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Thermal degradation and pyrolysis analysis of zinc borate reinforced intumescent fire retardant coatings

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ABSTRACT

This work aims at evaluating the potential of nano-sized zinc borate as substitution of boric acid for thermal degradation and gaseous products in expandable graphite based intumescent fire retardant coating IFRC systems. The thermal degradation and pyrolysis of intumescent flame retardant coatings was characterized by bunsen burner fire test, thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM), energy dispersive spectrometry (EDX), X-ray diffraction (XRD), fourier transformed infra-red analysis (FTIR), X-ray photoelectron spectroscopy (XPS) and gaseous emission analysis (Py-GC). Bunsen burner fire test reveals that the partial substitution of zinc borate (6.61 mass%) imparts a substantial improvement in thermal stability and reduces steel substrate temperature to 124 °C. From thermogravimetric analysis results, it was shown that this composition increases char residual mass from 39 to 46.14 mass%. The morphological structures of char residue were investigated by FESEM and it indicates that zinc borate promotes more continuous and compact char layers that hinder the heat diffusion and oxygen transmission effectively. XRD and FTIR results show that zinc borate develops a zinc-based glassy intumescent shield i.e. zinc bis (hydroxyanthrapyrimidine) dehydrate ($C_{30}H_{14}N_4O_4Zn{\cdot}2H_2O$) that strengthens the char. The new chemical species enhances the thermal stability of the freshly formed char at high temperature and provides an enhanced fire protection. XPS analysis shows the higher carbon contents in formulation IF-5 (6.6 mass%) and endorses high char residue. The Py-GC analysis confirms release of less toxic gaseous products in IF-5 formulation, considering their type and concentration, as compared to control formulation, and is considered as an environmentally safe intumescent formulation.

1. Introduction

Intumescent coatings are a blend of chemicals that swell and form a multiparous char layer over the surface of the substrate when exposed to the fire. Traditional intumescent systems contain three main ingredients. The carbon source performs as a char developer (e.g.pentaerythritol/Expandable graphite), the acid source works as a dehydrating catalyst (e.g. polyphosphate) and a blowing agent helps to form the porous barrier (e.g. melamine, guanidine [1]. This carbonaceous cellular/porous residue acts as a physical barrier between the heat source, the air, and the pyrolysis products, and prevents the substrate fire spread [2,3].

The carbonaceous char keeps its integrity up to 800 °C. When the temperature reaches above 600 °C, the charring layers degrade and the underlying substrate structure collapses. To overcome this problem different types of organic and inorganic additives have been used in the intumescent coating [4–7]. These additives play a key role to develop a foaming char on the surface of the combusting material within the intumescent coating at relatively low cost [8].

Moreover, intumescent coatings release gases upon degradation. Released gases expand the developed char network. This expansion in char assembly is the key factor that determines the heat shielding property of intumescent coating. The expansion process clearly depends upon the coating thickness, but also the speed of chemical reaction and the rate of heating. Therefore, the efficiency of an intumescent coating is also reliant on the reaction chemistry between the incorporated additives and their synergism with basic ingredients [9].

Zinc borate is a boron-based compound and possesses its own

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potentials as flame retardant additives in terms of thermal stability and smoke suppression [10–12]. Zinc borate degrades at 290 °C and does not release any toxic and corrosive elements during the combustion process. These properties make it attractive to be used as a fire retardant additive in intumescent coatings [13–16]. Hydrated zinc borate promotes the formation of a protective, cellular and vitreous char layer. This layer acts as a good thermal insulator and protects the underlying substrate from heat, oxygen, and converts the burning polymer into carbon. This phenomena minimizes the emission of combustible gases during gas phase reaction.

The chemical composition of zinc borate offers natural cooling effects by releasing water molecule at high temperature [17]. It dehydrates endothermically, absorbs heat from the vaporized water and locally dilutes oxygen and gaseous flammable components [18]. Zinc species in the condensed phase produces aliphatic hydrocarbons rather than benzene and other aromatics which increases the crosslinking reactions within the polymer, suppresses smoke during burning, and enhance the quality of char regarding its thermal stability [19].

Previously, zinc borate has been used by many researchers and manufacturers for flame retardant purposes. Rongcai Xi et al. studied its synergism with expandable graphite in terms of fire retardancy. A number of researchers investigated zinc borate as a fire retardant additive by using it with different polymers systems [13,20–28]. Zinc-based compounds e.g. zinc stannate ($ZnSnO_3$, ZS), zinc hydroxystannate (ZnSn(OH), ZHS), have been already used as a smoke suppression additives in intumescent coatings [29,30] However, zinc borate has not been reported for reducing the emission of aromatic compounds in intumescent fire retardant coatings. Zinc borate has the tendency to facilitate in gas phase reaction of combustion cycle and decreases the soot formation [31] which can possibly leads low smoke generation. On the other hand, its natural crosslinking property can support termination with aromatic compounds and convert them into aliphatic long chain hydrocarbon which in turn reduces toxicity [32,33].

