Fireproofing and heat insulating performance improvement of EG/ATH modified intumescent flame retardant coating treated under Co-60 radiation

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Abstract. New intumescent flame retardant (IFR) coatings with different fire retardants were prepared in this paper. Expandable graphite (EG) and Aluminium hydroxide (ATH) were respectively added into the conventional IFR coating system, which included ammonium polyphosphate (APP) / pentaerythritol (PER) / melamine (MEL). The fireproofing time and heat insulating properties of the additives acted as fire retardants were investigated via thermogravimetry analysis (TGA) and fire resistance test of homemade big panel test. The morphology of the char layer structure was achieved by scanning electron microscopy (SEM). The highlight of the paper was that the coating samples were pretreated under Co-60 radiation. The influence of radiation on the fire resistance time and char layer height was investigated. The results showed that the prepared IFR coatings can be used in Co-60 radiation for more than 90 min when encountering fire. It would be a reference for radiation shielding in nuclear environment.

1. Introduction

In recent decades, as energy shortage and environmental pollution are becoming more and more serious, importance is attached to the use of renewable energy. Thus nuclear energy has a very good prospect. However, the accidents happened reminds people of the risk of nuclear power plant. As was reported in Fukushima disaster [1,2], this disastrous accident was mainly due to earthquake and tsunami, damaging nuclear power plant’s cooling system. Then the explosion and fire happened, causing much fire in that scene. With so much radiation in the nuclear power plant, it’s hard for people to take rescue in such harsh environment. Thus rescue robots are widely used in nuclear power plant to withstand high-dose-rate radiation, high temperature and humidity [3]. To protect the rescue robots from fire and radiation, a new kind of intumescent flame retardant coating for fire and heat isolation, and part of radiation shielding is essential. The coating is also supposed to decrease the weight of the whole prototype.

In case of nuclear power plant accident, fire disaster may occur. The temperature of the aluminum alloy of robots shell substrate will exceed the melting point (600 °C), when it is exposed to the fire within 10 minutes [4]. Intumescent flame retardant coating is regarded as the most efficient and economical way to protect aluminum alloy substrate against fire. It was peripherally attached to the substrate as protective clothing. The coating will react once the fire and heat emerges [5-7]. As the chemical reaction occurs, the coating will expand and form a layer of char to prevent the flame from reaching the surface of protected substrate, slowing down the heat transfer to the aluminum alloy...
substrate \textsuperscript{18-13}. This kind of protection is useful in the way of the generation and collapse of pore in the intumescent char layer. When fire exists, the coating will become expandable and the flame or smoke burning and diffusing will be avoided. Thus, fire can be put out. Then the aluminum alloy substrate can maintain a low temperature under its melting point. To reduce the impact of oxidation and improve thermal insulation and fire retardant properties, different fillers with good incombustibility are considering to be added into the coatings \textsuperscript{14,20}.

In this paper, a kind of intumescent flame retardant (IFR) coating system, which is based on APP, PER and MEL, is achieved. To the best of our knowledge, this system of the three active ingredients is sensitive in harsh environment. It is unsatisfactory due to its bad performance in being easily oxidized and short-time flame retardance \textsuperscript{18}. Traditional flame retardant coating is not durable when exposed to external brutal scenes such as in nuclear power plant accident \textsuperscript{21}. So here, two popular materials, EG and ATH are added to the traditional flame-retardant system. As was reported in literature, EG, as the additive in the coating, perform extremely bad flammability and has no effects in the thermal degradation of composite coating \textsuperscript{18}. It can be easily oxidized at high temperature and be intumescent. ATH, usually used as fire retardants in this kind of coatings, can easily appear thermal decomposition \textsuperscript{22}. When the coating is exposed into fire, the components of the coating will react. After the reacting process, it will absorb the heat and send out H\textsubscript{2}O and CO\textsubscript{2}, which can maintain a low temperature of the substrate and intensify the structure of the char layer.

Because the study of effects of radiation on IFR coating is scarce, the main objective of this paper is to study the properties of the IFR under radiation condition and to investigate the performance and effects of the addition of EG, ATH and EG/ATH on heat insulation performance, residue weight and microscopy of the intumescent char layer.

2. Experimental section

In this research, many trials were conducted to figure out the appropriate proportion of the traditional IFR coating combined with APP, MEL and PER. The orthogonal design experimental method was used. The ratio of APP, MEL and PER was 5:3:3. After investigating the individual ratio and compound ratio of EG and ATH, the content of the final components of the IFR coating was determined. As a result, we chose 5 \% content of the EG and 9 \% content of ATH. The compound was also made up with 5 \% EG and 9 \% ATH.

