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Flame Retardancy Effects on Intumescent Coatings with Vinyl Acetate Copolymers

This research aimed to study the effects of fire combustion on materials coated with ethylene vinyl acetate and polyvinyl acetate copolymer emulsion resins with differing foam producing substance to dehydrating agent ratios. The flame retardancy of these materials was assessed by evaluating their heat release, CO and CO₂ emissions. Experimental results indicate that intumescent paint formulations significantly enhance the flame retardancy of painted plywood, thus reducing peak heat release rate and extending the time to reach peak heat release rate. Moreover, a low amount of foam producing substance enhances the fire retardancy of plywood panels. Furthermore, binder resin containing vinyl acetate monomer in intumescent coatings can enhance fire performance. In addition, low foam producing substance content can form an ideal char layer, which significantly reduces CO and CO₂ emissions. The mechanism to achieve more favorable fire performance was verified by carrying out thermogravimetric analysis, which demonstrated lower weight loss. The results of this study provide an improved understanding of the effects of intumescent coatings.

1 Introduction

In recent years, natural materials, such as wood and wood-based materials, have been prevalently used in residential and public buildings to conserve energy and reduce carbon emissions. Woods and resins are frequently used for building decorations. Because these materials are flammable and emit a considerable amount of smoke, the use of these materials raises crucial safety problems. Because fire can cause human fatalities and economic losses, the use of flame retardants is essential and is increasingly in demand (Girardin et al., 2017). Intumescent paints are flame retardant because they form a charred layer that acts as a physical barrier to prevent heat and mass transfer between gases and condensed phases (Bourbigot et al., 1996; Demir et al., 2005). The charred layer, which has low thermal conductivity, then forms a carbonaceous layer

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through cyclization and cross-linking with phosphate ester (Alongi et al., 2015).

When organic materials are exposed to heat, they burn, generating fire and smoke. The products of combustion are highly toxic and cause most fire fatalities (Biswas et al., 2007). CO and CO₂ are the primary toxic products. Several studies have determined that the fire performance of materials is based on their heat release behaviors (Gao et al., 2006; Anees and Dasari, 2018). Results of our previous study indicate that low binder resin (BR) contents increase the fire retardancy of coated plywood (Chuang et al., 2010). However, the flammability of coating films containing different ratios of foam producing substance (FPS) and dehydrating agent (DA) remains unclear. The mechanism of chemical reactions for various formulations is also unclear. Furthermore, the CO and CO₂ emissions of different intumescent formulations have rarely been reported. However, the fire performance of materials must be evaluated using the information on heat, CO and CO₂ generation.

Abbreviations

APP:	ammonium polyphosphate
BR:	binder resin
COav300:	average CO at 300 s
CO ₂ av300:	average CO ₂ at 300 s
CS:	carbonizing substance
DA:	dehydrating agent
EM:	the intumescent coating use ethylene vinyl acetate resin (EVA) as a binder resin
EVA:	ethylene vinyl acetate copolymer
FPS:	foam producing substance
HRRav:	average heat release rate
PER:	pentaerythritol
PHRR:	peak heat release rate
PM:	the intumescent coating use polyvinyl acetate copolymer resin (PVAc) as a binder resin
PVAc:	polyvinyl acetate copolymer
THR:	total heat release

In this study, different formulations containing the following four primary components were systematically investigated to understand the effects of intumescent gradients: (1) ethylene vinyl acetate copolymer (EVA) emulsion resin and polyvinyl acetate copolymer (PVAc) emulsion resin as binder resins (BR); (2) pentaerythritol as a carbonizing substance (CS); (3) melamine as a foam producing substance (FPS); and (4) ammonium polyphosphate (APP) as a dehydrating agent (DA). A cone calorimeter was employed to investigate the fire performance of plywood painted with different formulations, and CO and CO₂ emissions were evaluated. Furthermore, thermogravimetric analysis (TGA) was performed to study the thermal properties of flame-retardant paints further, and compare these properties with the flame retardancy of painted plywood. The relations between a char chemical structure and fire performance were also investigated.

