluated. Scanning Electron Microscope, X-Ray Diffraction technique and Thermo Gravimetric Analysis were conducted on the samples to study the morphology, the chemical components of char and the residual weight of the coatings. The formulation, FG08 containing 7.0 wt% glass fiber provided better results with enhanced thermal insulation properties of the coatings.

Keywords: component,intumescent coating, expandable graphite, fiber glass

INTRODUCTION

The use of fire-retardant coatings is one of the easiest, oldest and most efficient ways to protect steel substrates against fire [1, 2]. It is important to protect materials against fire in the construction and petrochemical industries to ensure safe evacuation of people from the building before the structural steel starts to deteriorate [3] when exposed to temperature above 450°C. It does not change the basic properties of the material (e.g. mechanical properties), can be easily processed and applied on several materials including metallic, polymers, textiles and wood [4].

Intumescent is defined as the swelling of certain substances when heated. Intumescent coatings form an expanded multicellular layer upon heating; namely char, which acts as thermal barrier that effectively protects the substrate against rapid increase of temperature and thereby maintaining the structural integrity of the building [5]. The physical structure of the charring layer play[2]s a very important role in the performance of flame retardant. Formation of homogeneous high volume of residual char of suitable thickness ensures longer fire-endurance time and better performance of the flame retardant coating. In recent years, price efficiencies and improvements in technology have created a situation for intumescent coatings to dominate the structural fire protection market [6-8].

Several studies have demonstrated the use of filler and binder as reinforcing agent that helped to increase the efficiency of the

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intumescent coatings in terms of providing longer fire protection to the structural steel. Smaller number of studies focused on the effect of using fiberglass to increase the thermal insulation properties of the intumescent coatings. Fiberglass has also used as reinforcement of the char strength. It helps to maintain the char integrity and provides higher mechanical resistance of the charring element. In terms of fire safety, fiberglass insulation is naturally noncombustible as it is produced from sand and recycled glass [9, 10].

The objective of this study was to investigate the thermal insulation properties of intumescent coating with varying amount of fiber glass added into the basic intumescent formulations. The optimum intumescent formulation with fibreglass, which provides the best thermal insulation properties against fire, was determined. The study on the thermal insulation property of the intumescent coating will allow determination of exact temperature at which the charring of the mixture begins.

MATERIALS AND METHOD

Materials

Ammonium polyphosphate (APP- Exolit AP422) containing 20% phosphorus used as acid source. Bisphenol A epoxy resin BE-188 (BPA) used as a binder with ACR Hardener H-2310 polyamide amine also known as tetraethylene tetramine (TETA). Melamine (MEL) used as blowing agent and boric acid (BA) as flame retardant additive. Short fiberglass (FG) of length 3.0 mm was used.

Preparation of Intumescent Formulations

Expandable graphite (EG) used as the carbon source was prepared by grinding and sieving the graphite powder into smaller particle size of 300µm. A mixture of concentrated sulfuric acid (98%), acetic acid (37.5%), (150g), graphite powder (75g) and potassium permanganate (5.25g) were stirred at room temperature for 1h. The treated graphite was filtered, washed with distilled water until pH level was close to 6-7 and dried at 100-110°C in the oven for approximately 4h.

APP, MEL and BA were weighed and grinded into smaller particles to prevent the formation of bubbles in the coating. Bisphenol A epoxy resin BE-188 (BPA) and hardener was weighed and mixed together in the Ultra Turrax mixer to achieve a homogenous mixture. This was followed by addition of expandable graphite and fiberglass into the mixture and stirred well until uniform dispersion was achieved. The coatings were then applied on 3.5 mm thick steel plates of dimensions 15 x 50 mm^2 and were left for curing at room temperature for 2 weeks. Eight formulations of the intumescent coating developed in this study are shown in Table 1.

