SYNERGISTIC EFFECTS OF ZINC BORATE AND HALLOYSITE NANOTUBES (HNTS) ON CHAR MORPHOLOGY AND GASES EMISSION OF EPOXY BASED INTUMESCENT FIRE RETARDANT SYSTEMS

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ABSTRACT

In this study, Zinc Borate (ZB) and Halloysite nanotubes (HNTs) are simultaneously integrated in the in expandable graphite (EG) based intumescent fire retardant coatings. The synergistic effect between the ZB and HNTs on fire performance, char morphology, and thermal degradation of IFRC were investigated. The IFRC of ZB/HNTs (5.5:1.5) showed noticeable improvement in char quality. Similar ratio of incorporated additives showed significant reductions in the phenolic gasses emission of IFRC. FESEM results showed that a solid and dense char layer was formed in ZBH (5), which hindered the transfer of heat to substrate and hold combustible gases in the condensed phase reaction. It is concluded that the combination of ZB and HNTs is proved to be a supportive synergism in development of environment friendly intumescence coating systems.

Keywords: zinc borate, halloysite nanotubes, char morphology, fire performance, thermal stability, intumescent fire retardant coatings.

INTRODUCTION

Intumescent Fire retardant coatings are easiest and oldest way to protect steel structures from reparations of fire accidents. An intumescent formulation require to be optimized in terms of physical (char strength, expansion, viscosity, morphology, heat conductivity etc.) and chemical (thermal stability, reactivity) properties in order to form an efficient protective char which will be able to protect steel substrate [1] . Pervious works have already been completed on the chemical characterization of Intumescent fire retardant coatings for the assessment of their thermal stability [2], [3],and [4] but only few papers deal with the investigation of the gaseous emissions during intumescence degradation[5]and[6]. Polymer epoxy resins are an essential part of Intumescent coatings formulations. They perform well as a binder in intumescent fire retardant systems but with one limitation. On thermal degradation they release toxic gases, like phenols, aniline, toluene, ammonia etc. to the environment which are health risk for people entrap in fire locations. One of the main challenges is to find out the optimum ratio between all additives of Intumescent formulations to reduce the gaseous emission while keeping the fire performance high. Reduction in toxic gaseous emission can be attained by choosing the suitable additives that can chemically convert aromatic hydrocarbons into aliphatic compounds [7] . Some fillers such as wollastonite, kaolin clay, and alumina can involve in endothermic reactions at high temperatures, are previously used to enhance the fire performance. It has been proven that zinc borate perform well as a flame retardant additive and suppress smoke when used with in different polymers like PVC [8], polyamide [9], polyolefin [10], epoxy, phenolic, and various elastomers [11]. Similarly, the use of different clays in intumescent fire retardant coating formulations is well known technique, to decrease their flammability. Clays are usually compounded in high fractions with the polymer to create best hindering effect through sturdiest char [12, 13] Since 1990s, several nano clays, montmorillonite clay OMMT, and two fibrous clay minerals; palygorskite (PAL), halloysite (HAL), and sepiolite (SEP) was have been reported as synergists in IFRs.

Previous studies reported that improvement in the fire retardant properties of IFRC can be achieved by the addition of hallyosite nanotubes in intumescent coating formulation[14]. The zinc borate contribution has also been recognized in development of glassy char layer at the surface of the polymer during condensed phase of combustion reaction, and protects steel substrate [15]. This effectively reduces the infusion of volatile compounds through the external char, and limits them from entering the gas phase., Zinc borate is also known as natural smoke suppressant agent and it has been acknowledged for its capabilities to suppress smoke that often arise during the burning of a polymers. In addition ,It has a natural tendency to break aromcity of phenolic comounds used in Intumescent fire retardant formulations, through crosslinking[15]. On the other hand, halloysite nanotubes ($Al_2Si_2O_5(OH)_4$) contain 39.8% alumina and 46.3% silica. These both element can emerge heat shielding effect dynamically[16].

Current Study reveals the synergist effects of halloysite nanotubes and zinc borate on the char morphology and gaseous emissions of Intumescent fire retardant coatings.

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EXPERIMENTAL

Materials and methods

Boric acid (B.A), Melamine (Mel), Hallyosite Nanotubes (HNTs), and Expandable graphite, and were purchased from Sigma Aldrich (M) Sdn Bhd. Malaysia. Ammonium poly phosphate (APP) was provided by Clariant (Malaysia) Sdn Bhd. Binder system bisphenol epoxy resin BE-188 (BPA) and ACR Hardener H-2310 polyamide amine were bought from Mc-Growth chemical Sdn Bhd. Malaysia. Structural steel A36M was provided by TSA industries (Ipoh) Sdn. Bhd. Malaysia.

