

Effects of graphene content on formation and characteristics of char layer in intumescent coating

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Abstract. This study provides a better understanding of the role and mechanism of graphene nano-platelets used as a flame-retardant filler in a commercial intumescent acrylic-based formulation. Through thermogravimetric analysis, the morphology and mechanical properties of the char layer as well as the influence of graphene on the expansion ratio and compression force are clarified. The achieved results demonstrate that graphene accelerates the burning of the coating and affects the structure of the char layer. The fire test was carried out in an electric furnace at a temperature of up to 800 °C for our fabricated samples, the swelling images show that the expansion ratio of the graphene-loaded coating is lower than that of the coating without graphene. On the other hand, during the combustion, the speed of air release occurring in a short time also contributes to forming bigger holes in the char layer, so the hardness of the graphene-loaded char layer is lower than that of the char layer without graphene coating.

Keywords: flameretardant coating, intumescent, graphene, char layer.

Classification numbers: 2.3.1, 2.5.3, 2.9.3.

1. INTRODUCTION

Intumescent polymer coatings are used to enhance the fire resistance of load-bearing structures and structural steel, it is a common method and widely used in practice [1 - 5]. A basic

intumescent system is composed of three main components: i) an acid source (ammonium polyphosphate); ii) a carbon source (same as pentaerythritol); and iii) a gas-generating agent (mostly melamine is used). In addition, the intumescent system also includes film-forming agents (organic polymers) and other reinforcing additives. The swelling process usually starts at around 250 °C to produce a charred layer that is then stabilized at 600 °C [6 - 12].

A basic component of an intumescent coating system produces a porous and soft layer that does not maintain long-term insulation [13 - 15]. To improve the fire resistance of the intumescent coating, fillers have been studied such as expandable graphite, graphene or carbon nanotube (CNT) [16 - 19], nano-sized SiO₂ or TiO₂ particles [20 - 22], Al(OH)₃ [23], 4A zeolite [24], glass filler [25], bentonite clay [26] and silicotungstic acid [27], etc. for creating a carbonized layer with a stable microstructure. However, they have not brought the expected improvement in thermal insulation for the carbonized layer, but also increased the product cost.

Recently, the graphene has been receiving extensive research attention because of its environmental friendliness, low density, and high strength. In the field of polymer materials, especially protective coatings, graphene with a flake-like structure and good UV resistance has been studied and incorporated into protective coating systems to increase longevity and resist environmental impacts [16 - 18]. In the last few years, several research groups focusing on graphene-filled intumescent systems have published some favorable results [16]. Thus, the study group used graphene fabricated in the Center for High-Tech Development, Vietnam Academy of Science and Technology to evaluate the influence of this graphene on thermal properties, carbonized layer formation as well as durability.

2. MATERIALS AND METHODS

2.1. Materials

The flame retardant additives used in this study included ammonium polyphosphate (NH₄ PO₃)_n with n>1000 (APP) provided by Clariant (Germany), pentaerythritol (PER) supplied by Perstorp (Singapore), and melamine (MEL) - a product of Er Sheng (China). The binding polymer was a thermoplastic acrylic resin with an average molecular weight of 60,000 g/mol from Mitsubishi, (Japan). Xylene solvent and titanium dioxide (rutile) were commercial products of China and Korea. Graphene was manufactured by the Center for High-Tech Development, Vietnam Academy of Science and Technology.

2.2. Preparation

a. Preparation of graphene

In this study, the graphene was used in the form of graphene nano-platelets (GNPs) fabricated by thermal shock technique from commercial GICs (graphite intercalation compounds) with a purity of 98 %, using intercalated H₂SO₄. First, the GICs were spread thinly on an electrode and vibrated with a frequency of 5 - 15 Hz. The electrode tray consisted of two electrode rods with a diameter of 2 mm placed opposite and parallel to each other on an insulating ceramic plate. The electric current flowing through the GIC particles located between the electrodes rapidly increased the temperature of the material (up to 500 °C) according to the Joule effect. The GICs were subjected to thermal shock and then expanded into graphene nano-platelets. The GNPs were obtained in a powder form and were graphene/graphite sheets with a

diameter of 100 - 150 μm , a thickness of 0.5 - 15 nm, a purity of 99 %, and a specific surface area of 80 - 100 m^2/g .

b. Preparation of intumescent coating

The coating was prepared by the high-speed stirring method. The binding agent (acrylic resin) was dispersed in xylene before adding flame retardant additives (APP, MEL, PER). The mixture was homogenized for 8 hours at a stirring speed of 1500 rpm on a Velp Scientifica stirring device which could reach a speed of 2000 rpm and a power of 120 W. The composition of the material is listed in Table 1. The intumescent coating was sprayed onto steel plates ($50 \times 100 \times 2$ mm) and completely dried at room temperature for 3 days in a ventilated environment before burning experiments. The average thickness of the samples was 500 μm .

