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Effect of Boric Acid with Kaolin Clay on Thermal Degradation of Intumescent Fire Retardant Coating

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Abstract: In this study, we have discussed the thermal behaviour of intumescent coating. Intumescent coating is an insulating system designed to decrease heat transfer from a fire to substrate structure to maintain its integrity. The coating was based on Expandable Graphite (EG), Ammonium Poly Phosphate (APP), melamine, boric acid, kaolin clay ($Al_2Si_2O_5(OH)_4$), bisphenol. A epoxy resin BE-188 (BPA) and ACR hardener H-2310 polyamide amine as curing agent. Different formulations were developed to study the heat shielding effect. The C4 formulation showed better result on the heat shielding effect; it is further modified by adding kaolin clay 3-5 wt% in the next three formulations. Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM) was done to study thermal analysis and char morphology of the formulations. The result showed that by adding the filler kaolin clay, the fire retardant time of coating was extended. The result showed that thermal behaviour of intumescent coating formulation was improved with 5 wt% of kaolin clay.

Key words: Intumescent coating, fire retardant expandable graphite, kaolin clay, heat shielding

INTRODUCTION

Intumescence is a strategy in flame retardancy which involves the formation on heating of a swollen multicellular thermally stable char insulating the underlying material from the flame action (Camino and Delobel, 2000). It was known that steel structures are not stable at 500°C as it will lose its structural properties within that temperature. If the load bearing elements reach the temperature of 550°C, the structure will collapse and therefore, this failure will lead to explosion as load bearing elements contain a highly flammable material such hydrocarbons and natural gas.

In recent years, the release of toxic gases and smoke during the burning of halogenated flame retardant materials (Han *et al.*, 2007). To find alternative flame retardants due to increasing environmental and health concerns surrounding by using halogenated flame retardants. Expandable Graphite (EG) shows attractive applications as intumescent fire retardant as its large increase in volume with expansion factors more than 200 mL g⁻¹ (Duquesne *et al.*, 2002).

In previous studies expandable graphite was used as synergistic effect with APP-PER-MEL and polyethylene coatings. Because of performance of anti oxidation of APP-PER-MEL coating was not suitable (Li *et al.*, 2007). The synergistic effect is likely to come from reaction between pyrolyzing additives.

In this study, EG used as a carbon source, APP as an acid source, melamine as a blowing agent and boric acid Kaolin Clay are as an inorganic additives.

The objective of this study is to investigate the effect of boric acid and boric acid kaolin on the heat shielding effect of coating, residue weight and structure of char of EG-APP-Mel-boric acid-epoxy-hardener intumescent coating formulations.

MATERIALS AND METHODS

Materials: Kaolin Clay supplied from Jinyang Shanxi Jinyang Calcined kaolin Ltd. China. Bisphenol A epoxy resin BE-188 (BPA) and ACR Hardener H-2310 polyamide amine purchased from Mc-Growth Chemical Sdn. Bhd. (MGC) Selangor, Malaysia. Ammonium poly phosphate supplied by clarinet Germany, Flake Graphite supplied by Insutex Industries Sdn. Bhd. Malaysia, Boric acid, structural steel coupons.

Preparation of intumescent formulation: Expandable Graphite was prepared by the mixing of flake graphite with acetic acid, sulphuric acid and $KMnO_4$ 1: 2: 0. 5: 0. 07 with weight percentage, respectively in a conical flask. The flask was stirred at 25°C for 1 h (Tushinsky *et al.*, 2002; Bhagat, 2001; Wang *et al.*, 2007). The mixture was washed with distilled water. Leave the expandable graphite to dry in the oven at 60°C which is further used as a carbon source in the intumescent coating composition.