Table 1: *Weight percentage of intumescent ingredients.*

Intumescent formulations	**Ingredients (wt. %)**
FG01	*APP = 11.1, EG = 5.5, MEL = 5.5, BA = 11.1, Epoxy Resin = 66.8*
FG02	*IF1 + 1 Fiber Glass*
FG03	*IF1 + 2 Fiber Glass*
FG04	*IF1 + 3 Fiber Glass*
FG05	*IF1 + 4 Fiber Glass*
FG06	*IF1 + 5 Fiber Glass*
FG07	*IF1 + 6 Fiber Glass*
FG08	*IF1 + 7 Fiber Glass*

Analysis and Characterization

The intumescent coating samples were burnt at three different temperatures; 450ºC, 650ºC and 850ºC for two hours using Carbolite Electric Furnace.

A Bunsen burner was used to fire the intumescent samples according to the UL-94

standard. In every test, the coated steel was wired with a digital thermocouple to record temperature of the steel substrate. The temperature versus time measurements was recorded using an electric data logger. The temperature of the steel plate was measured for 60 minutes at an interval of 1 minute. The charring layer and the morphological structures of the inside and outside of char were observed and analyzed using Carl Ziess SUPRA V55.

The composition of the residual char of intumescent coating was analyzed by XRD and measurements were performed on a Diffractometer Bruker AXS D8 Advance, Germany using Cu Kα radiation and a nickel filter (k = 0.150595 nm) in the range ($10 < 2\theta < 90$).

The residual weight of intumescent coatings was analyzed using TGA. Thermogravimetric analysis of samples (approximately 10mg) was carried out at 10°C/min under N_2 over the whole range of temperature (50°C–800°C) using Perkin-Elmer TGA Q50.

RESULTS AND DISCUSSIONS

Char Expansion Test

Heating at 450 ºC and 650ºC

The intumescent coating sample, FG07 showed the highest expansion followed by samples FG06 and FG08. After the fire test, the coatings swelled and expanded into charring elements that protected the substrate steel from severe fire. The char had a very rough surface with large cracks. The microstructure of samples FG07 and FG08 were examined using SEM. Figure1 (a,b) shows the burnt samples of coating FG07 and FG08 at 650ºC. Figure1 (c) shows the graph of expansion ratio shown by each sample burnt at 450ºC and 650ºC.

Heating at 850ºC

White powder (ashes) was obtained after burning the coating in furnace at high temperature i.e. 850ºC. The ashes were formed due to the high fire temperature inside the furnace. Figure 2 shows the burnt intumescent coating samples of FG07 and FG08. Glass fibers are not susceptible to oxidize, but began to soften around temperatures of 650°C to 970°C and melt above 1225°C.

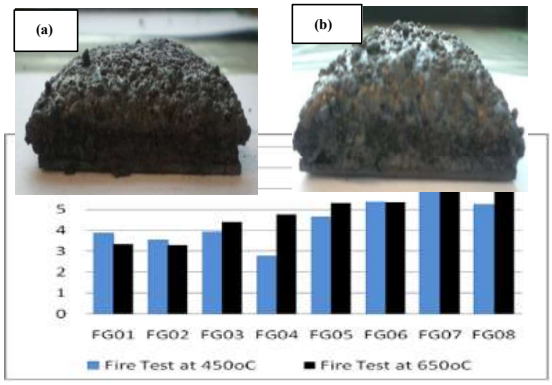

Figure 1: *(a,b) Char obtained after 650ºC for FG07 and FG08, (c) Expansion ratio of coating burnt at 450ºC and 650ºC.*

Figure 2: *Char of FG07 (left) and FG08 (right) after fire test at 850ºC.*

Thermal Insulation of Coating

The thermal properties of the intumescent coating with and without fiberglass were compared and shown in Figure 3 (a). The coating without fiberglass was observed to reach the highest back steel temperature of 367ºC while the coating FG04, FG05 and FG06 had 346, 329 and 278ºC after 60 minutes fire test, respectively. The coating FG07 and FG08 with 6.0 wt% and 7.0 wt% of glass fiber recorded the lowest temperature of substrate i.e. 217°C and 189°C after 60 minutes exposure to fire.