Sample preparation

All intumescent ingredients were mixed with their particular weight percentage as quantified in Table-1 and grinded well to homogenous the size distribution of all particles. The shear mixer was used for the mixing of materials with epoxy and hardener at 40 rpm for 40 min (Figure-1(a)). In general, Inurement coating performance and adhesion depends upon the surface preparation. Most disappointments in the performance of Intumescent coatings can be credited to poor surface morphology. Intumescent fire retardant coatings rely on the physical roughness of the substrate surface. This surface must not have any be dust, dirt, oil, grease, rust, corrosion and other contaminants over them. For this purpose, sandblasting has been done before application of Intumescent Fire retardant coating according to ISO 8503 standard.

The sandblasted steel plates of cross-sectional area 100 cm^2 were used as a substrate. The coating was applied using brush on the steel substrate as shown in Figure-1(b). An average thickness of coating was maintained at 1.5 mm and it was measured by digital Vernier caliper.

Prepared samples were cured for 24 hours at room temperature. In order to get char for FESEM analysis cured samples were burnt in carbolite furnace according to ISO 8430 standard. Table-1 showed six intumescent coating formulations (ICF) prepared to study the Synergism of Hallyosite Nano Tubes (HNTs) and zinc borate on char morphology and thermal degradation of IFRC coatings. The char was characterized by FESEM. The gasses emission was determined by using gas chromatography Technique.

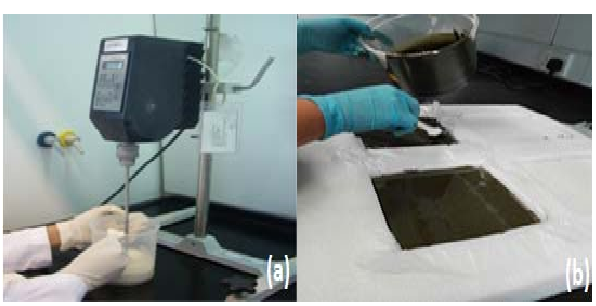

Figure-1. (a) Mixing of intumescent coating formulations. (b) Applying procedure of intumescent coating formulations on steel substrate.

Table-1. Weightage of ingredients in HNT and ZB reinforced Intumescent fire retardant coatings.

Formulation Names	(APP) (wt. %age)	(MEL) (wt. %age)	(BA) (wt. %age)	(ZB) (wt. %age)	(EG) (wt. %age)	HNTs (wt. %age)	Epoxy (wt. %age)	Hardener (wt. %age)
ZBH(0)	11.76	5.5	11.11	0	5.5	1.5	43.45	20.75
ZBH(1)	11.76	5.5	10.11	1	5.5	1.5	43.45	20.75
ZBH(2)	11.76	5.5	9.11	2	5.5	1.5	43.45	20.75
ZBH(3)	11.76	5.5	8.11	3	5.5	1.5	43.45	20.75
ZBH(4)	11.76	5.5	7.11	4	5.5	1.5	43.45	20.75
ZBH(5)	11.76	5.5	6.11	5	5.5	1.5	43.45	20.75

CHARACTERIZATION

Field emission scanning electron microscopy

Porosity and morphological structure of char was observed and analyzed by field emission scanning electron microscope (FESEM).

Pyrolysis gas chromatography mass spectroscopy analysis

The gaseous products of decomposition from the pyrolyzed samples of intumescent coating were identified with GCMS. The Py-GC/MS were carried out using a PYRO-CHEM WILKS pyrolyser, Hewlett Packard 5890 Series II gas chromatograph, and TRIO 1000 mass spectrometer. The gas chromatographic column (BPX 5, provided by SGE, nominal diameter 25 mm, 0.25 mm bore/0.25 mm thickness film) was heated from 40 °C to 220 °C at 20 °C/min in 10 min (180 C, 9 min), the initial temperature was held for 5 min. The sample (10 mg) was placed in the pyrolyser. The pyrolysis process was carried out at 25 °C–800 °C in 10s paralysis products in the gas phase were injected into the Py-GC–MS by syringe to characterize the gaseous products. Gas chromatography was carried out and the gaseous products were identified during degradation of the intumescent coating.