Table 1: Weight percentage composition of coating

No	EG	APP	Mel	Boric acid	Kaolin clay	BPA+ACR hardener*
C1	10	30	10	10		40
C2	10	20	20	10		40
C3	10	25	10	15		40
C4	15	20	10	15		40
KC5	15	20	10	12	3	40
KC6	15	20	10	11	4	40
KC7	15	20	10	10	5	40

*Noted that (BPA+ACR hardener) refers to curing agent

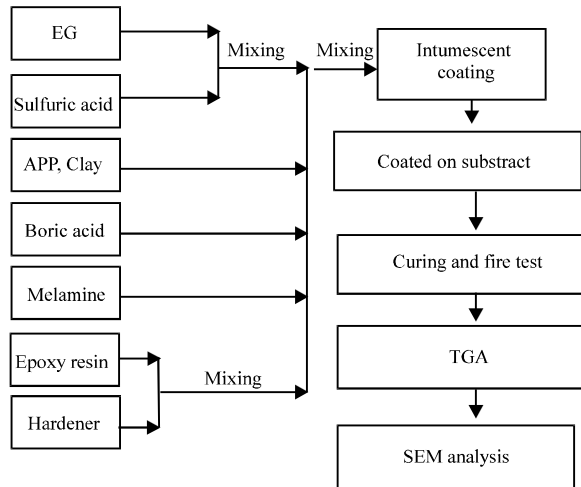


Fig. 1: Experimental flow chart

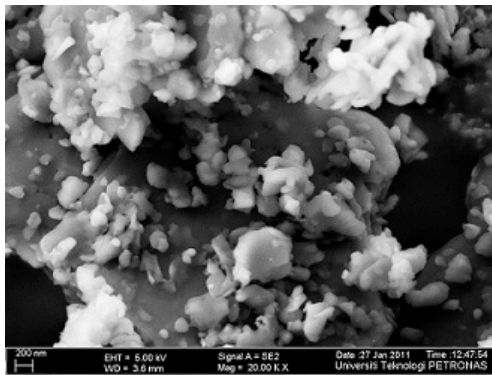


Fig. 2: The FESM image of kaolin clay

Figure 1 showed the experimental flow chart. The intumescent ingredients are mixed with their weight percentage composition homogeneously by using high shear mixer. C1, C2, C3 and C4 are controlled formulations with EG-APP-Mel-boric acid-epoxy-hardener. C4 formulation is further modified by adding 3-5 wt% of Kaolin Clay (KC) described in the Table 1. The Field Emission Scanning Electron Microscopy (FESEM) image of Kaolin clay is illustrated in Fig. 2. The formulation was coated manually on the steel substrate. The coated substrate was cured in the oven at 60°C for 4 h. Bunsen was used for fire test.

Analysis and characterization

Heat shielding effect: Bunsen burner was used as a fire test source by using the standard UL 94. K-type thermocouple is used to measure the temperature with AMS-850 data logger. The flame temperature of bunsen burner is 780°C.

Scanning electron microscopy (SEM): Charring layer and their morphological structures were observed and analyzed by AMARY 1000 SEM.

Thermogravimetric analysis (TGA): The Thermogravimetric analyses of samples (approximately 10 mg) were carried out at 20°C min⁻¹ under N₂, over the whole range of temperature (50-900°C) by TGA Q50.

RESULTS AND DISCUSSION

Heat shielding effect: In this study, four samples with different compositions of intumescent ingredients were prepared. After the fire testing was done, it was found that C4 that contains 15% of expandable graphite, 20% of ammonium polyphosphate, 10% of melamine, 15% of boric acid and 40% of epoxy-hardener mixture gives the best intumescent effect after fire testing being performed onto the samples. By using similar composition with C4, another three coatings were prepared by adding kaolin clay 3-5wt%.

The temperature time curves and data for the fire proofing time of flame retardant coatings are illustrated in Fig. 3, 4 and Table 1. The uncoated mild steel plate can only sustain its properties for about 9 min after the fire. Figure 3, formulation 1, it has the back side substrate temperature 426°C after 60 min. Formulation 2 has the back side substrate temperature of 395°C while formulation C3 and C4 has the back side substrate temperature 378 and 377°C after 60 min, respectively. From the result obtained, formulation C4 has the lowest backside substrate temperature followed by formulation C3, C2 and C1. This is because of the weight percentage of every component for each formulation. As shown in the Table 1, by comparing formulation C1 and C3 when boric acid is constant, the back side substrate temperature of formulation C3 is lower than formulation C1; this is because of the weight percentage of each component used. Formulation C4 gives the best intumescent effect as it contains 15 wt% percentage of expendable graphite. Expendable graphite will gives a better intumescent effect that lead to better intumescent effect.