2 Experimental

2.1 Materials

Two commercial emulsion resins, namely EVA and PVAc copolymer, were used as BRs. The viscosity of EVA and PVAc copolymer was 2,000 and 15,000 cps, respectively, and the total solid content of EVA and PVAc copolymer was 55% and 44% w/v, respectively. These emulsion resins were obtained from Yeou Shuenn Products Co., Ltd., Kaohsiung, ROC. Pentaerythritol (PER) and melamine were used as a carbonizing substance (CS) and foam producing substance (FPS), respectively. These two materials were purchased from Sigma-Aldrich (Darmstadt, Germany). Ammonium polyphosphate (APP), which was used as a dehydrating agent (DA), was purchased from U-Way C.E.T. Co., Taipei, ROC. The degree of polymerization (*n*) of APP in this study was approximately 1000. An intumescent paint was coated on a 4-mm thickness red lauan (*Parashorea spp.*) plywood panel.

2.2 Sample Preparations

In this study, two sample groups were investigated. The sample numbers were named by different binder resin; the one sample group was named as EM series which used the ethylene vinyl acetate resin (EVA) as the binder resin. The samples which used the polyvinyl acetate copolymer resin (PVAc) were named as PM series. In Table 1, the EM and PM series had identical solid weight ratios (w/w) of the binder resin (BR)

and carbonizing substance (CS) and varying ratios of foam producing substance (FPS) and dehydrating agent (DA). In our previous study (Chuang et al., 2010), the better formulation of binder resin/carbonizing substance was 15/35% (w/w), which promoted fire performance. Hence, the ratio of foam producing substance and the dehydrating agent was changed to investigate their char-forming performance. The required weight of each of the four major components was combined and stirred at 600 min⁻¹ for 4 h.

The coating amount was at 360 g m⁻² (i.e., each plywood panel was coated with 32.4 g of the paint after three equal coatings). A preconditioning procedure for moisture content control is specified in ASTM E 1354-99.

2.3 Flammability Tests

A cone calorimeter (Fire Testing Technology Ltd., East Grinstead, UK) was used to evaluate the efficiency of the flame retardant, as specified in the ASTM E 1354 method. The specimens were placed horizontally with an external igniter, and the flux of the cone heater was set at 50 kW m⁻². The total test time was 1200 s and the HRR_{av} was calculated at 1200 s. The PHRR exhibited two major exothermal peaks, and the first and second stages of the PHRR were calculated. Moreover, CO and CO₂ analytical equipment were employed. According to CNS 14705-1, when the THR300 value is less than 8 MJ m⁻², the coating film passes the regulatory standards and can become a flame-retardant material.

The char residue after the cone calorimeter test was observed by a scanning electron microscope (Hitachi S-4800, Hitachi, Tokyo, Japan). The voltage of the scanning electron microscope was 10 kV, and thin gold was sprayed on the surface of char before observation.

2.4 Thermogravimetric Analysis

The thermogravimetric analysis (TGA) was performed using a TA-2950 analyzer (TA Instruments, New Castle, DE). Flame-retardant coating films were placed in a ceramic sample pan, and the vapor around the sample was purged with nitrogen gas. The gas flow was set at 60 ml min⁻¹. The sample weight was 5.0 mg, and the heating rate was 10 °C min⁻¹. The heating experiment was conducted at temperatures ranging from 40 to 700 °C. The TGA was performed to calculate mass loss and obtain the derivative thermogravimetric (DTG) curves.

