

Effect of Kaolin Clay and Alumina on Thermal Performance and Char Morphology of Intumescent fire retardant coating

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Abstract. Intumescent fire retardant coating (IFRC) have been developed by using ammonium polyphosphate, expandable graphite, melamine, boric acid, kaolin clay and alumina as fillers bound together with epoxy resin and cured with the help of curing agent. Five different formulations were developed with and without using fillers. Cured samples were burned in furnace at 500°C for 2h for char expansion. Bunsen burner test was performed for 1h using UL-94 vertical burning test to investigate the thermal performance of IFRC. The resultant char obtained after burning of coated samples were characterized by using field emission scanning electron microscopy for char morphology. Char composition was analyzed by using fourier transform infrared spectroscopy. Thermogravimetric analysis was carried out to investigate the residual weight of coating. Results showed that formulation with 0.5 weight % of kaolin clay and 0.5 weight % of alumina provide best thermal performance, uniform and multi-porous char structure with high anti-oxidation property.

1 Introduction

Steel is an important part of any construction industry like buildings, bridges, cars, off shore and onshore structures etc [1, 2]. At elevated temperature, the mechanical properties and load bearing ability of steel declines. In case of fire, the temperature of unprotected steel reaches to critical temperature within no time and within 45 min whole of the structure ruins causing loss of lives, assets etc. In order to protect steel against fire, two types of fire protection system such as active and passive fire protection system have been used.

Intumescent originates from the word “intumescence” means swelling of certain substance in case of fire. It is one of the easiest and oldest method of protecting structural steel against fire and presents several advantages like it does not modify the intrinsic properties of the material [2], does not alter the performance of substrate and it can be applied on several materials like wood [3, 4], polymer [5] and metals [6] etc. It contains three basic ingredients such as acid source, carbon source and blowing agent [7]. Intumescent fire retardant coating (IFRC) forms on heating an expanded multi-cellular char layer having thickness better than the original thickness of coating which acts as a thermal barrier, protects the substrate from fire and mass loss from substrate to the fire. Conventionally coating was based on ammonium polyphosphate (APP) as acid source, pentaerythritol (PER) as carbon source and

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melamine (MEL) as blowing agent. The performance of coating was not adequate and char was easily oxidized at high temperature [8, 9].

Kaolin clay had better intumescence and by using 5% as filler the thermal efficiency of IFRC was enhanced [10]. When alumina was used as filler the residual weight was significantly increased and it improved the thermal efficiency of IFRC [11]. Flame retardancy of polypropylene in intumescent system with ammonium polyphosphate was decreased by using alumina filler [5]. However, the combined effect of both alumina and kaolin clay fillers with expandable graphite was not investigated in intumescent system yet. In this research work, expandable graphite was used as carbon source and combine effect of these two fillers towards thermal efficiency, char morphology and anti-oxidation of IFRC was studied.

2 Materials

APP, EG and MEL were used as acid source, carbon source and blowing agent respectively. BA used as an additive. Kaolin clay and alumina were used as fillers. Bisphenol A with polyamide amine acts as curing agent. Four formulations were prepared i.e. IF1, IF2, IF3, IF4 and IF5 as shown in Table 1.

Table 1. Preparation of intumescent coating formulations

Formulations	APP	EG	MEL	BA	Kaolin clay	Alumina	Curing agent
IF1	11.14	5.57	5.57	11.14	0.00	0.00	66.58
IF2	11.14	11.14	5.57	5.57	0.00	0.00	66.58
IF3	11.14	5.57	5.57	11.14	0.50	0.50	65.58
IF4	11.14	5.57	5.57	11.14	1.00	1.00	64.58
IF5	11.14	5.57	5.57	11.14	1.50	1.50	63.58

3 Preparation of intumescent fire retardant coating

First of all APP, BA, MEL and fillers were ground using grinder for 1 min. After that epoxy, all ground material and EG were mixed using shear mixture for 20 min at 40 rpm. Adding hardener and mixed it for further 10 min at same rpm until uniform dispersion achieved. Formulations were then coated on steel substrate using brush and placed at room temperature for curing.

4 Results and Discussions

4.1 Furnace test

Furnace test was performed to investigate the char expansion using CARBOLITE ELECTRIC FURNACE. The samples were left in furnace for 2 h and divided into three segments. In first the sample were heated to 500°C with heating rate 20°C/min. Second segment is the dwell time of 1h at 500°C to ensure complete burning of coating. Last segment is the cooling of samples from 500°C to room temperature in 35min. Physical structure of char was also investigated besides char expansion. IF1 which was without filler have good expansion but the char contained cracks and poor adhesion with substrate. IF2 has the highest expansion due to high wt. % of EG but the char was loose and fragile. In order to improve the char characteristics, fillers were added. By adding fillers (IF3) the expansion was better as compared to IF1 as shown in fig 1(a). The physical structure of char was uniform, exhibited good adhesion with substrate and also good cohesion among the char. IF4 and IF5 have good expansion as compared to IF1 but the cracks were formed inside the char. Good expansion provides better thermal insulation and anti-oxidation of char at higher temperature. Physical structure was also important for better thermal insulation apart from char expansion. If the coating has good expansion but cracks were formed inside the char then it will lead to the heat of flame to penetrate inside the char to the substrate resulted in poor char integrity at high temperature.

