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THE SYNERGISTIC EFFECT OF HYBRID FLAME RETARDANTS ON PYROLYSIS BEHAVIOUR OF HYBRID COMPOSITE MATERIALS

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Abstract

The aim of this investigation is to comprehensively understand the polymeric composite behavior under direct fire sources. The synergistic effects of hybrid flame retardant material on inhabiting the pyrolysis of hybrid reinforced fibers, woven roving (0°- 45°) carbon and kevlar (50/50 wt/wt), and an araldite resin composites were studied. The composites were synthesised and coated primarily by zinc borate (2ZnO.3B2O3.3.5H2O) and modified by antimony trioxide (Sb_2O_3) with different amounts (10-30 wt%) of flame retardant materials. In the experiments, the composite samples were exposed to a direct flame source generated by oxyacetylene flame (~3000ºC) at variable exposure distances of 10-20 mm. The synergic flame retardants role of antimony trioxide and zinc borate on the composite surface noticeably improves the flame resistance of the composite which is attributed to forming a protective mass and heat barrier on the composite surface and increasing the melt viscosity.

Keywords: Synergistic effect, Inorganic retardants, Pyrolysis behavior, Hybrid materials.

1. Introduction

Flame retardants (FRs) are chemical materials used to diminish the spread or intensity of fire, i.e. protection to the fire fighters. The ultimate function of flame retardants is to decrease the potential of ignition and delay the spread of a flame [1, 2]. To produce a composite material with good flame resistance, two parameters need to be addressed as type of halogen source (aliphatic versus aromatic) and type of polymer used in that material. Four primary substances those commonly used as fire retardants are halogenated, phosphorus, nitrogen and inorganic flame retardants [3, 4]. The inorganic flame retardants involve metal hydroxides, such as aluminium hydroxide [Al $(OH)_3$], magnesium hydroxide [$Mg(OH)_2$], ammonium polyphosphate [NH_4 $PO_3]_n$, boron salts, inorganic antimony, tin, zinc, molybdenum compounds and elemental red phosphorous. Additionally, zinc borate (ZB) is an effective inorganic flame retardant while it is principally used in smoke suppression, promoting charring, and multifunctional flame retardants in combination with other halogenated or halogen free flame retardant systems to boost flame retardants properties [5, 6]. The mode of action for the zinc borate appears to be a combination of the effect of the formation of a conspicuous glassy inorganic layer and an increase in char formation perhaps through the formation of borate esters as well as the blocking off of volatile fuel release. Borates and boric acid can also give off water which provides a heat sink, fuel diluents, a propellant for the fuel out of the flame zone and blowing agent for the glassy in tumescent coating. The zinc borate can possibly display a synergistic effect with antimony oxide in fire retardancy [1, 7]. Antimony oxides are known to exist in several different compositions and display polymorphism, Sb_2O_3, Sb_2O_4, and Sb_2O_5. Antimony trioxide (Sb_2O_3) is cubic phase, colourless and orthorhombic phase which has white colour. Moreover, antimony trioxide dissolved slightly in water and dissolved in potassium hydroxide, dilute hydrochloric acid and with many organic acids [5, 8, 9].

To better understanding the pyrolysis and flammability for fibre composites and factors affecting these features such as surface spread flame, fire penetration, ease of ignition, fuel contribution and oxygen index i.e. the minimum oxygen content that support combustion). Various practical results from selected studies included diverse flame retardants systems have been given here. A comprehensive review on flame retardants for polypropylene (PP) has been addressed [10]. Five different types of generic flame retardant systems (phosphorus containing, halogen-containing, silicon-containing, metal hydrate and oxide and nanocomposite flame retardant formulations) have been identified in that study. It has been showed that the combination of halogen-antimony and phosphorus-bromine is the most effective flame system among others.