Table 1. Composition of intumescent coating.

unit: wt.%

Ingredient	Name				
	G0	G005	G01	G03	G05
Acrylic resin	20	20	20	20	20
APP	39	39	39	39	39
PER	13	13	13	13	13
MEL	13	13	13	13	13
TiO ₂	15	15	15	15	15
Graphene	0	0.05	0.1	0.3	0.5

2.3. Methods

a. Sample burning

Samples were burned in a Carbolite furnace using a heating cycle shown in Figure 1. The temperature was kept constant at 50 °C for 15 minutes, then raised to 800 °C and the dwell time was 30 minutes to completely burn the samples. After that, the samples were cooled for about 30 minutes to prevent their cracking (Figure 2).

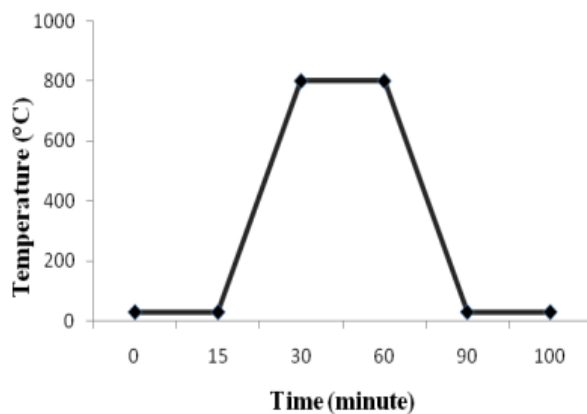


Figure 1. Heating cycle for burning test.



Figure 2. Coating samples after combustion.

b. Thermogravimetric analysis (TGA)

The thermal properties and weight loss of the coating samples were evaluated on a TGA Setaram thermogravimetric analyzer from room temperature to 800 °C at a heating rate of 10 °C/min in air.

c. Observation of charred layer morphology

The morphology and structure of the carbonized layer were observed by imaging the sample surface after coating. A Hitachi S-4800 Field Emission Scanning Electron Microscope (FE-SEM) was used for obtaining the inner structure of the carbonized layer.

d. Determination of the swelling coefficient and hardness of the charred layer

The ratio between the thickness of the charred layer after burning and the thickness of the sample before burning is calculated for determining the swelling of the intumescent coating. The thickness of the initial coating was determined on a magnetic gauge with a maximum accuracy of 1 µm, and the thickness of the charred layer was obtained on a caliper with an accuracy of 0.1 mm.

The hardness of the carbonized layer was measured through compressive stress on a GOTECH AI-7000M material tester with 1 kN force sensor at a compression speed of 10 mm/min. The compressive stress of the charred layer was determined at the times when the compressibility reached 10 %, 20 %, and 30 % compared to the thickness of the initial charred layer (Figure 3). At higher compressions, the charred layers were often broken or the compressive force was unstable.

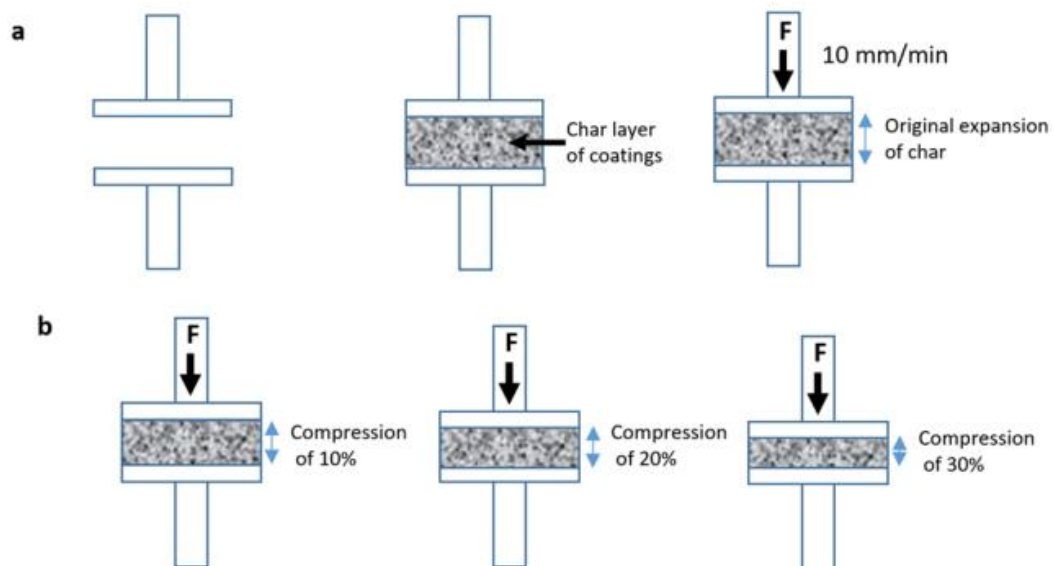


Figure 3. Compression test for determining the hardness of char layer.