Initially the temperature of FG07 and FG08 increased rapidly within first 10-18 minutes of fire test. It was reached to 160°C after ten minutes and 185°C after another 8 minutes of fire test. After the formation of carbonaceous char on the substrate, the temperature was gradually increased. It was concluded that the use of glass fiber in the intumescent coating formulations helped to enhance the thermal insulation properties of the coating, prolong the lifetime of steel structures and imparted the strength of the char.

Thermogravimetric Analysis (TGA)

TGA curves of sample FG01, FG07 and FG08 had showed three steps of thermal degradation as shown in Figure 3(b). In the range of 0-200ºC, the residual weight was 96 -90%; this weight loss was attributed due to H_2O being released from cured epoxy resin and the decomposition of boric acid into meta boric acid. The residual weight was 90-75% in the range of 200-350ºC due to decomposition of melamine and APP releasing N_2, H_2O and NH_3 gas. In the range of 350-500ºC, APP decomposed into polyphosphoric acid and meta phosphoric acid, epoxy and hardener decomposed into CO_2 and H_2O; resulting reduction in residual weight to 35-31%. At this stage, it might be possible that APP was reacted with boric acid to form a thermally stable compound i.e. boron phosphate [8]. The FG01 contained the final residual weight 19.73%. Sample FG08 with 7.0 grams of fiberglass had 26.58% and FG07 with 6.0 grams of fiberglass left 24.13% residues of char at 800ºC. It shows that FGO8 had 10 percent higher residual weight compared to FG07 and 34.71 percent higher than FG01. The residual weight was enhanced due to increase in the weight percentage of fiberglass. The former gave enough charring to allow a good char expansion in the fire test.

The TGA results were confirmed by DTGA curves of FG08 illustrated in Figure 3(c) which indicated six steps of thermal degradation at 117, 138, 279, 341, 404 and 454ºC. The first degradation at 117ºC indicated the degradation of cured epoxy, and conversion of boric acid into meta boric acid; while the second degradation at 138ºC was the conversion of meta boric acid into boron oxide. Melamine decomposed at 279oC. The decomposition of BPA epoxy resin, EG and APP occurred at 341ºC, 404ºC and the degradation of polyamide hardener occurred at 454ºC.

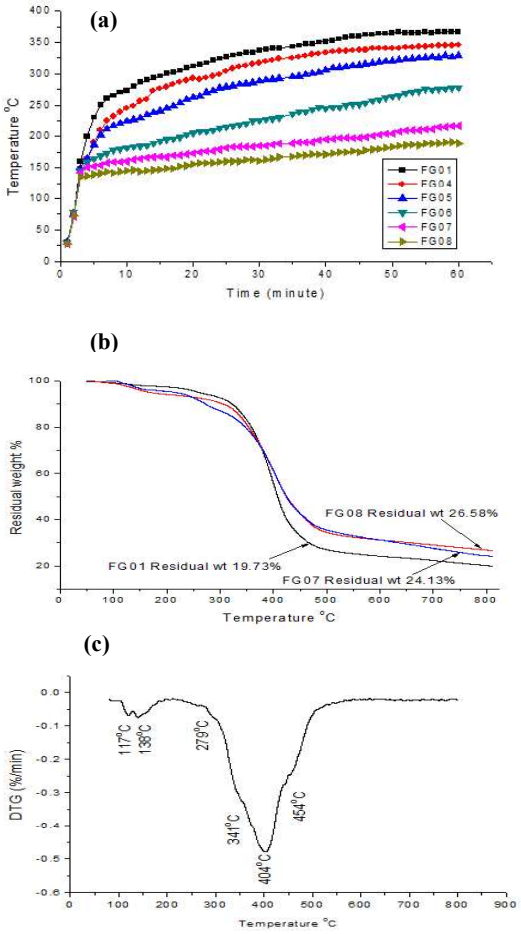

Figure 3: *(a) Temperature vs time for formulations, (b) TGA curves and (c) DTGA curves for sample FG08*

Scanning Electron Microscopy (SEM) Microstructure of Char Obtained at 450ºC

SEM micrograph of char of FG07 showed bubbles, holes and cracks on the outer layer.