Hribernik et al. [11] coated the surface of a regenerated cellulose fibre with a layer of silica (SiO_2) using a sol-gel process. It was observed that the flammability of the coated fibre was lower than those the untreated counterpart. This is because SiO_2 increased the temperature at which the fibre started to decompose by 20°C and hindered significantly the flow of oxygen to the generated volatiles during the thermal decomposition. Zhao et al. [12] synthesized a novel flame retardant containing three flame-retardant elements, phosphorous (P), nitrogen (N), and sulphur (S) by using melt condensation reaction. By increasing of the flame retardant content, the flame retardancy of the system increased but the char yield decreased. Besides, other investigators attempted to benefit from the feature of the synergistic between inorganic substrates. Thus, the effects of hydroxy silicone oil (HSO) as a synergistic agent on the flame retardancy of intumescent flame retardant polypropylene composites was studied via [13]. To that end, the HSO reacted with polypropylene and formed silicon phosphate and ceramic-like structure which in turn increased the efficiency of the intumescent char shield and improved the fire performance of the system.

Furthermore, Qu et al. [14] studied the effects of inorganic tin compounds (Zinc hydroxylstannate (ZHS), Sb_2O_3, tin dioxide (SnO_2), and tin monoxide (SnO) and their mixtures on the flame retardant and smoke suppressant properties of flexible poly-vinyl chloride (PVC). Via applying the limiting oxygen index (LOI) test, the flame retardant and smoke suppressant actions of the PVC showed a significant enhancement in its flame retardancy. This behaviour could ascribe to the partial replacement of Sb_2O_3 in flexible PVC by ZHS which resulted in a noticeable synergistic improvement in flame retardant behavior. However, to the best of our knowledge there is by far no particular study has dealt with the synergistic effect for both the coated flame retardant and the reinforced fibre in fibre-composite materials. Therefore, the efforts have been focused on testing the flame retardancy for the araldite polymer resin-based hybrid carbon-kevlar fibres. Araldite resin has been chosen due to its low shrinkage, high dimensional stability, high mechanical strength, and the highly compatible testing. Besides, its applications in architecture and bonding thin pre-cast concrete joints.

Within this study, the effects of synergistic antimony oxide and zinc borate as hybrid flame retardant coated the surface of carbon-kevlar fibers reinforced araldite resin composite on its pyrolysis behavior is identified via using the heat erosion test.

2. Experimental

2.1. Materials and preparation of test specimens

Zinc borate ($2ZnO.3B_2O_3.3.5H_2O$) and antimony trioxide (Sb_2O_3) supplied by Akrochem, Ohio and NL Industries, Texas, respectively were used as flame retardant material. Araldite resin type CY223 having appearance of amber viscous liquid, mild odour at 20°C and density of 1.15 g/cm^3 was used with 40 wt.% of concentration as polymer matrix-reinforced by 60 wt.% hybrid carbon-kevlar (50/50 wt/wt, 0°-45°) woven roving fibres. The composite laminate of 10 cm×10 cm×1 cm was built up in metal mould by a conventional hand lay-up technique. The resultant composite was coated by hybrid flame retardants, primarily by zinc borate followed by different toughened percentages of antimony trioxide (10, 20, 30 wt. %) consecutively using spray-coating deposition technique to make a total coating layer of 4 mm as illustrated in Fig.1.

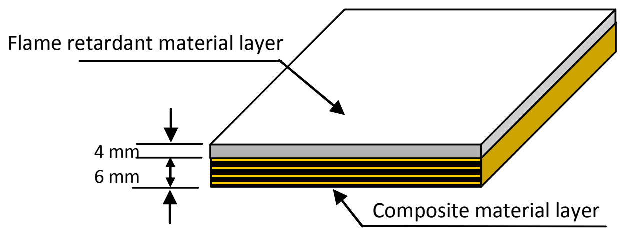

Fig. 1. Thermal Erosion Test's Specimen.

2.2. Thermal erosion test

A direct source of flame generated by oxyacetylene torch with temperature almost of 3000ºC was depended in order to conduct the thermal erosion test. A special system for that purpose was designed in situ as shown in Fig. 2. The functional procedure for this system is fixing the coated composite material in various distances of 10, 15 and 20 mm in front of the flame source. The measurements of the face surface temperature and the opposite surface temperature of the coated composite were done via a thermocouple as indication for the pyrolysis resistance of the composite.

