Research and manufacture water-based fire retardant coating mixture using graphene additive for natural wood

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ABSTRACT

Intumescent fire-retardant coatings, especially water-based intumescent fire-retardant coatings, are increasingly attracting attention due to their environmentally friendly properties. In this work, we have successfully manufactured a water-based fire retardant coating mixture using graphene additive for natural wood with three main ingredients (ammonium polyphosphate acidifying agent, pentaerythritol carbonizing agent, melamine blowing agent), and some additives including graphene. We investigated the influence of graphene content on the fire retardant effectiveness of the mixture when coated on natural wood (pine wood) according to UL94-V standard. Test results show that the content of graphene contributes to enhancing the fire retardant effectiveness of the manufactured mixture. SEM imaging method was used to analyze and explain the test results. Some specifications of the manufactured mixture are also analyzed and evaluated. The findings of this research provide a solution to enhance fire resistance for natural wood structures using environmentally friendly materials.

Keywords: Water-based fire retardant coating mixture; Intumescent coating; Graphene; Natural wood.

1. INTRODUCTION

Fires are always a serious threat to human life and property. Passive fire protection is one of the commonly used solutions to prevent and reduce the impact of fires [1]. This solution is increasingly receiving attention due to its ability to prevent structural collapse, slow down the combustion process of materials, thereby prolonging the evacuation time for people and valuable assets [2]. In the past, inorganic intumescent flame retardant coatings were widely used because of their low cost, but they had limitations in durability and water resistance. These days, organic intumescent coatings are becoming more popular because of their outstanding advantages, such as fireproof performance, aesthetics, ease of application, better water resistance, and more stability in weather conditions. Therefore, they can be used for coating both indoors and outdoors [1]. Organic intumescent flame retardant coating film is based on three main components, including acid agent, charring agent and swelling agent [3]. Water-based intumescent fire-retardant coatings are organic intumescent fire-retardant coatings with water-based adhesives, they are both environmentally friendly and have good fire resistance for many different solid materials [4].

Graphene-based flame retardant additives are a new research direction in flame retardant materials in recent years [5, 6]. Graphene is a two-dimensional material which is composed of layers of carbon atoms arranged as a honeycomb network, and it has unique electron and photon transport behavior. Graphene has excellent thermal conductivity (5000 $Wm^{-1}K^{-1}$), high Young's modulus (1 TPa) and mechanical hardness (130 GPa), large theoretical specific surface area (2630 m^2g^{-1}), high charge carrier mobility (200000 $cm^2V^{-1}s^{-1}$), and optical transmittance (98%) [5]. With excellent thermal conductivity, graphene allows heat to pass through and dissipate very quickly [7]. Besides, graphene has high mechanical strength, so it has the ability to increase the durability of carbon films, which are formed during the combustion process of flame retardant additives [8]. Thanks to its unique two-dimensional layered structure, graphene can promote the formation of a continuous dense layer of char during the decomposition process. Many studies have shown that graphene can not only enhance the fireproof properties of the mixture but also enhance the mechanical properties of the mixture [6], so graphene has been researched and applied in fire retardant coatings for polymer [9], steel [10], cotton [11].

In this study, having used graphene additive and three main components, including ammonium polyphosphate acidifying agent, pentaerythritol carbonizing agent, and melamine blowing agent, we successfully research and manufacture a water-based fire retardant coating mixture for pine wood. After being manufactured, the mixture is coated on pine wood samples. Then, these wood samples were burned to evaluate the fire retardant effectiveness of the mixture according to UL94-V standard. In addition, SEM images of the coating film before and after combustion are taken to analyze and explain the experimental results. Finally, some specifications of the manufactured mixture are also analyzed and evaluated.