RESULTS & DISCUSSION

Char morphology of HNTs and ZB reinforced intumescent fire retardant coatings

The FESEM images in Figure-3 showed the comparison between surface morphology of the char from the burnt Intumescent fire retardant coatings formulations. A number of holes and cracks were present on the char residues surface of ZBH (0). Intermittent and loose residues showed poor charring performance for the flame retardant coating formulations. In comparison, the fire residue surface of ZBH (4) and ZBH (5) was continuous,

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denser and intumescent. The difference between the results indicated that the residues of ZBH (4) and ZBH (5) were denser and more intumescent, thus zinc borate with synergism of HNTs were greatly contributed to the development of better quality char.

Similarly, FESEM images of ZBH (0) on higher magnifications, divulged big size pores in char outer surface while ZBH (4) and ZBH (5) have smaller size of pores (Figure-3). The average pore size observed at char surface of ZBH(0) is 22 µm while in ZBH(4) and ZBH (5) this number is reduced up to 11.49 µm. Literature states that char with less than 40 µm pore size can provide better resistance due to its ability to entrap gas bubbles and offer spongy char. But the lowest pore size provide more better insulation[18].

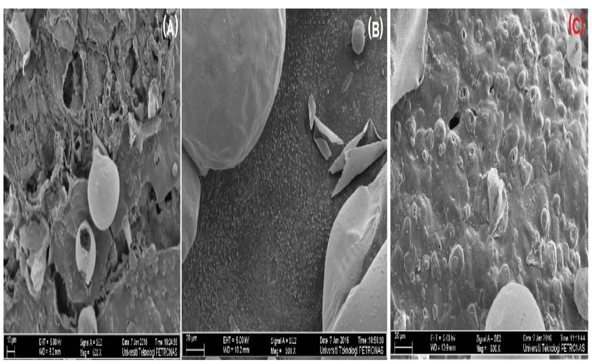

Figure-2. Cracked and discontinuous char surface of ZBH (0), presented (A), smooth homogeneous char structure of ZBH (5) shown in (B) and (C) at 500 X magnifications respectively.

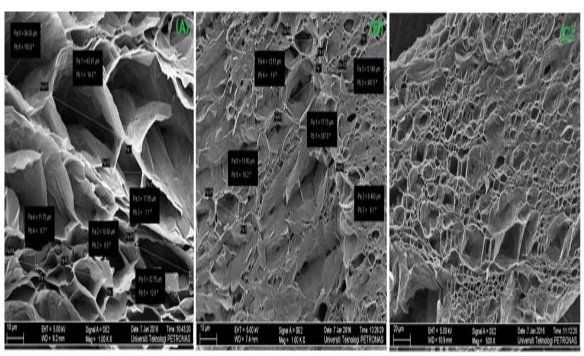

Figure-3. Opened pored char surface of ZBH (0) presented in (a), minor pored regular char structure of ZBH (5), shown in (B), and (C) at 1000 X magnifications respectively.

Gaseous emission analysis of HNTs and ZB reinforced intumescent fire retardant coatings

The Gasses emission of HNTs and ZB reinforced Intumescent fire retardant coatings have been studied by pyrolysis–gas chromatography at 800 °C and shown in Figure-5 and 6. It was shown that, as is generally thought, the decomposition of phenol base epoxy resins consist of breaking the bonds between aromatic rings and produce phenolic compounds during burning [19]. Thus, the main degradation products in case of ZBH (0) are phenol and its methyl derivatives, as well as small amounts of aromatic hydrocarbons. According to OSHA standards the phenol is consider as highly detrimental gas for environment.

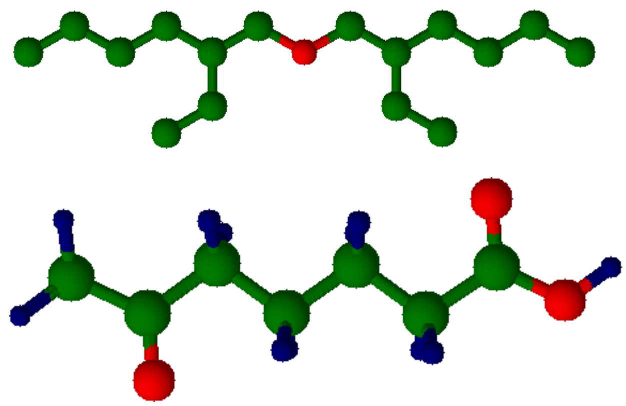

Figure-4. Non aromatic structure of Bis (2-ethylhexyl) Ether (C16 H34O) and Hexanedioic acid.