However, the intumescent performance was good and substrate temperature was also low. The outer layer was smooth and confirmed a good intumescence. Bubbles were formed due to emission of N_2, NH_3, CO_2 gases and dehydration of water occurred during the burning process of the intumescent coating [11]. The graphite flakes were appeared in the inner surface that produced a heat barrier to protect the steel (substrate). Small holes were observed due to the heat dissipation that occurred and prevented transference of heat from fire to the surface. Figure 4 shows SEM micrograph of the outer surface of the char which showed small bubbles.

Figure 4 shows the outer surface of the char of FG08 coating.

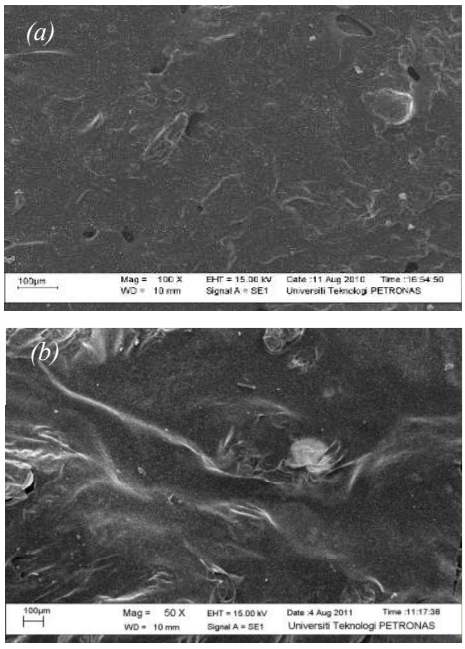

Figure 4: *SEM micrograph of char, (a) inner surface-FG07 and (b) outer surface-FG08.*

The sample demonstrates a good intumescent behavior. The outer surface was smooth with bubbles, small cracks and folding structures. The formation of bubbles was due to the emission of N_2 and ammonia gases during burning process. The FG08 char swells nicely since there are emissions of N_2, NH_3 and CO_2 gases and dehydration of water which occurred inside the charring layer [12]. Graphite flakes appeared in the inner surface which acts a heat barrier to protect the steel substrate.

Microstructure of Char Obtained at 650ºC

The SEM micrograph of char for sample FG07 burnt at 650ºC showed formation of large holes and white powder on the outer surface with cracks in the inner surface of the charring layer. The presence of white powder (ashes) as in Figure 5(a) on the surface was the result of heating at 650 ºC of the coatings which turned small portions of the coating into ashes. The surface of the coating swells properly due to emission of gas from the holes. Large holes within the char were helpful to minimize the heat penetration from the source to the surface of substrate. Figure 5(b) shows the SEM micrograph of chars of inner surface for sample GF08.

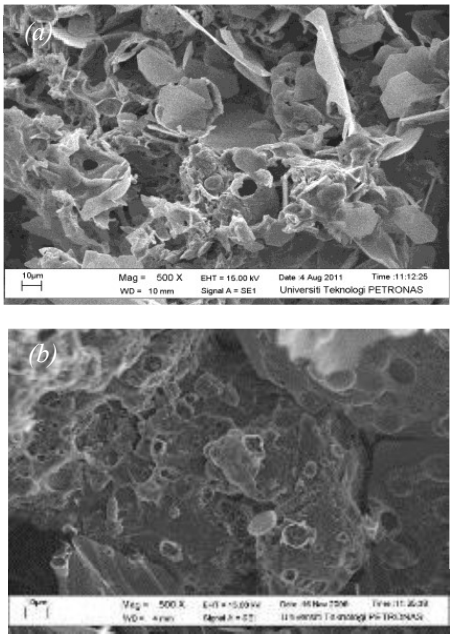

Fig. 5: *SEM micrograph of char, (a) outer surface-FG07 and (b) inner surface-FG08.*

The formation of holes, folding structure and white powder on the charring layer can be observed. The outer surface of the coating was smooth with small holes and the presence of white powder (ashes) due to high temperature of the fire test at 650 ºC. Inside

the coating, the emission of N_2, NH_3 and CO_2 gas and dehydration of water occurred. Small holes were observed too which were helpful to prevent the heat from transferring to the surface.