2. PREPARATION OF MATERIALS AND PRODUCTION

2.1. Chemicals and equipment

2.1.1. Chemicals

The three main components of the coating mixture are ammonium polyphosphate (APP), chemical formula $[NH_4PO_3]_n$ with n > 1000, molar mass MW = 97.01 g/mol; pentaerythritol (PER), molecular formula $C_5H_{12}O_4$, molar mass MW = 136.15 g/mol; melamine (MEL), molecular formula $C_3H_6N_6$, molar mass MW = 126.12 g/mol. APP and PER are manufactured by Shifang Changfeng Chemical Co., LTD., China. MEL which is manufactured by Sichuan Golden-Elephant Sincerity Chemical Co., Ltd., China with purity ≥ 99.5%. Graphene which is made in Vietnam is of density 0.015 g/ml, diameter 10-20 µm, particle size less than 5 nm, and purity 99%. Other additives include fatty alcohol ethoxylate 8 (FA8+EO) dispersing aid (made in Indonesia); TiO_2 whitening agent which is manufactured by Cosmo, Korea is of purity ≥ 98%, particle size 0.3-0.05 µm); carbonxyl methyl cellulose (CMC) thickener which is manufactured by Shanghai Jizhi Biochemical Technology Co., Ltd., China with chemical formula $C_8H_{16}O_8$, and molar mass MW = 240.20800 g/mol); bentonite anti-sediment agent (made in Vietnam); triethanolamine gloss agent (TEA) (made in Malaysia); EG-S926 anti-foaming agent (made in China); $CaCO_3$ porosity additive (made in Vietnam). These chemicals are dispersed in distilled water (once time) with ethylene vinyl acetate copolymer (EVA) film-forming agent which is manufactured by Shanghai Jizhi Biochemical Technology Co., Ltd., China bears with chemical formula $(C_4H_6O_2.C_2H_4)x$, and molar mass MW = 114.14200 g/mol to create a water-based fire-retardant coating mixtures for natural wood. The chemical ingredients of the mixtures are presented in table 1.

Table 1. *Chemical ingredients of fire retardant coating mixture samples.*

Ingredients (% by weight)	Samples				
	M0	M1	M2	M3	M4
APP	17.5	17.5	17.5	17.5	17.5
PER	7	7	7	7	7
MEL	7	7	7	7	7
EVA	8	8	8	8	8
Water	54.49	54.39	54.29	53.99	53.49
Graphene	0	0.1	0.2	0.5	1
Other additives	6.1	6.1	6.1	6.1	6.1
Other additives include FA8+EO (0.01%), TiO_2 (2%), CMC (1%), Bentonite (1%) TEA (1%), EG-S926 (0.5%), $CaCO_3$ (0.5%)					

2.1.2. Equipment

The equipment used to produce a water-based fire retardant coating mixture using graphene additive for natural wood includes volumetric flasks; electronic scale (PA2102, Ohaus, USA); distilled water jet tank; glass rod; stirrer (high-speed dispersion homogenizer, AD500S-H, Angni, China); sample rack.

The equipment used to evaluate the fire retardant effectiveness of the coating mixture according to the UL94-V standard includes a sample clamp, a Bunsen burner connected to the gas tank, a stopwatch (PC894, made in China); pine wood samples with dimensions of (125x13x13) mm, and a paintbrush.

The Hitachi S-4800 scanning electron microscope was used as the equipment to determine the morphology and structure of the coating before being burned and the char layer after combustion according to the UL94-V standard.

2.2. Production and measurement

2.2.1. Production and evaluation process

The process of production of water-based fire retardant coating mixture and evaluation of the fire retardant effectiveness of the mixture for natural wood is carried out according to the steps shown in figure 1, specifically including: (i) preparing materials in a determined ratio; (ii) mix and stir with a high-speed dispersion homogenizer at 6000 rpm for 1 hour to form a homogeneous mixture; (iii) paint the produced mixture once on pine wood samples that have dimensions of (125x13x13) mm; (iv) let the pine wood samples naturally dry for 2-3 days (laboratory conditions, no wind, humidity 60-80%, temperature 25-30 ^oC); (v) evaluate the fire retardant effectiveness of the coating mixture according to the UL94-V standard.

2.2.2. Evaluation of the fire retardant effectiveness of the manufactured mixture for natural wood

Evaluation of the fire retardant effectiveness of the manufactured coating mixtures for natural wood (pine wood) is conducted according to the UL94-V standard (figure 1). For each type of produced mixture, we need to determine the total burning time of 5 pine wood samples coated by that mixture. These pine wood samples are placed vertically and fixed at one end by a clamp. Place the Bunsen burner under the end of the pine wood samples so that the distance between them is equal to 10 mm and the flame of the burner impacts the pine wood sample vertically by 10 mm. Burning time and combustion time are determined as follows: first burn for 10 seconds, record the combustion time of the pine wood sample until it turns off. Immediately, then burn a second time and do the same. The total combustion time of each pine wood sample is its total combustion time after two times burning. The total combustion time of 5 pine wood samples of the same type will be used to evaluate the level of fire resistance according to the UL94-V standard.