No.	Binder resin	Carbonizing substance	Foam producing substance	Dehydrating agent
EM1/PM1	15	35	15	35
EM2/PM2	15	35	25	25
EM3/PM3	15	35	35	15

Table 1. The different formulation of intumescent coatings with various vinyl acetate copolymer resins in solid weight ratio (w/w)

2.5 Statistical Analysis

SAS (version 9.2, 2012) software (SAS Institute Inc., Cary, NC) was employed for all statistical analyses. The THR, CO emissions, and CO₂ emissions were statistically analyzed to evaluate the correlation between different components and combustion time (i. e., 100, 200, 300, and 400 s). A linear regression equation was applied to combustion data. The goodness-of-fit was evaluated according to r^2 (determination coefficient), the level of significance (P value), and a standard error (SE). The different amount of FPS and correlations with combustion times were compared using the least significant difference (LSD) testing. LSD values were calculated using the SE and t-test at appropriate degrees of freedom with a 95 % confidence level.

3 Results and Discussion

3.1 Cone Calorimeter Test of Different Coatings on Plywood Panels

Figure 1 shows experimental results of HRRav, THR (Fig. 1A), PHRR (Fig. 1B), time to PHRR (Fig. 1C) and Effective heat of combustion (Fig. 1D). The experimental results indicate that the first peak was attributed to the ignition of the flame-retardant paint, whereas the second peak resulted from the burning of plywood. PHRR is the most significant parameter characterizing flame retardancy enhancement in the samples. Because of the importance of the formulations of the four components, tests for the EM and PM series were employed to study the impacts of the ratio of the altering of foam producing substance and dehydrating agent on the flame retardancy of painted plywood. According to Fig. 1A and B, better flame retardancy of the EM series was achieved by EM1 (Table 1). Since the PHRR values were low, larger intervals were observed between the peak heat release occurrences and longer

time to peak heat release as given in Fig. 1C. Comparison of the THR, HRRav and time to PHRR, flame retardancy can be ranked in the following order: EM1 > EM2 > EM3.

The same trend was observed for the PM series. PM2 exhibited extraordinary flame retardancy because of the intumescent layer (Fig. 1). Similarly, as the PHRR values were low, larger intervals between the peak heat release occurred, and longer time to the peak heat release, the flame retardancy of PM series was ranked as PM2 > PM1 > PM3. Low PHRR and THR values indicate that the flame retardancy of painted plywood improved during combustion. The experimental results indicate that the longer time between the two PHRRs corresponded with the improved durability of the formed char for EM1 and PM2 under fire combustion. Wladyka-Przybylak and Kozłowski (1999) concluded that a coating of flame-retardant paint resulted in the production of incombustible gases, which blocked access to oxygen. Moreover, insufficient dehydrating agent cannot provide an esterification reaction. On the other hand, excessive foam producing substance can release incombustible gases; however, it may not form an ideal char layer. Several reports pointed out that the ideal char layer of intumescent coating was a great deal of integrated honeycomb pores (Gu et al., 2007; Qian et al., 2019). Therefore, digital photographs and SEM images were used to better understand the morphology of the intumescent char layer with different formulations.

Figure 2 show digital photographs and SEM images of char residues. In Fig. 2A, PM2 showed a higher swell layer than other formulations. On the other hand, PM3 and EM3 have many more cracks on the surface than other formulations at the same test time. As given in Fig. 2B, SEM images also indicated that EM3 and PM3 have many channels and apertures. The above structure of EM3 and PM3 demonstrated the non-ideal char structure. Therefore, the gas and molten substance of underlying materials can overflow to enter the flame region. Furthermore, the experimental results indicated that the excessive foam producing substance could not form an ideal char