3. RESULTS AND DISCUSSION

3.1. Fire characteristics

To understand the coating performance during combustion, thermogravimetric analysis was carried out on the initial coating sample. Figure 4 shows the decomposition of coating samples with and without graphene during increasing temperatures. The analysis results show that the charred layer formation includes two stages. The first stage is in the temperature range of 200 °C to about 400 °C and the second one is above 500 °C to 650 °C. From 200 °C, APP begins to decompose to polyphosphoric acid and releases NH₃. A large amount of ester is produced from a reaction of PER with polyphosphoric acid. At temperatures above 250 °C, the binder melts to form a liquid/viscous matrix. Above 300 °C, a decomposition of melamine releases NH₃, allowing the binder and ester to form a char layer at 300 - 440 °C. As the temperature increases up to 500 °C, carbon dioxide is generated and escapes from the char layer.

The two weight-loss stages of the coating can be distinguished more clearly in the graphene-containing samples, which illustrates that graphene contributes to accelerating the combustion of the coating in the first stage. This fact can be somewhat detrimental to the thermal insulating of the coating as the combustion of a coating containing graphene releases more heat than non-graphene coatings. The presence of graphene not only accelerates the combustion of the coating but also forms a loose and porous carbonized layer.

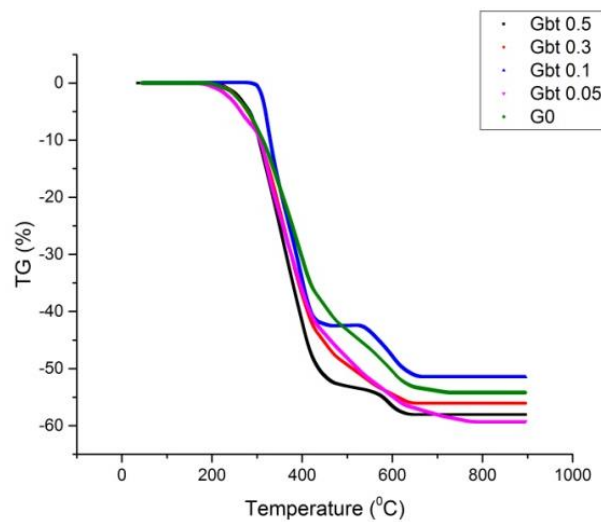


Figure 4. Thermogravimetric analysis of coating samples.

3.2. Observing the morphology and structure of the charred layer after burning

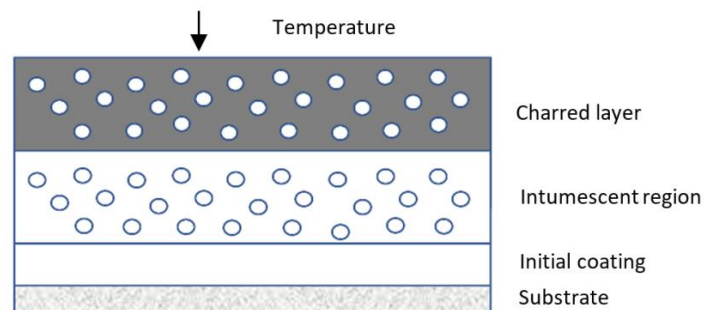


Figure 5. The process of combustion and the formation of a charred layer.

The charred layer formation plays an important role in the efficiency of the thermal insulating and protection performance of materials. The simultaneous reactions take place continuously in a melted state of a mixture of the coating during charred layer formation (as described in Section 3.1). Besides, the swelling and charred layer formation process usually occurs from the outside, which is directly exposed to the heat source to inside of the coating (as depicted in Figure 5). Figure 6 shows the images of the coating after burning and SEM image of the charred layer.