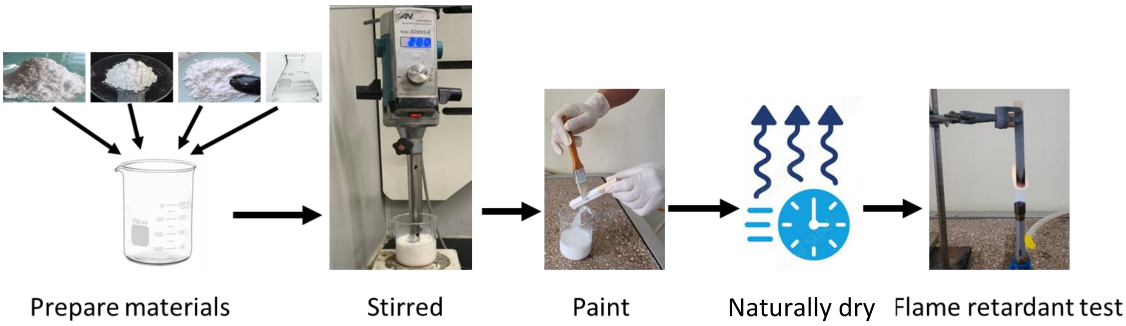

Figure 1. *The process of production of water-based fire retardant coating mixture and evaluation of the fire retardant effectiveness of the mixture for natural wood according to the UL94-V standard.*

The morphology and structure of the coating before burning and the char layer after combustion tested according to the UL94-V standard are investigated SEM image method using Hitachi S- 4800 scanning electron microscope.

3. RESULTS AND DISCUSSION

Figure 2 shows images of pine wood samples coated with manufactured fire retardant coating mixtures as in table 1. In which G0 is a pine wood sample coated with fire retardant coating mixture without graphene additive; G1, G2, G3, G4 are pine wood samples coated with fire retardant coating mixtures with graphene content of 0.1%, 0.2%, 0.5%, 1%, respectively. It can be seen that the G0 sample is white while the G1, G2, G3, and G4 samples are gray; pine wood samples coated with fire retardant coating mixtures with higher graphene content have a darker gray color because graphene is black. Because the graphene content is not large, the surfaces of the fire retardant coatings have a relatively similar uniformity. Details of the bond between the coating films and the pine wood substrates are shown in the SEM images in figure 4. Naturally dried pine wood samples are burned to evaluate the fire retardant effectiveness of the coating mixtures according to the UL94-V standard. Figure 3 shows G0, G1, G2, G3, and G4 pine wood samples after two burns, each burn lasts 10 seconds. Each pine wood sample is burned for the first 10 seconds and then the flame is taken out of the pine wood sample. If the pinewood sample does not combust, it is burned immediately for the next 10 seconds; if the pine wood sample combusts, take the flame out of the pine wood sample, wait for the pine wood sample to extinguish itself, then it is burned immediately for the next 10 seconds. For each sample of fire retardant coating mixture in table 1, we conducted a test with 5 same type pine wood samples, the total combustion time after each burn of 10 seconds is summarized in table 2.