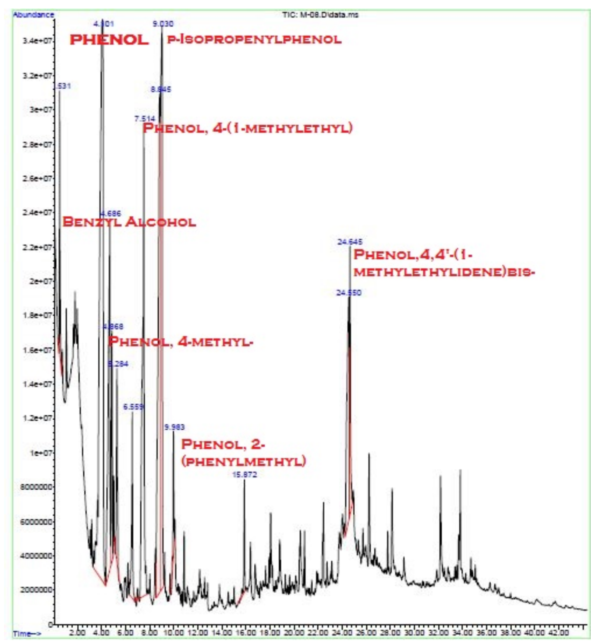

Figure-5. Gas chromatograph of ZBH (0).

In the case of ZBH (4) and ZBH (5), the GC–MS analysis identified Cyclobutanol Benzaldehyde, Benzyl Alcohol, Dibutyl phthalate, Benzene, 1-ethyl-3, 5-dimethyl-, Hexanedioic acid, octadecyl ester and bis (2-ethylhexyl) ester. Gas chromatograph of ZBH (5) is given in Figure-6.

Hexanedioic acid, octadecyl ester and bis (2-ethylhexyl) ester are ester based compounds and it is assumed that they may be synthesized in a gas phase reaction due to presence of Zn^{+} specie offered by zinc borate. Zn species has tendency to enhance crosslinking

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and convert aromatics rings into aliphatic hydrocarbons [20]. Formation of ZnO after esterification also expected. It is assumed that zinc borate helped in breaking all the aromatic rings and convert them into ester based compounds. Long chain structures of Hexanedioic acid, and bis (2-ethylhexyl) esters, the two major gaseous products in case of ZBH (5), are given in Figure-4.

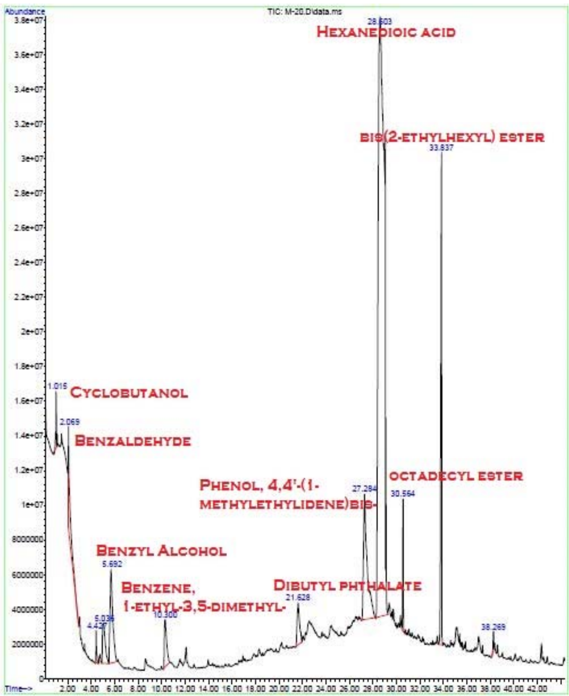

Figure-6. Gas chromatograph of ZBH (5).

CONCLUSIONS

The smoke suppressant property of multifunctional fire retardants additive zinc borate showed very well enactment when used in synergism with halloysite Nano tubes. Hallyosite nanotubes developed aluminosilicate network over the surface of char and preserve the carbon of char. On the mean time zinc species attacked accessible aromatic rings present in the phenolic epoxy and convert them into long chain esters which actually help the networking phenomena of aluminomsilicates network present in HNTs. Hence, the findings from this study revealed that the synergism between two flame-retardant additives, zinc borate and hallyosite nanotubes drastically reduced the phenolic gaseous emission, while keeping the char quality high in intumescent fire retardant systems.

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