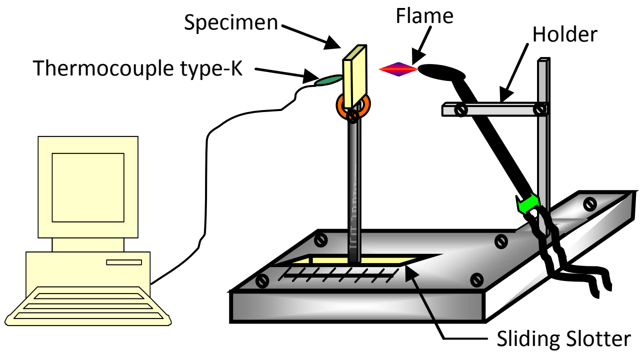

Fig. 2. Thermal Erosion System Applied in this Study.

3. Results and Discussion

The relationship between surface temperatures of the coated composite and the exposure time for the direct flame at distance of 10 mm away from the flame was shown in Fig. 3. It is obviously clear from the figure that the surface's temperature of the composites increases with increasing the time of exposure to flame. While, the composites endure longer time before deforming by fire which is ascribed to that zinc borate forms a glassy char at high temperatures and releases water of hydration from its chemical structure which in turn prevents the flame propagation [4, 5, 15]. Consequently, the coated composite steadfastly stays longer and the fire spread decreases [3, 6]. Besides, this ability of the coated composite to withstand the direct fire promotes after introducing the antimony trioxide into the zinc borate, while the antimony oxide plays a synergistic role with the zinc borate even at low additions like 10% and the subsequent coated composites will have much better retardancy if compared to the solely coated materials via antinomy oxide.

The addition of ZB into Sb_2O_3 induces the phase transformations that happen within the internal structure of the trioxide which finally results in enhancement of the composite's flame retardancy, i.e. the retardant action of the composite against fire increases with increasing antimony trioxide content [4, 9, 14, 16]. The surface behavior of the coated composites via different fire retardants were shown in Figs. 4, 6 and 8. From these images particularly in the vicinity of trigged area by direct source fire, it can be observed many black and white regions. The black ones are referring to the complex char occurred due to the strong interaction between the resin-intumescent-fibres [17].

Additionally, to further identify the effects of hybrid coated layers on the pyrolysis behaviour of the composites, the results of the thermal erosion for the composites coated tested in three different distances from the direct source of the oxyacetylene flame (10, 15 and 20 mm) were demonstrated in Figs. 3, 5, and 7.

The trends of these figures followed the same deviation with slight changes in the surface temperature which increases with longer exposure time. In the meantime, the time required to decompose the flame retardant layer increases due to reducing the combustion gaseous. In other words, with the increase of intumescent level, due to introducing of 10%, 20 %, and 30 % antimony trioxide into zinc borate, the time-to-ignition (TTI) increases [17]. This perhaps due to the mode action of this oxide with glassy coating layer which results in flame retardancy enhancement. In general, using FRs materials tend to reduce the heat distortion temperature and melt dripping for polymer based composite at high temperature [15].

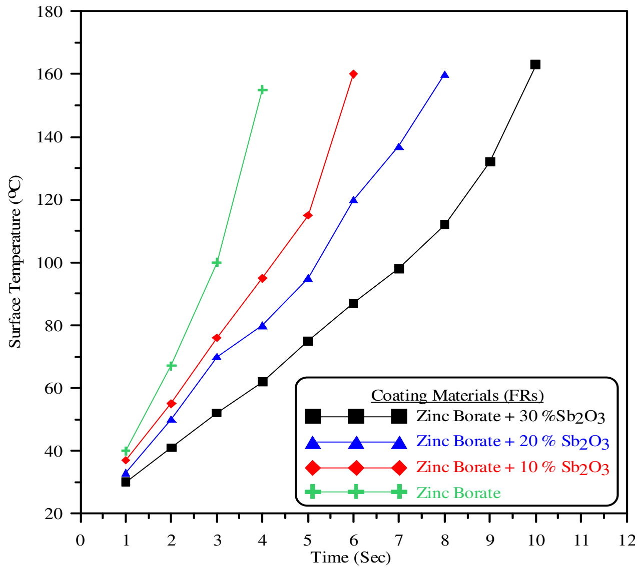

Fig. 3. Surface Temperature versus Time with Distance of 10 mm from the Flame Exposure Source.