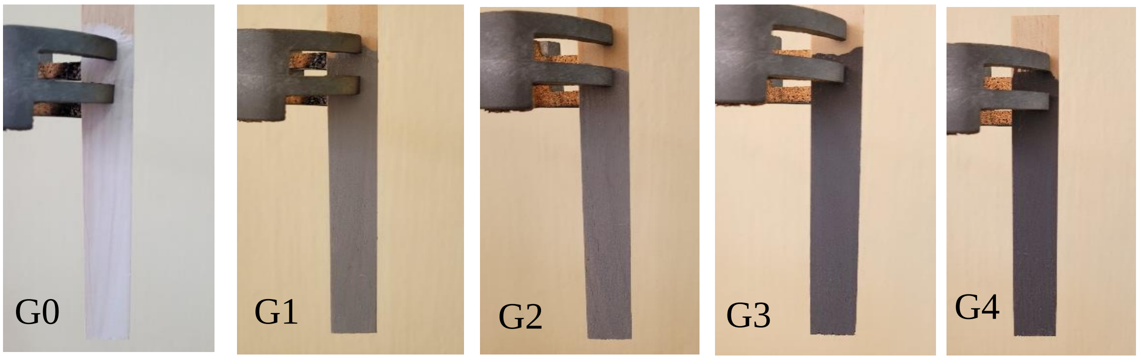

***Figure 2.** Wood samples are coated with manufactured coating mixtures, as shown in table 1.*

***Table 2.** The combustion time of pine wood samples was tested for fire retardancy according to the UL94-V vertical fire measurement method.*

Sample	Characteristic	Total combustion time after first burning (seconds)	Total combustion time after second burning (seconds)	Testing according to UL94-V standard
G0	Coat M0	5	33	Reached V0
G1	Coat M1	0	20	Reached V0
G2	Coat M2	0	5	Reached V0
G3	Coat M3	0	3	Reached V0
G4	Coat M4	0	2	Reached V0

From the summarized results in table 2, it can be seen that all tested pine wood samples reached V0 level of the UL94-V standard (total combustion time after 2 burns is less than 50 seconds). However, with the G0 sample, the total combustion time is the greatest (33 seconds); for samples coated with fire retardant mixtures with increasing graphene additive contents, the total combustion time gradually decreases. When the graphene content in the fire retardant coating mixture is 0.1%, the total combustion time according to the tested results is 20 seconds.

When the graphene content in the fire retardant coating mixture is up to 0.2%, the total combustion time rapidly decreases to 5 seconds. Continuing to increase the graphene content in the fire retardant coating mixtures to 0.5% and 1%, the total combustion time continues to decrease gradually until zero. Thus, it can be seen that when the graphene content in the fire retardant coating mixture increases to 0.2%, the fire retardant effectiveness of the coating mixture is almost saturated. Therefore, in this study, 0.2% graphene content in the fire retardant coating mixture is chosen as the optimal ratio. The images of pine wood samples after being burned in figure 3 show that at the part of pine wood samples affected by the fire, the coating films have swelled, which prevents heat from transferring to the pine wood surface. To illustrate the effect of the content of graphene on the swollen layers, SEM images of the swollen part on the pine wood samples after being burned are taken and presented in figure 5.

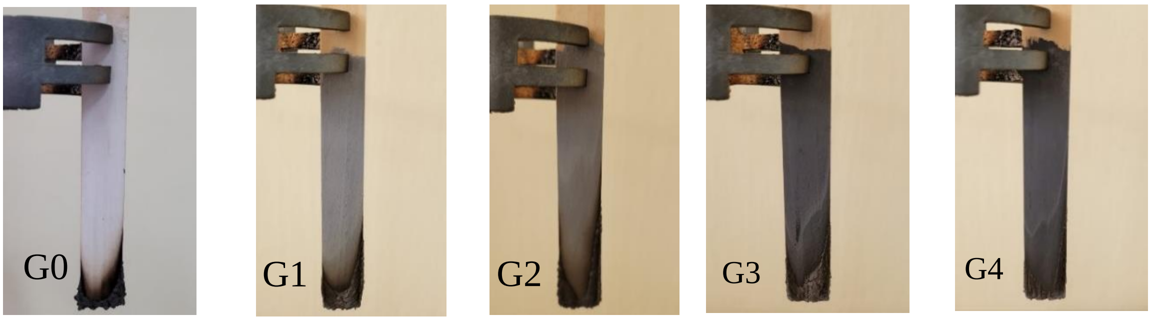

Figure 3. *Pine wood samples coated with fire retardant coating mixtures after burning.*