As C4 formulation was modified with 3 to 5 wt% of Kaolin clay, the fireproofing time of the coating was increased dramatically. The result showed that the temperature was lowered to 336, 304 and 302°C after

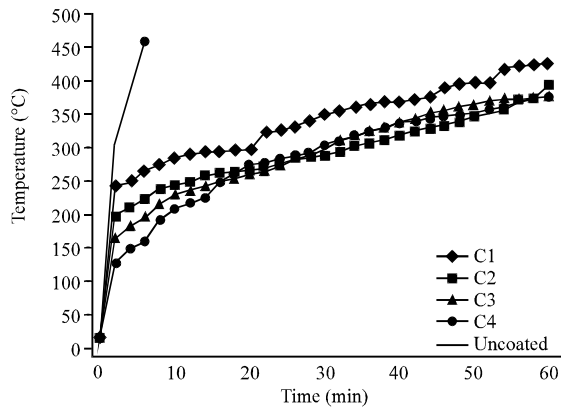


Fig. 3: Thermal behaviour of coating EG-APP-Mel-B.A- epoxy and hardener

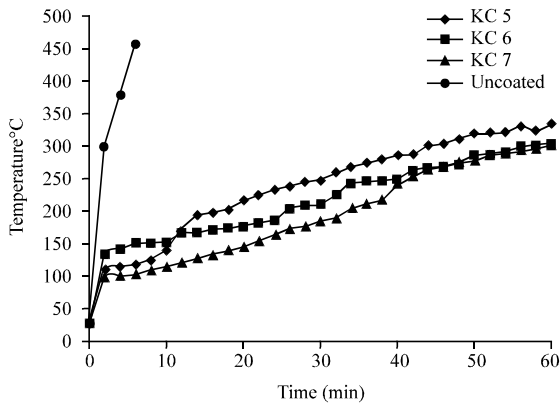


Fig. 4: Thermal behaviour of formulation modified with kaolin clay

60 min of kaolin clay coating KC5, KC6 and KC7, respectively. However, for samples containing Kaolin Clay, it shows that formulation KC7 gives the best intumescent effect as the temperature at the back of the steel is 302°C after 60 min fire test. A ceramic-like B₂O₃ layer would slow mass and heat transfer to the pyrolysis zone while the water vapour produced would serve to quench the flame, hence reducing its intensity (Nyamboa *et al.*, 2009).

This proved that, Kaolin clay as nano clay showed a better intumescent effect. This is the effect of adding the reinforcement material that will create a ceramic like protective barrier on the surface of the insulating material. Thus, it will give a better intumescent effect.

Scanning electron microscopy (SEM): The SEM micrograph of chars from the formulation C3 C4 presented in the Fig. 5 and 6, respectively. The multiporous structure