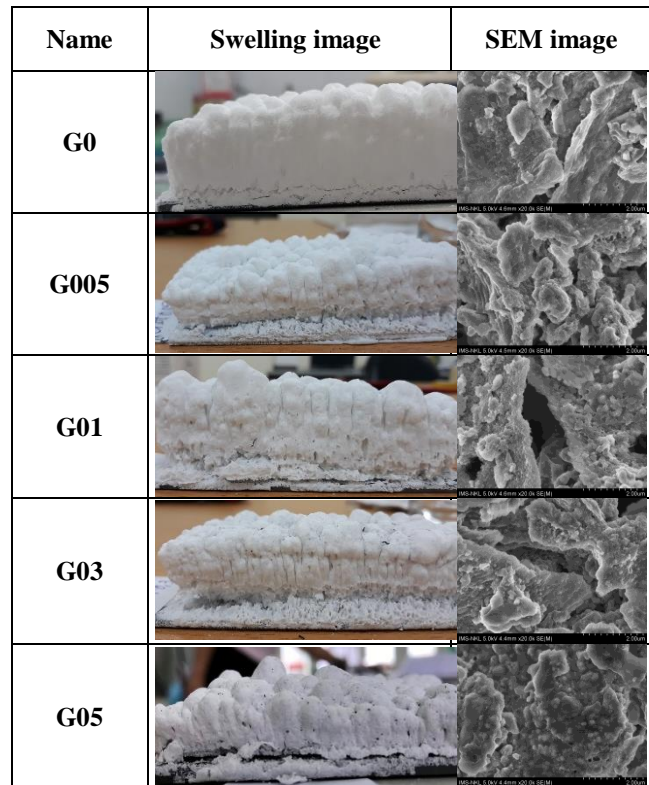


Figure 6. Image of the intumescent coating after burning and SEM image of the charred layer.

As mentioned in Section 3.1, graphene contributes to accelerating the combustion of the coating, causing faster decomposition and swelling reactions. The images of the charred layer after the combustion are shown in Figure 6, demonstrating that the charred layer structure of the graphene-containing coatings is not compacted as the non-graphene coating. Besides, the delamination of the charred layer with the substrate can be realized clearly in graphene-added coatings. It can be predicted that there is strong outgassing in the intumescent region that is not directly exposed to the heat source, which is the main difference compared to the non-graphene cases.

3.3. The expansion ratio and hardness of the carbonized layer

The thick intumescence improves the thermal insulation of the charred layer for the substrate, while the hardness of the charred layer maintains the insulation for a longer period. In general, the thicker the intumescence, the smaller the hardness of the charred layer. In this study, the effect of graphene content on the intumescence and the hardness of the charred layer were

evaluated by compressive stress. The obtained results confirm that the coating with graphene has lower swelling and hardness than the non-graphene coatings.

The effect of graphene content shows that the intumescence is highest for the coating containing 0.1 % graphene (expansion of 39.47 times). Meanwhile, the coating with a graphene content of 0.1 % has the compressive force of the charred layer reaching the highest value at 10 % strain (4.2 N), as shown in Tables 2 and Tables 3. It can be seen that the presence of graphene accelerates the burning and intumescent process in the layer of materials that is not directly exposed to the heat source. It adversely affects the intumescence as well as the hardness of the charred layer.

Table 2. Swelling coefficient of coating samples.

Name	G0	G005	G01	G03	G05
Expansion ratio (times)	47.84	37.96	39.47	37.09	36.67

Table 3. Compression forces at different ratios compared to the initial thickness of the charred layer.

Name	Compression force at 10 % (N)	Compression force at 20 % (N)	Compression force at 30 % (N)
G0	7.4	8.7	9.2
G005	3.3	5.3	7.8
G01	4.2	6.0	8.7
G03	3.9	6.2	9.2
G05	2.7	5.5	9.6

4. CONCLUSIONS

The melting process of the APP-PER-MEL-based intumescent coatings takes place faster in the temperature range of 250 - 450 °C in the presence of graphene. This causes the intumescent thickness of the graphene-containing coatings to be smaller than that of the initial coating, simultaneously, the porosity inside the charred layer is larger due to the strong release of air in a short time. Then, their hardness is lower than the non-graphene coating. Among the coatings with different graphene contents, the coating with 0.1 wt.% graphene (G01) reveals the best results. It has the highest expansion ratio and compression forces. Besides, it increases the ignition temperature up to 300 °C.

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CRedit authorship contribution statement. All authors contributed to the conceptualization and realization of the study. Phan Ngoc Hong, Vu The Ninh, Tran Thu Trang, Nguyen Thi Lien, Giang Thi Phuong Ly and Nguyen Viet Dung conceived the idea. The experiments were carried out by Nguyen Tuan Hong, Nguyen Anh Duc, Nguyen Thi Ngoc Tu, and Le Van Duan. Phan Ngoc Hong, Nguyen Tuan Hong, Nguyen Anh Duc, and Nguyen Viet Dung analyzed and wrote the paper. All of the authors discussed and commented on the manuscript.

Declaration of competing interest. There are no conflicts to declare.

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