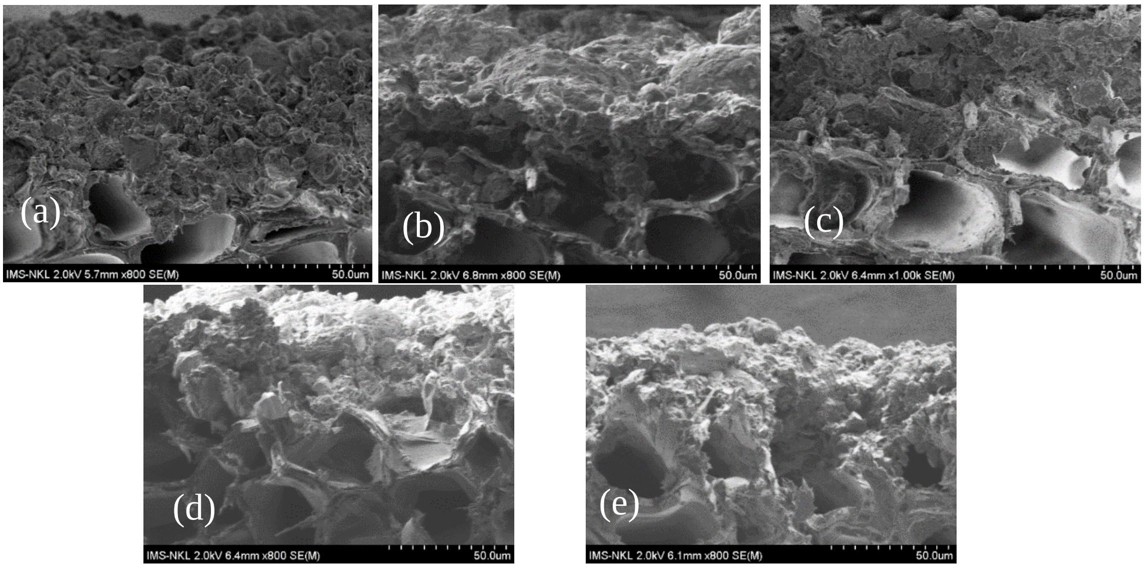

Figure 4. *SEM images of the cross-section of the bond between the fire-retardant coating and the pine wood surface of the samples before burning (a) G0; (b) G1; (c) G2; (d) G3; (e) G4.*

Figure 4 and figure 5 present SEM images of the bond cross-section between the coating and the pine wood surface of G0, G1, G2, G3, and G4 samples before and after burning. It can be seen that the coating films bond well with the pine wood surfaces, the thickness of the films are very thin and are all within 50 µm. For the samples in figure 4b, c, d, e, which are coated with coating mixtures using graphene additive, gaps and small holes appear on the surface the coating films less than those in the sample in figure 4a, the reason may be due to the graphene additive filling this gap. It can be concluded that compared to those without graphene additives the ability to prevent heat transfer to the surface of pine wood samples coated with a mixture using graphene additive is better. Also, the SEM images in figure 5 also show that when pine wood samples are affected by heat, all tested samples swelled strongly and thereby prevented the impact of heat on the pine wood surfaces. In figures 5b, c, d, e, the samples coated with the mixtures using graphene additive not only have the same swelling of the basic flame retardant components as the G0 sample but also appear a "maze effect". The "maze effect" can be explained by the fact that the carbon framework of graphene has high thermal stability and can act as a template for char promoting the formation of multiple overlapping layers of char. This effect enhances the resistance to heat transfer from the flame to the pine wood surface. These results are consistent with the obtained experimental results in table 3. The effect of the "maze effect" is much more clearly demonstrated on the SEM images in which the surface of coated films with 0.2% graphene additive before and after burning (figure 6 and figure 7).