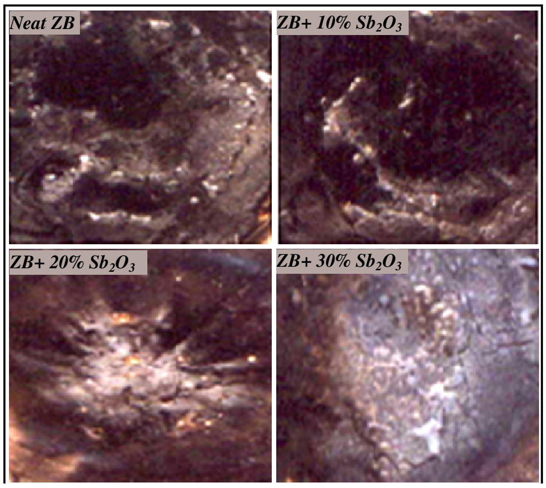

Fig. 4. Images of the Coated Composites by Zinc Borate (ZB) and Sb_2O_3 with Distance of 10 mm from the Flame Exposure.

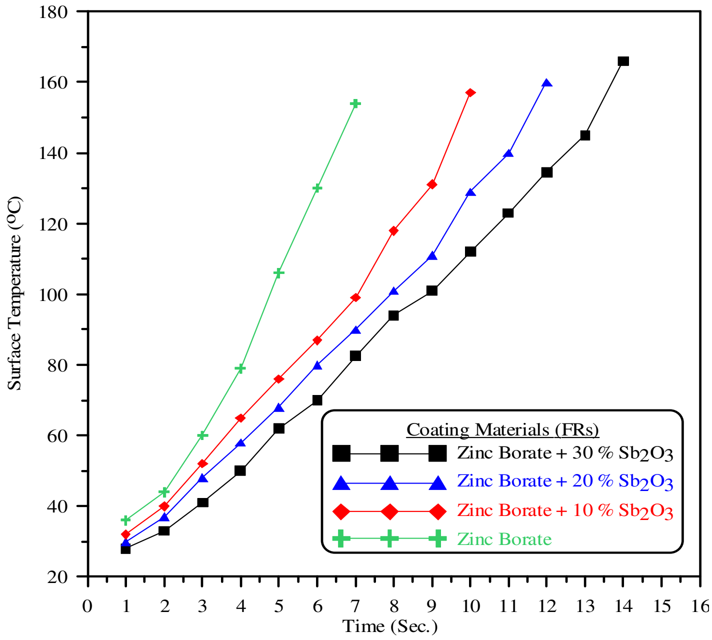

Fig. 5. Surface Temperature versus Time with Distance of 15 mm from the Flame Exposure Source.

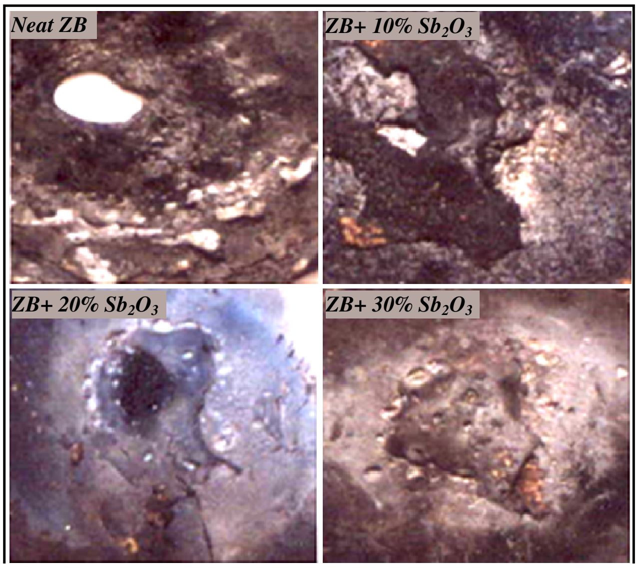

Fig. 6. Images of the Coated Composites by Zinc Borate (ZB) and Sb_2O_3 with Distance of 15 mm from the Flame Exposure.