2.1. Raw Materials and Performance

Considering two Benzene rings in this epoxy resin performed good radiation resistance and mechanical properties, bisphenol epoxy resin (E51) from Baling Petrochemical Company was used as matrix resin \textsuperscript{23}. The epoxy equivalent value of E51 was 184-210 g/Eq. It was usually used as fundamental resin and binder. Triethylenetetramine (TETA) was the curing agent of E51. It is a curing agent cured at room temperature. The purity of TETA acquired from Shanghai Aladdin Biochemical Technology Co. Ltd is CP, 68\%. The ratio of E51 and TETA we conducted was 5:2. In the traditional IFR coating system, APP, MEL and PER were used as acid source, blowing agent and carbon source respectively. They were bought from Shanghai Maclin Biochemical Technology Co. Ltd. EG provided by Qingdao Teng Shengda Carbon Machinery Co. Ltd expanded at a certain temperature and generated voluminous insulating layer as well. It was pretreated with H\textsubscript{2}SO\textsubscript{4} or HNO\textsubscript{3} that intercalated into the crystal structure of the graphite. These intercalated particles would expand in the perpendicular direction to the carbon layers in the crystal structure once came into high temperature \textsuperscript{17}. The particle size of EG was 50 meshes. EG was also used as a synergistic component of IFR coatings in some synthetic experiments \textsuperscript{21-24}. ATH with a particle size of 1-20 \textmu m was purchased from Shanghai Maclin Biochemical Technology Co. Ltd too. As the most commonly used mineral flame retardant, ATH is preferred because of its low toxic smoke releasing. All the auxiliaries like dispersion agent, antifoaming agent, film forming agent and flatting agent were bought from BYK Additives & Instruments, Germany.
2.2. Sample Preparation

IFR coating was prepared in accordance with the following method. Table 1 demonstrated the weight proportion of the IFR coatings.

2.2.1. Pretreatment

Before the experiment, all powder ingredients were dried at 80 °C for 4 h. The E51 was heated at 60 °C to gain good fluidity and to be well dispersed in solvent.

2.2.2. Weighing and mixing

The materials were weighed according to the proportion in Table 1 with electronic balance FA2004 made by Shanghai Fangrui Instrument Co. Ltd. The powders were mixed and ground in a mortar of large scale until the mixed powders were thin enough. Afterwards, the mixed powders were poured into the pre-weighed resin and stirred via a magnetic stirring for 20 minutes. Finally, the curing agent TETA was added to the mixture.

| Coating Number | E51(g) | TETA(g) | APP(g) | PER(g) | MEL(g) | EG(g) | ATH(g) |
|----------------|--------|---------|--------|--------|--------|-------|--------|
| No.1           | 12     | 4.8     | 12.08  | 7.25   | 7.25   | 0     | 0      |
| No.2           | 12     | 4.8     | 12.08  | 7.25   | 7.25   | 2.14  | 0      |
| No.3           | 12     | 4.8     | 12.08  | 7.25   | 7.25   | 0     | 3.85   |
| No.4           | 12     | 4.8     | 12.08  | 7.25   | 7.25   | 2.14  | 3.85   |

2.2.3. Brushing

The designed plate was shown in figure 1(a). It was made of aluminum alloy. The highlight of the design was its stack structure with three stages. The height of each stage was 1 mm. These stages were filled in to get proper thickness of the coating. This structure can ascertain the thickness of the coating and minimize the error of the experiment. The specific parameters of the plate were shown in figure 1(b). A rolling brush without brush hair was used to assure that there was no residual left on the coating. The compound coating was prepared layer by layer. In this process, the first layer was brushed for a while. After the surface of the first coating dried, another layer was brushed on the plate. After several times of the brushing and drying, a coating of 3 mm thickness was achieved.

2.3. Measurements and instruments

The coating samples were dried and totally hardened at ambient temperature for a week. To ensure full curing, the coating samples were tested by Thermogravimetry Analysis (TGA) method. Then all the coating samples were examined to get char layer formation by flame resistance test. We took the test under the guidance of big panel burning method in GB 12441-2005. Figure 2 illustrated the experimental installation process. As is shown in figure 2, the distance between fire and coating surface was 7 cm. The temperatures of the coating samples in two sides (front side and back side) were measured by thermocouples and recorded by AIGLENT 34970A data collecting instrument.
Meanwhile, the expansion of the char was measured too. After fire resistance test, the char surface morphology of combustion residues would be observed and analyzed by Scanning Electron Microscope (SEM). In order to investigate the property changes of the prepared flame retardant coatings before and after Co-60 radiation, the samples were placed in the Co-60 environment for 6 hours with the dose rate of 5kGy/h.