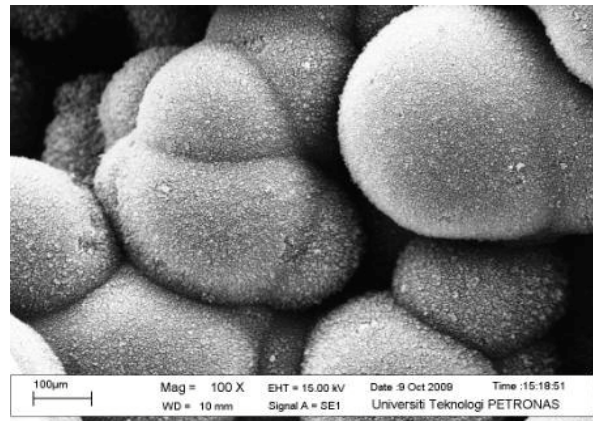


Fig. 5: SEM image of formulation C3

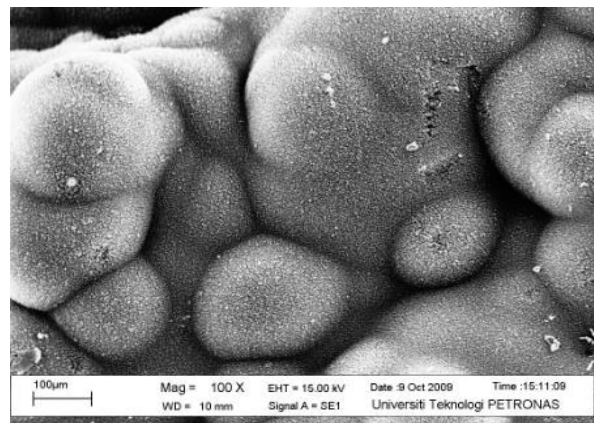


Fig. 6: SEM image of formulation C4

the char layer depends on the resistance of the substrate to fire. The expansion of the char and structure are very important to common fire resistant properties of coating (Li *et al.*, 2007). From Fig. 5 and 6, microstructure of C3 and C4 showed that the formation of bubbles. These bubbles expand the char due the emission of N₂ and ammonium gases (Jimenez *et al.*, 2006). It explains the dehydration charring of APP, Boric Acid and frothing of melamine proceeds in the range of rather appropriate temperature. The intumescent charring layers with bubbles act as the effect of the flame retardant, heat insulation and protecting inner matrix materials. can obstruct heat transferring to the substrate and protect the substrate from heat. Transfer speed of heat through. From Table 1, KC6, KC7 and KC8 modified the C4 EG-APP-Mel-B.A formulation with 3, 4 and 5 wt% of Kaolin are more compact than C3 and C4. The SEM images show the thick char structure of KC6, KC7 and KC8, respectively

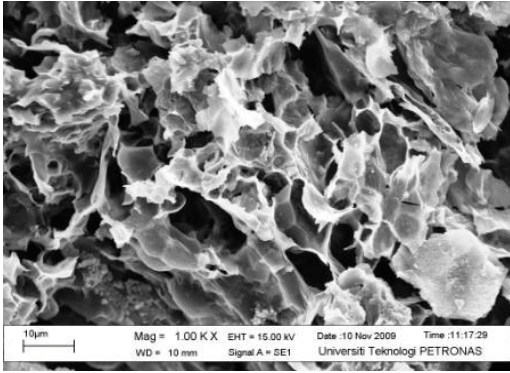


Fig. 7: SEM image of formulation KC5

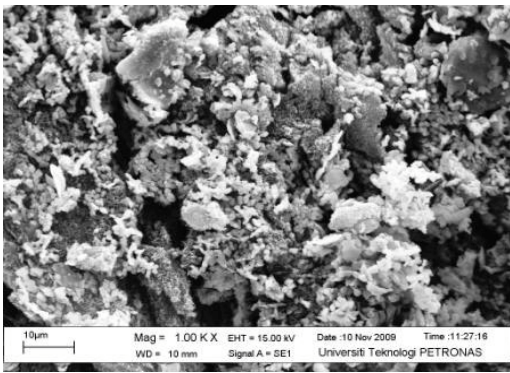


Fig. 8: SEM image formulation KC6

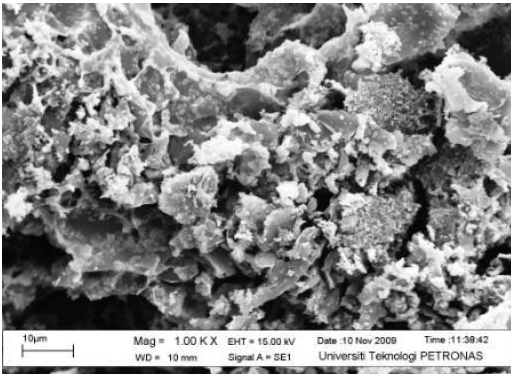


Fig. 9: SEM image formulation KC7

in Fig. 7-9. The cause is that kaolin Clay ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) acts as a filler hindered the expansion of EG-APP-Melboric acid coatings. The different aperture surface tensions in the route of gas cavities lead to the irregularity of swelling, the surface tension rely on the viscosity and regularity of the coating. Li *et al.* (2007) reported that

anti-oxidation of the coating was improved by adding EG and MoSi_2 and SEM images showed that a good synergistic effect was obtained through a ceramic-like layer produced by MoSi_2 enclosed on the surface of open-cellular structural char.