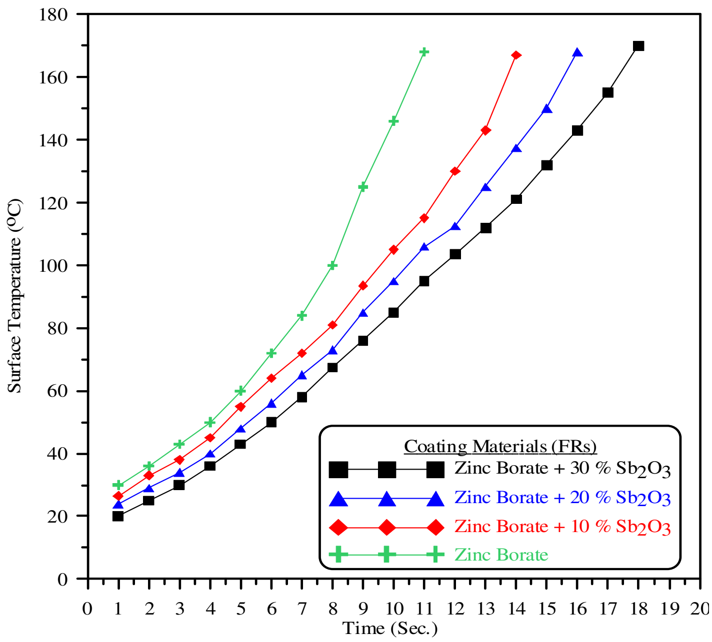

Fig. 7. Surface Temperature versus Time with Distance of 20 mm from the Flame Exposure Source.

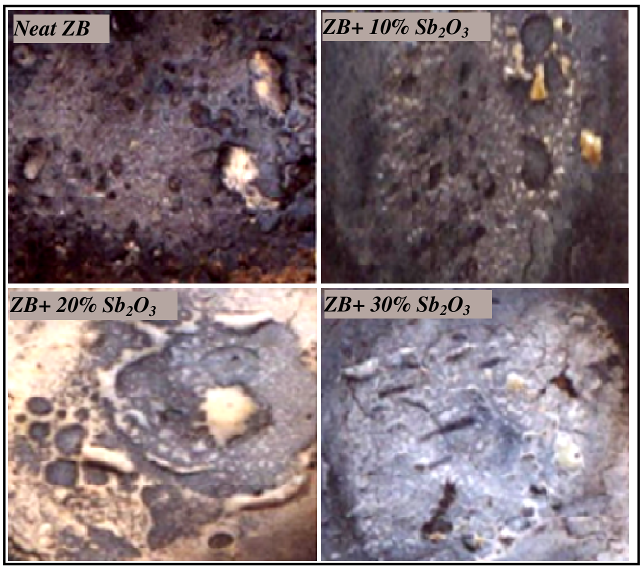

Fig. 8. Images of the Coated Composites by Zinc Borate (ZB) and Sb_2O_3 with Distance of 20 mm from the Flame Exposure.

4. Conclusions

The attempt was made to investigate the synergetic effect of using zinc borate modified by 10, 20, and 30 wt. % of antimony trioxide as flame retardant material on the pyrolysis behavior of hybrid fibers carbon-kevlar (50/50 wt/wt) reinforced araldite polymer composite by conducting the heat erosion test. The results of the time required to break down the coated layer of the composite increased due to forming the complex char from the interaction between the resin-intumescent-hybrid carbon/kevlar fibres which created due to the synergistic effect of the zinc borate and antimony trioxide flame retardant material.

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