In this study, the use of zinc borate for the cross-linking of polymer for suppression of aromatic compounds was explored. It investigates the effects of zinc borate on the thermal degradation according to the ASTME-119 procedure, char morphologies, and degradation products of Intumescent formulations. Char morphology of designed formulations were investigated by field emission scanning electron microscopy (FESEM). Thermal degradation of zinc borate reinforced intumescent formulations was evaluated by thermogravimetric analysis (TGA). The composition of char residue was analyzed by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Emission of gases during degradation were characterized by Pyrolysis gas chromatography (Py-GC).

2. Materials and methods

Nano-sized zinc borate, boric acid (B.A), melamine (Mel), and expandable graphite (EG), wollastonite (W) and alumina were purchased from Sigma-Aldrich (M) Sdn Bhd. Malaysia. The binder system bisphenol-A epoxy resin BE-188 (BPA) and ACR Hardener H-2310 polyamide amine were purchased from Mc-Growth chemical Sdn Bhd. Malaysia. Ammonium polyphosphate (APP) was purchased by Clariant (Malaysia) Sdn Bhd. TSA industries (Ipoh) Sdn. Bhd. Malaysia provided the structural steel A36 M.

Nano-sized zinc borate used in this study was examined under transmission electron microscope (TEM). The TEM micrographs are shown in Fig. 1. The zinc borate exhibits a porous structure which can entrap blowing gases and enhance intumescence phenomena of residual char.

The single-crystal structure of zinc borate Zn $[B_3O_4\ (OH)_3]$ illustrates a complex network of polytriborate chains, Fig. 2. Zinc atoms are attached to the network through coordination and further integrated by hydrogen bonding. Hydrogen bonding enhances the thermal stability of this compound [34].

2.1. Sample preparation

Table 1 depicts the mass percentages of all the intumescent components used in this study. They were mixed with epoxy resin thoroughly using a shear mixer operated at 40 rpm for 30 min. Sandblasted steel plates of the cross-sectional area of 10 × 10 cm^2 were used as a substrate and coated by using a brush keeping the average thickness of coating up to 2 mm for each substrate. Thickness of coating was measured by digital coating thickness measuring gauge.

The coated substrates were cured for 24 h at room temperature. Table 1 shows all intumescent coating formulations prepared in order to study the effects of zinc borate on its thermal degradation, char expansion, heat shielding, and char morphology and gases emission. TGA analysis was performed to evaluate the thermal degradation behaviour of the coatings. The compounds present in the residual char were identified using XRD and FTIR. The Py-GC analysis was conducted to record the degradation products of Intumescent formulations.

3. Characterization

3.1. Furnace fire test

In order to examine the char structure and its expansion, the coated substrates were burnt in a carbolite furnace. The temperature was kept at 800 °C for 60 min to ensure the sample has burnt completely [35]. The samples were cooled in the furnace for approximately 120 min to avoid thermal shocks to the char. The char expansion was measured at four points using a digital Vernier calliper, and the average char expansion is reported.

3.2. Field emission scanning electron microscopy

The morphology of the char samples was examined using SUPRA 55VP field emission scanning electron microscope (FESEM).

3.3. Bunsen burner fire test (ASTM E-119)

The evaluation of the heat diffusion from fire to the steel substrate was performed by conducting the fire test for each coating formulation according to ASTM E-119 standard [36]. The fire test of the coated steel substrate was carried out by using a portable Bunsen burner and the distance between the burner and coated substrate was kept 7 cm [35,37]. Three thermocouples of type K were connected to Anarittsu Data logger, Input Channel 6 Model AM- 8000 K with Anarittsu software and the back of the coated substrate to record temperature. The temperature of the steel plate was recorded for 60 min with a step of 1 min. Butane gas was used during the Bunsen burner test, the temperature of the flame was determined using a K-type thermocouple, and the temperature was recorded by a data logger. The butane gas had a maximum temperature of 1350 °C. Fig. 3 represents the setup of the fire test used in this study.

3.4. Thermogravimetric analysis

TGA Q50 Perkin Elmer was used to perform the thermogravimetric analysis of intumescent coating samples (approximately 10 mg). In order to determine the residual mass of the char for each coating formulation, this characterization was carried out at 10 °C/min under N_2, over the whole range of temperature (50–830 °C)

3.5. X-ray diffraction

XRD analyse the compounds present in the residual char of the intumescent coating after the fire test. These measurements were carried out on a Bruker Diffract meter AXS D8 Advance using Cu K radiation and a nickel filter (k ¼ 0.150595 nm) in the 2θ range of 10°–90°. The