4.2 Bunsen burner test

Heat insulation test was performed by using Bunsen burner test. Three K type thermocouples were attached to the backside of the steel substrate and other end connected to the ANARITSU 800AM DATA LOGGER. The temperature of flame used was more than 1100°C. Backside temperature of substrate was recorded after every 1 min. It was observed that the backside temperature of bare steel plate reaches to more than 450°C within 5 min. In order to protect steel substrate IFRC was used. The mean backside substrate temperature of IF1 which was without filler was reached to 267°C after 1h and for IF2 was 284°C. When the coating was modified with fillers, the thermal efficiency increased significantly with the final backside substrate temperature after 1 h was only 105.5°C for IF3. The final backside substrate temperature after 1h for IF4 and IF5 were 154.7°C and 160.1°C respectively as shown in fig. 1(b). IF3 had better thermal insulation and char expansion as compared to other formulations studied.

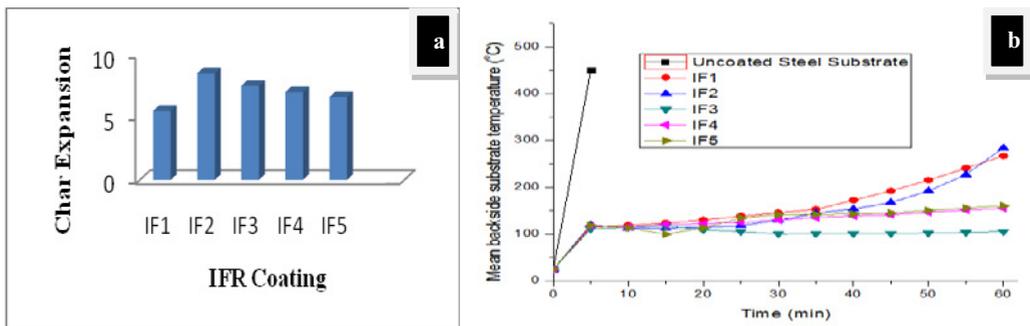


Figure.1. (a) Char expansion, (b) Backside steel temperature Vs time

4.3 Field emission scanning electron microscopy (FESEM)

The exfoliated char obtained after fire test was characterized by using SUPRA 55VP manufactured by Carl Zeiss AG, Germany for char morphology and microstructure. The microstructure for IF1, IF2 and IF3 is shown in fig 2(a, b, c). IF1 which was without filler has uneven and non-uniform structure. The microstructure of IF2 has big hole size which aids in transference of heat from these big holes to the metallic substrate [12]. IF3 showed dense and multi-porous char structure with even cell size distribution and has best thermal insulation among other formulations. The average cell size is 9.28 μ m which helps in reducing the heat of flame to penetrate inside to the substrate. The multi-porous char structure is desirable because it blocks the heat transference to the substrate as shown in fig 2(b). Cell size diameter must be within 50 μ m in order to achieve good thermal insulation of char [13].

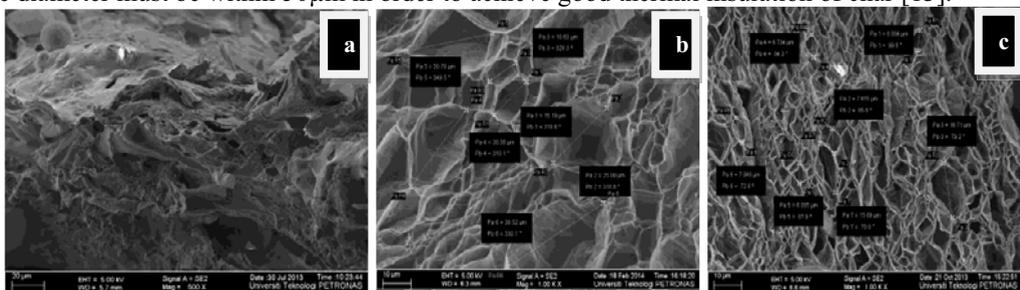


Figure2. Microstructure of char, (a) IF1, (b) IF2, (c) IF3

4.4 Fourier transform infrared spectroscopy (FTIR)

FTIR was carried out by using Spectrum One manufactured by Perkin Elmer Inc. Sample was prepared by mixing the char sample with KBr and characterized for chemical functional groups present in the char. IF3 has highest thermal insulation as compared to other formulations. The bending peak at 3431.44cm^{-1} represents O-H group due to epoxy. Bending vibration peak at 2359.95cm^{-1} represents nitrile group C-N. Melamine is used as blowing agent which contained amide group and at the decomposition temperature it dehydrates to nitrile group [14]. Bending peak at 1630.62cm^{-1} represents amino group NH_2 . Region $1400\text{-}800\text{cm}^{-1}$ represents phosphate P-O-P and it is present at the bending vibration peaks at 1192.71cm^{-1} and 1085.79cm^{-1} . Bending peak at 624.99cm^{-1} represents the B-O-P group. Boric acid dehydrated into boron oxide and boron oxide further reacted with the decomposition products of APP to form boron phosphate and it is represented by B-O-P group. The bending peak at 546.48cm^{-1} represents the Al-O group as alumina is used as filler during the preparation of IFRC as shown in fig. 3(b).