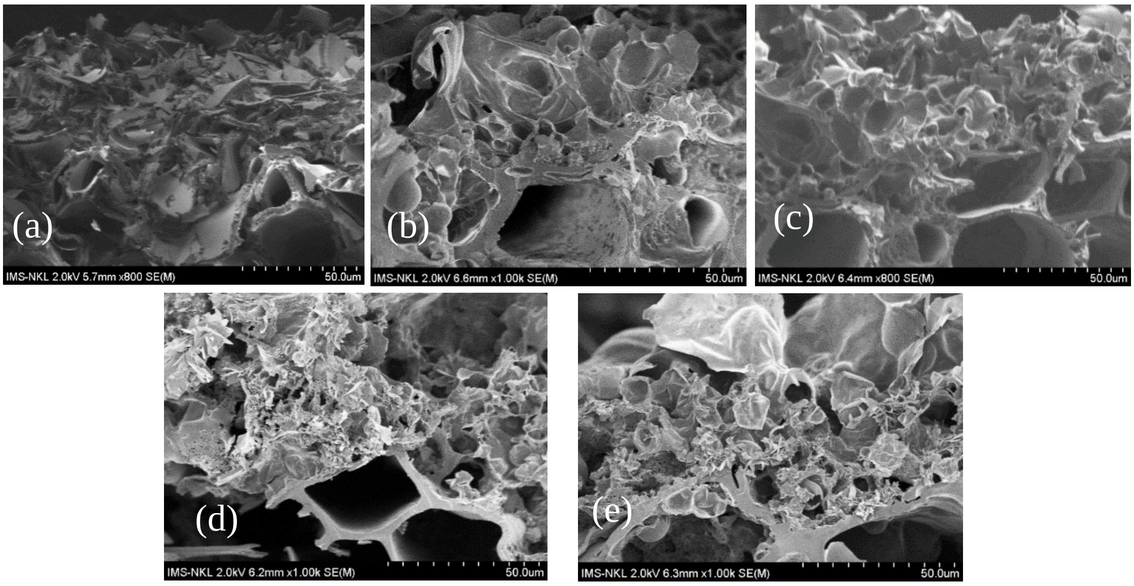

Figure 5. *SEM images of the cross-section of the bond between the fire-retardant coating and the pine wood surface of the samples after burning (a) G0; (b) G1; (c) G2; (d) G3; (e) G4.*

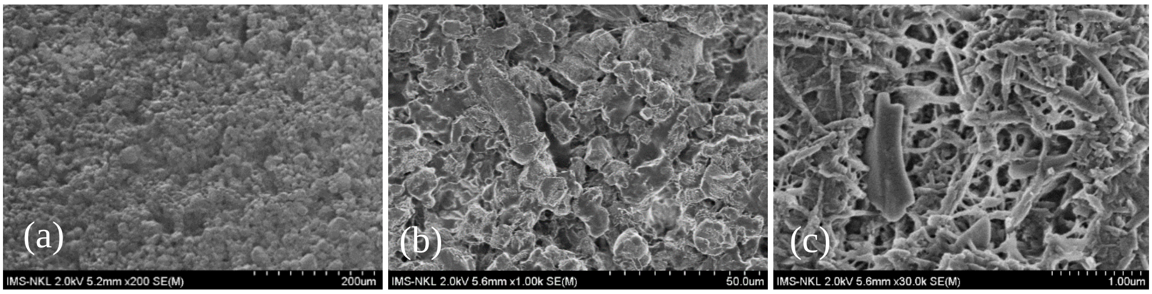

Figure 6. *SEM images of the surface of the coat film of G2 sample before burning with magnifications (a) 200 times, (b) 1000 times and (c) 30000 times.*

The SEM image with 200x magnification in figure 6a shows that the surface of the coating film is flat with particles of uniform size. When the magnification is increased to 1000 times and 30,000 times, it can be seen that the surface of the coating film is still relatively uniform. In addition, gaps between particles and particle clusters are also observed, which can allow heat transfer from the heat source to the surface of the protected object. However, when the coating film is affected by heat, those gaps no longer exist, instead, the charred layer has many continuous sheets which have large areas, overlapping each other as shown in figure 7b, c. It is this charring into many overlapping layers that prevents heat transfer from the fire to the pine wood surface.

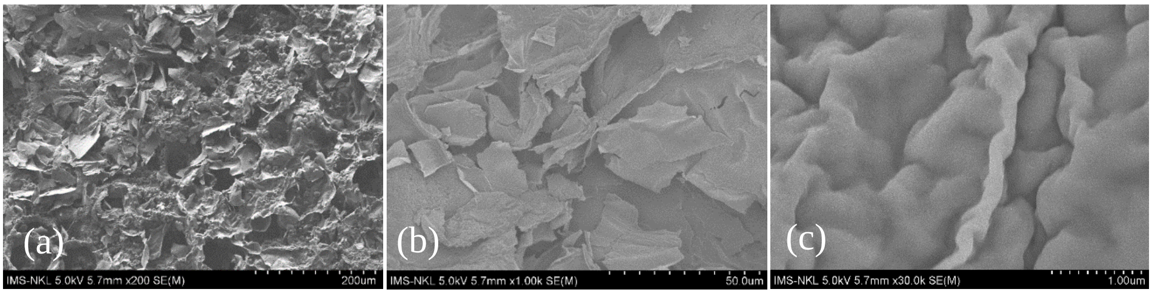

Figure 7. *SEM images of the surface of the char film of G2 sample after burning with magnifications (a) 200 times, (b) 1000 times and (c) 30000 times.*