X-Ray Diffraction (XRD)

XRD analysis was carried out to investigate the residual char composition of the intumescent coating after fire test at 450ºC. After the residue char of the intumescent coating was oxidized at high temperature; amorphous carbon and inorganic materials were left [13].

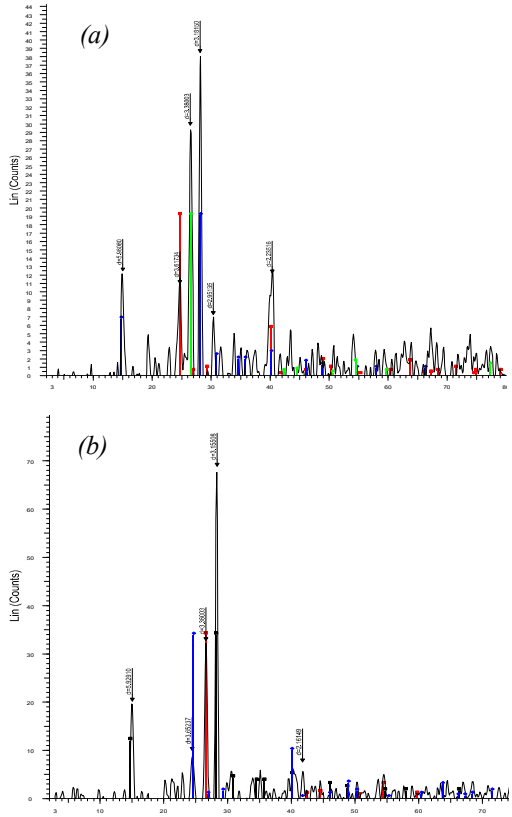

Fig. 6: *XRD curve of residue char of sample FG08 at burnt at 450ºC.*

The inorganic compounds were considered as forming the main protective layer at later stages of burning. The facial residue of samples FG07 and FG08 were analyzed using XRD technique. Figure 6 showed the XRD peaks of the facial residue char of sample FG07 and FG08 burnt at 450ºC. Several XRD peaks of the residue char at 5.929, 3.61734, 3.38003, 3.18150, 2.95135 and 2.23516 were assigned according to JCPDS card.

The peak at 5.929 was assigned to boron oxide. The peak at 3.65237 assigned to boron phosphate and at 3.3803 assigned to graphite. The major peak at 3.15807 assigned to sassolite and 2.16149 were assigned to boron phosphate oxide. The dehydration of boric acid yielded boron oxide while the reaction between APP and boron oxide yield some boron phosphate in the charring element. The formation of sassolite (mineral acid of boric acid H_3BO_3) that has been shown due to the dehydration to support the formation of B_2O_3, glass-like material which increase fire retardancy of char [8].

CONCLUSIONS

Study was focused on the preparation of the expandable graphite as char former and fiberglass as an insulating reinforcement in order to enhance the thermal insulation property of the coating. This investigation led to the following conclusions; varying amount of fiberglass ranging from 1.0-7.0 wt% was reinforced into the basic intumescent coating formulations. Formulation FG08 with 7.0 wt% glass fiber recorded the best results in terms of the enhanced thermal insulation property of the coatings. It recorded the best expansion during fire test at 450ºC and 650ºC with 5-7 times more than the original thickness. The lowest back steel temperature was 200ºC during thermal test. Thermal insulation test illustrated good coating characteristics after examined using SEM. These coatings also recorded the presence of graphite, boron oxide and boron phosphate after XRD testing and with good residue after degradation analysis using TGA. The residual weight enhanced due to increase in weight percentage of fiberglass in the intumescent coating. Thus, it was concluded that the addition of fiberglass into the basic intumescent formulations helps to enhance the thermal characteristic of the coating and

assists to maintain the structural properties of substrate materials for longer time.

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