4.5 Thermogravimetric analysis (TGA)

Thermo gravimetric analysis was carried out by using Pyris 1 TGA manufactured by Perkin Elmer. The heating rate was $10^\circ\text{C}/\text{min}$ in the range of $30\text{-}800^\circ\text{C}$ under N_2 atmosphere. TGA curves have four decomposition stages. In the first stage from $0\text{-}200^\circ\text{C}$, 15% of weight loss occurred mainly due to decomposition of volatilized solvent and some molecules of epoxy resin. Also, boric acid dehydrated to metaboric acid in the range of $100\text{-}140^\circ\text{C}$ and further metaboric acid dehydrated to boron oxide at $140\text{-}180^\circ\text{C}$ [2] which is a hard intumescence glass. During second stage $200\text{-}350^\circ\text{C}$, 12 weight loss occurred. APP started to decompose by releasing ammonia and water vapors. EG was decomposed above 200°C and released carbon dioxide. MEL was decomposed to release ammonia which blows the charring layer formed by the chemical reaction between the decomposition products of APP, EG and boric acid. In third stage, $350\text{-}550^\circ\text{C}$, 20-25% weight losses occurred due to the decomposition of APP and converted into polyphosphoric and metaphosphoric acid. Boron phosphate was formed due to chemical reaction occurred between the decomposition products of APP and boric acid, which is a thermally stable compound and decompose above 1200°C . In fourth stage, $550\text{-}800^\circ\text{C}$, non-combusted residual char layer was formed which provides thermal insulation and also intumescence layer shrink in this stage and degrade slowly. The final residual weight at 800°C for IF1, IF2 and IF3 was 29.007, 25.387 and 35.186 wt. % respectively as shown in fig. 3(a). By adding the fillers, residual weight increased significantly besides thermal insulation. Higher residual weight enhanced anti-oxidation property of coating so that the char will sustain higher temperature for longer time.

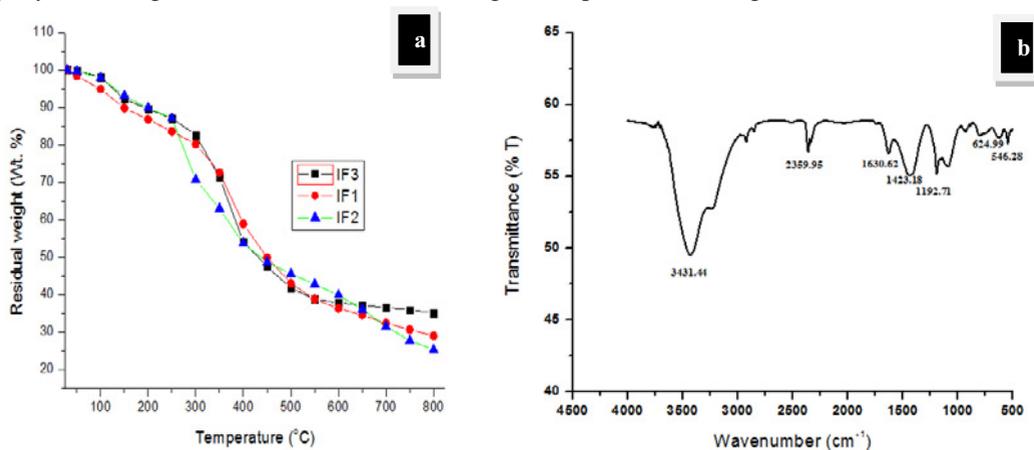


Figure 3. (a) TGA curves for IF1, IF2 and IF3, (b) FTIR spectra of IF3

5 Conclusion

This paper described the thermal efficiency of alumina and kaolin clay filler based IFRC towards protecting unloaded structural steel. Multi-cellular char was formed due to interaction among APP, EG and MEL. Results showed that by using small quantity of fillers; physically good char structure with uniform expansion was achieved as illustrated by furnace test and it was stable for 2h. The backside temperature of steel substrate after 1h was only 105.5°C and has very good thermal insulation property. FESEM showed dense and multi-porous char structure with less cell size diameter. FTIR represents the functional group B-O-P, P-O-P and Al-O. Higher residual weight was achieved i.e. 35.186 wt. % by adding small amount of fillers providing better anti-oxidation property. By increasing the wt. % of EG i.e. IF2, highest char expansion achieved compared to other formulations studied but thermal efficiency and residual weight decreased. It is concluded that only char expansion is not important other factors like thermal efficiency, residual weight and microstructure are also important. By adding fillers, thermal insulation and anti-oxidation property enhanced up to certain extent of fillers.

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