The SEM results show that the char of the coating modified by Kaolin is covered by a ceramic like open cellular protective layer on the steel substrate showed in Fig. 7.

Thermogravimetric analysis: The degradation of a pure APP has already been described by Camino and Luda (1998). Ammonium Polyphosphate (APP) will start to degrade to yield ammonia above 200°C (Cullis and Hirschler, 1981). Boric acid degrade into two step, first step $100\text{-}140^\circ\text{C}$ it is decomposed into metaboric acid and boron oxide at $140\text{-}200^\circ\text{C}$ in the second step (Jimenez *et al.*, 2006). Melamine will start to degrade at 290°C with the yield of ammonia and N_2 (Jimenez *et al.*, 2006). Graphite will start to degrade when temperature reached at $250\text{-}650^\circ\text{C}$ (Duquesnea *et al.*, 2001). However, the Kaolin clay will only degrade when the temperature is above than 1350°C (Lee *et al.*, 1989). Figure 10 TGA curve of C4 showed the decomposition of EG, APP, melamine, boric acid, epoxy and hardeners and the weight loss of the formulation is about 39% in the later stages.

It is also shown that the weight loss of the formulation C4 is 1% at the beginning of the experiment ($20\text{-}230^\circ\text{C}$), the moment is mostly due to fraction substance and resin decomposing, other volatilization vaporizing. The medium-term of the experiment ($230\text{-}510^\circ\text{C}$) is the key weight loss region that the coating begins to decompose largely, the weight loss gets to about 54%. The coating melts, APP decomposes to release NH_3 , H_2O and phosphoric acid (the catalytic effect is considered as a benefit since to be efficient the intumescent protective layer has to be formed in the early stages of a fire. For both resin/APP mixtures, a thermally stable protective layer is formed later on in the higher temperature range) thermally degrades, dehydrates to release poly-metaphosphoric acid and pyrophosphoric acid with other organic materials which contains hydroxy groups, dehydrates, to form the charring framework. At the same time, the vesicant ammonia begins to release NH_3 gas over 296°C (Gu *et al.*, 2007).

As the TGA maximum temperature is 900°C , the final weight percentage for samples with Kaolin clay are is slightly higher than samples without Kaolin clay because the kaolin clay will only degrade when the temperature reach 1350°C . Thus, Kaolin clay will remain in the residual char.

The results of the TGA show the similar behaviour of thermal degradation for each of the samples as the sample contains the same intumescent materials showed in

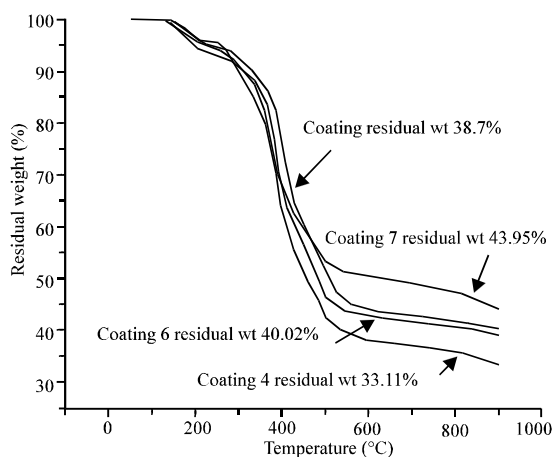


Fig. 10: TGA curve formulation C4, KC5, KC6 and KC7

Fig. 10. However, the rate of weight percentage loss slightly different as the weights percentages of each formulation are differ from each other. The remaining weight percentage of C4, KC5, KC6 and KC7 have 33.11, 38.7, 40.02 and 43.95%, respectively.

Based on these TGA result, it was observed that KC7 has the highest percentage of residual weight (43.95%) at the temperature 900°C. This shows that KC7 gives the best in tumescent effect compared to other formulations.