Table 3. *Some specifications of the manufactured mixture (M2).*

Number	Specifications	Unit	Test method	Quality level	
				No-burn® Original [12]	Manufactured mixture M2
1	pH	-	TCVN 8826:2011	6	7.5
2	Density	g/ml	ASTM D1475:2008	1.08	1.21
3	Solid content	%	TCVN 10519:2014	30.6	41.5
4	VOC content	g/l	ISO 17895:2005	18	38
5	Drying time: - surface - completely	min	TCVN 2096:2015	105 630	95 590

Some specifications of the manufactured mixture (M2) are measured, including pH, density, solid content, VOC content, and drying time. The measurement method and measurement results are presented in table 3. The results show that M2 mixture has specifications quite similar to the specifications of the No-burn® Original product [12]. The drying time of this mixture is much smaller than that of No-burn® Original paint. This result can be explained by the fact that M2 mixture has a higher solid content. Although the VOC content of M2 mixture is higher than that of No-burn® Original product, the VOC content of 38 g/l is still relatively low. This result can be expected because the coating mixture uses an aqueous solvent, which has a small component of EVA binder which can be a major contributor to the VOC content. This result is a demonstration that the manufactured mixture has environmentally friendly properties.

4. CONCLUSIONS

In this study, we have presented our outcome in successfully manufacturing a water-based fire retardant coating mixture using graphene additives for natural wood. Different contents of graphene additive were investigated to clarify the influence of graphene on the fire retardant effectiveness of the mixture when coated on natural wood (pine wood) according to UL94-V standards. SEM imaging method was used to analyze and explain the experimental results. The results show that the content of graphene affects the fire retardant effectiveness of the mixture and is optimized at 0.2% graphene content. Results of analysis and evaluation of some specifications such as pH, density, drying time, solid content, VOC content show that the manufactured mixture is environmentally friendly. The findings of this research provide a solution to enhance the fire retardant effectiveness for natural wood structures using environmentally friendly materials.

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TÓM TẮT

Nghiên cứu chế tạo hỗn hợp tạo màng phủ chậm cháy hệ nước sử dụng phụ gia graphene cho gỗ tự nhiên

Màng phủ chậm cháy trương phồng, đặc biệt là màng phủ chậm cháy trương phồng hệ nước, đang ngày càng được quan tâm do tính chất thân thiện môi trường của chúng. Trong nghiên cứu này, chúng tôi đã chế tạo thành công dung dịch tạo màng phủ chậm cháy hệ nước sử dụng phụ gia graphene cho gỗ tự nhiên với ba thành phần chính (tác nhân axit hóa ammonium polyphosphate, tác nhân than hóa pentaerythritol, tác nhân nở phồng melamine) và một số phụ gia khác trong đó có graphene. Chúng tôi đã khảo sát sự ảnh hưởng của hàm lượng graphene đối với hiệu quả chậm cháy của hỗn hợp khi phủ lên gỗ tự nhiên (gỗ thông) theo tiêu chuẩn UL94-V. Kết quả thử nghiệm cho thấy hàm lượng của graphene có tác dụng tăng cường hiệu quả chậm cháy của hỗn hợp chế tạo được. Phương pháp ảnh SEM được sử dụng để phân tích và giải thích các kết quả thử nghiệm. Một số chỉ tiêu kỹ thuật của hỗn hợp chế tạo được cũng được phân tích và đánh giá. Kết quả nghiên cứu này cung cấp một giải pháp tăng cường khả năng chống cháy cho các kết cấu gỗ tự nhiên sử dụng vật liệu thân thiện môi trường.

Từ khóa: Màng phủ chậm cháy hệ nước; Màng phủ trương phồng; Graphene; Gỗ tự nhiên.