Figure 2. The experimental installation (a) Fire resistance test (b) The Co-60 radiation test

3. Results and discussion

3.1. TGA test of the coating samples
Thermal degradation of the coating samples was analyzed by TGA. The TGA test was carried out under Nitrogen atmosphere with a heating rate of 10 °C/min under temperatures from room temperature to 600 °C. Figure 3 illustrated the results of samples before and after Co-60 radiation.

Figure 3. TGA test results of different formulations before and after Co-60 radiation. (a) TGA curves of No.1 coating sample without fire retardants, (b) TGA curves of No.2 coating sample with EG, (c)
TGA curves of No.3 coating sample with ATH, (d) TGA curves of No.4 coating sample with both EG and ATH.

As can be seen from figure 3(a), the TGA curve of No.1 coating before radiation was similar to that sample after radiation at a temperature range of 250 °C to 600 °C. But the weight loss of them was quite different. The sample before radiation showed the ultimate residual weight 44.84 % at 450.43 °C, while the sample after radiation was 44.28 % at 462.6 °C. Obviously, Co-60 radiation caused the coating sample to decompose earlier at a lower initial temperature, with a weight percentage from 93.75 % at 212.54 °C after radiation to 88.34 % at 245.43 °C before radiation.

Figure 3(b) illustrated the No.2 coating with the additive of EG. From this picture, the curves were consistent from RT to 195 °C. The radiation will not influence the coating in that temperature range. The beginning decomposition statuses were marked in the graph at 225.63 °C and 215.72 °C, with the corresponding percentage of 90.12 % and 88.92 %. However, ignoring the weight loss value, the tendency of the curves was similar on the time or temperature scale. When the thermal decomposition finished, the final values were 45.12 % at 441.5 °C and 43.28 % at 451.32 °C respectively. The decomposition time after radiation was longer than before radiation. It illustrated that the addition of EG was adoptive in the coating. The fire resistance time will be longer by adding EG in the coating.

Figure 3(c) demonstrated the properties of the coating with the addition of ATH. The No.3 coating samples before and after radiation decomposed at nearly same temperature. One sample before radiation decomposed from 89.86 % at 224.41 °C. The other after radiation was from 89.82 % at 223.45 °C. Their decomposition process was definitely same from 300 °C to 600 °C. In the final step of the thermal decomposition, the residual weight of the coating was 46.34 % at 454.41 °C before radiation and 44.45 % at 448.45 °C after radiation. With the addition of ATH, the thermal decomposition of No.3 coating was faster after radiation than that of before radiation. It can be explained that ATH could enhance the synergism of the coating and maintain a good thermal decomposition property after Co-60 radiation.

Figure 3(d) showed the excellent performance of the coating with EG and ATH. The initial decomposition state was close to each other, with a mass residual rate of 89.82 % at 245.92 °C before radiation and 90.18 % at 238.89 °C after radiation. This indicated that the coating after radiation started to decompose earlier. However, at the end of the thermal decomposition, the statue of the sample before radiation finished in advance at 458.43 °C with a higher residual weight of 45.28 %, while the compared one after radiation finished later at 460.58 °C with a lower residual weight of 44.85 %. This result illustrated that the coating after radiation presented a longer time of thermal decomposition.

Above all, figure 3 indicated the different functions of the additives. Without additives, the weight loss was extremely higher than any other coating examples after radiation. With the addition of EG, the thermal decomposition time after radiation was prolonged. Moreover, the weight loss didn’t substantially change. This conclusion can be explained from figure 3(b) and figure 3(d). However, as was shown in figure 3(c), the time of thermal decomposition was decreased with the addition of ATH. These results demonstrated the similar thermal degradation pathway of these coating samples. And the weight loss of this degradation process can be contributed to the evaporation of unvolatilized solvent, water molecules and some other reacted substances. The shorter time in the thermal degradation of coating with added ATH showed that the ATH can be used as the catalyst of the intumescent flame retardant coating system. A rapid heat decomposition reaction may occur when it is exposed to a fire. Hence, the results of thermogravimetric analysis exhibited the thermal degradation process of coatings. They decomposed, absorbed heat, swell and form the protective char layers at different temperature ranges. The cooperated and synergistic reactions provided a good fire resistance property. The related data analysis is shown in table 2.
Table 2. Temperature difference and weight loss of coating samples before and after Co-60 radiation.

| Coating number | Figure 3 | Before radiation | After radiation |
|----------------|----------|------------------|-----------------|
|                |          | ∆T(°C) | ∆wt(%)      | ∆T(°C) | ∆wt(%)      |
| No.1           | a        | 205     | 43.5       | 250.06 | 49.47       |
| No.2           | b        | 215.87  | 45         | 235.6  | 45.64       |
| No.3           | c        | 230     | 43.52      | 225    | 45.37       |
| No.4           | d        | 212.51  | 44.54      | 221.69 | 45.33       |