CONCLUSION

The fire retardant time of EG-APP-Mel-B.A coating modified by 5% wt kaolin clay was lowered the temperature of back side of substrate by various degrees. The KC7 showed the best result and the temperature of the backside of substrate was 302°C after 60 min. SEM result showed the structure of residue char was improved by adding kaolin clay. TGA showed that kaolin clay can enhance residue weight higher than that of EG-APP-Mel-boric acid-epoxy and hardener formulation C4. The largest improvement was achieved with 5 wt% of kaolin clay. Kaolin clay is a reinforcement material that will create a ceramic like protective barrier on the surface of the insulating materials. Thus, the efficiency of the heat transfer can be reduced and this will give a better effect of intumescent into the coatings.

REFERENCES

Bhagat, V.J., 2001. Behavior of Expandable Graphite as a Flame Retardant in Flexible Polyurethane Foam. Polyurethane Foam Association (PFA), Arlington, VA., USA.

Camino, G. and M.P. Luda, 1998. Mechanistic Study on Intumescence. In: Fire Retardancy of Polymers: The Use of Intumescence, Le-Bras, M., G. Camino, S. Bourbigot and R. Delobel (Eds.). Royal Society of Chemistry, Cambridge, pp: 48-63.

Camino, G. and R. Delobel, 2000. Intumescence. In: Fire Retardancy of Polymeric Materials, Grand, A.F. and C.A. Wilkie (Eds.). Marcel Dekker, New York, pp: 217-243.

Cullis, C.F. and M.M. Hirschler, 1981. The Combustion of Organic Polymers. Clarendon Press, Oxford, pp: 419.

Duquesne, S., M.L. Brasa, S. Bourbigot, R. Delobel and G. Camino *et al.*, 2001. Thermal degradation of polyurethane and polyurethane/expandable graphite coatings. *Polym. Degrad. Stab.*, 74: 493-499.

Duquesne, S., R. Delobel, M.L. Brasa and G. Camino, 2002. A comparative study of mechanism of action of ammonium polyphosphate and expandable graphite in polyurethane. *Polym. Degrad. Stab.*, 77: 333-344.

Gu, J.W., G.C. Zhanga, S.L. Donga, Q.Y. Zhanga and J. Konga, 2007. Study on preparation and fire-retardant mechanism analysis of intumescent flame-retardant coatings. *Surface Coatings Technol.*, 201: 7835-7841.

Han, Z., L. Dong, Y. Li and H. Zhao, 2007. A comparative study on the synergistic effect of expandable graphite with ammonium polyphosphate and IFR in polyethylene. *J. Fire Sci.*, 25: 79-91.

Jimenez, M., S. Duquesne and S. Bourbigot, 2006. Intumescent fire protective coating: Toward a better understanding of their mechanism of action. *Thermochim. Acta*, 449: 16-26.

Lee, H.L., H.J. Lim, S. Kim and H.B. Lee, 1989. Thermomechanical properties of β -sialon-sialon synthesized from kaolin. *J. Am. Ceramic Soc.*, 72: 1458-1461.

Li, G., G. Liang, T. He, Q. Yang and X. Song, 2007. Effects of EG and MoSi₂ on thermal degradation of intumescent coating. *Polym. Degrad. Stab.*, 92: 569-579.

Nyamboa, C., E. Kandareb and C.A. Wilkie, 2009. Thermal stability and flammability characteristics of ethylene vinyl acetate (EVA) composites blended with a phenyl phosphonate-intercalated layered double hydroxide (LDH), melamine polyphosphate and/or boric acid. *Polym. Degrad. Stab.*, 94: 513-520.

Tushinsky, L.I., I. Konsensky, A. Plokhov, V. Sindeyev and P. Reshedko, 2002. Coated Metal: Structures and Properties of Metal Coating Composition. Springer, UK.

Wang, Z., E. Han and W. Ke, 2007. Influence of expandable graphite on fire resistance and water resistance of flame-retardant coatings. *Corrosion Sci.*, 49: 2237-2253.