3.2. Fire resistance test: big panel burning method

In figure 4, the temperature of both sides of the plate without coatings was showed. As can be seen from figure 4, the biggest temperature difference of the two sides was 15.3 °C. As time went by, the temperature of the two sides was almost the same. And it was fast enough to reach the specified temperature 300 °C in just 555 s. The short fire resistance time emphasized the importance of intumescent fire retardant coatings. Therefore, fire retardant coatings were necessary to protect the aluminium alloy plate.

![Figure 4](image)

**Figure 4.** Temperature in both sides of plain aluminium alloy plates in fire condition

The heat insulation property of flame retardant coatings was examined by the fire resistance test. The experimental installation was shown in figure 2(a). Fire resistance test coating samples were pretreated before and after radiation. Co-60 radiation test was presented in figure 2(b). When the back side temperature of the coating samples reached 300 °C, the corresponding time was defined as fire resistant time. The height of char layer was measured by vernier caliper. The curves of the temperature as a function of time were obtained by thermocouples of Agilent data collecting instrument. Table 3 illustrated the fire resistance time and char layer intumescent height. To investigate the fireproofing time and heat insulation property of the coating samples, a contrast test with a plain aluminium alloy was made. These results were shown in figure 4.

Table 3. The experimental testing and char layer height of the coating with 3 mm thickness before and after Co-60 radiation

| Coating number | Before radiation | After radiation |
|----------------|------------------|-----------------|
|                | Fire resistance  | Char layer      | Fire resistance  | Char layer      |
|                | time(min)        | height(mm)      | time(min)        | height(mm)      |
| No.1           | 125              | 13              | 90              | 10              |
| No.2           | 150              | 20              | 94              | 15              |
| No.3           | 128              | 15              | 116             | 13              |
| No.4           | 130              | 32              | 110             | 25              |
As can be seen from table 3, the whole tendency of flame retardant coatings after radiation was slightly influenced by Co-60 radiation. Both of the fire resistance time and char layer height were consistently decreased after the radiation of Co-60. Moreover, ignoring the spalling of the coating exposed to fire in long time, the intumescence was significantly improved with the addition of EG in No.2 coating. The decrease of fireproofing time may result from the loose and fragile properties of intumescent char layer. However, when the APP-PER-MEL No.1 coating was modified with ATH, the coating was well bonded with the aluminium alloy. And the fire resistance time and char layer height didn’t vary much after radiation. Thus, with the addition of both EG and ATH, the coating can combine the good performance of each other. Then it presented good adhesion and flame retardant properties.

3.3. Morphological structures of intumescent chars obtained from coatings with SEM test before and after Co-60 radiation
As can be seen from figure 5, a clear view of the microscopic structure of the char layer after big panel fire test can be observed. It demonstrated that the coatings were slightly broken to pieces after Co-60 radiation. Figure 5(a) showed the char layer was not compact. There were no holes. Some cracks appeared. In figure 5(b), there was wormlike expanded graphite formed by EG with the diameter of 250 μm. A continuous and multiporous char layer structure can be observed in figure 5(d), which looked like honeycomb. This porous structure can form an insulating layer to block heat transferring to the alloy plate. In figure 5(d), the EG was embedded in char structure. And the EG in No.4 coating can act as fiber to enhance the structure of char layer and protect it from deforming. The cracks of No.4 coating were fewer than No.3 coating. Figure 5(c) showed the structure of coating with ATH. When compared with figure 5(a), No.3 coating was more compact and homogeneous. The residual char layer was flaky. Therefore, the char structure can provide a shield to protect the substrate from radiant heat and fire. The longer fireproof time of the No.4 coating can meet the heat insulation and flame retardant requirements.

4. Conclusion
The main conclusions of the paper are as follows:
(1) All the performance of coating samples decrease after Co-60 radiation. The TGA, fire resistance test and SEM characterization method were used to explain the specific details.
(2) TGA and fire resistance test showed that with different additives of flame retardants, the coating samples presented different performances respectively. EG can dramatically improve the intumescent char layer height and block heat transferring, but decrease the adhesion ability with alloy plate. ATH can be used as both catalyst and the flame retardant in the intumescent system. While EG and ATH are simultaneously added into the system, the merits of each other can be obtained.
(3) The SEM analysis indicated that the coating with the addition of ATH and EG can prevent the coating from falling off and form an intumescent char layer structure with porous holes to insulate heat and fire.

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