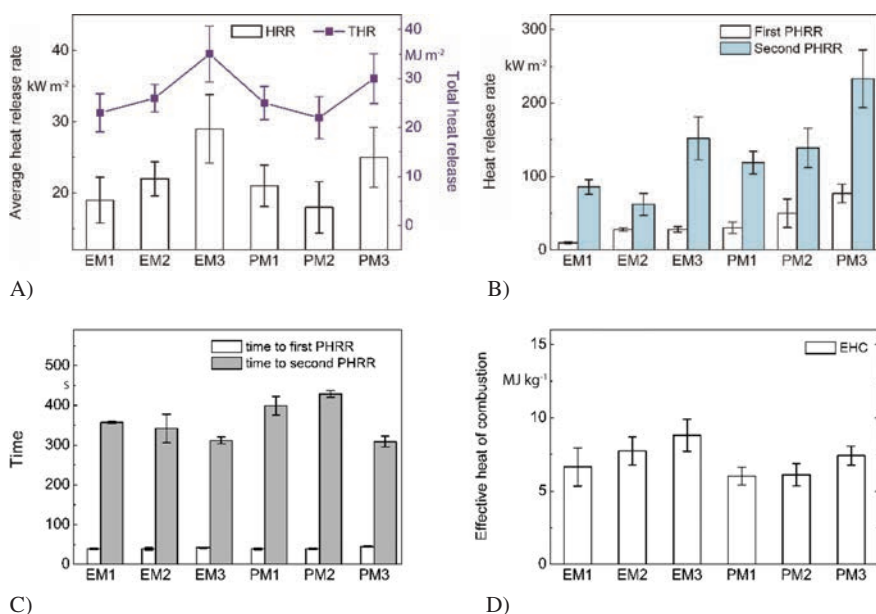
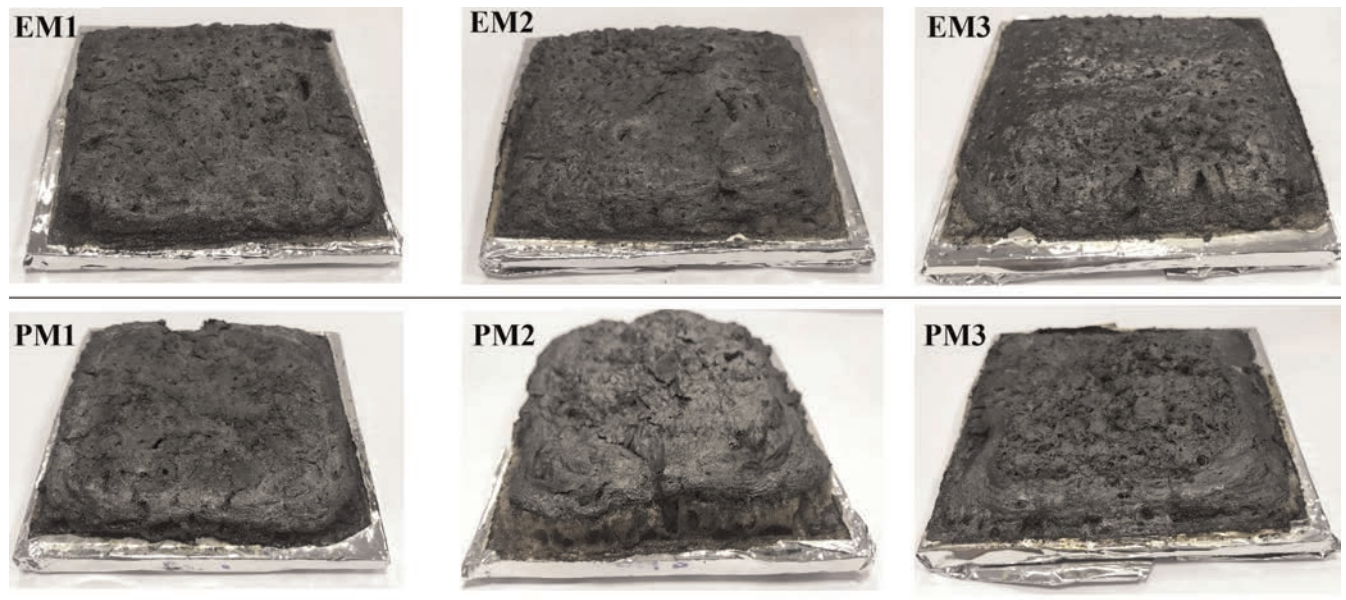


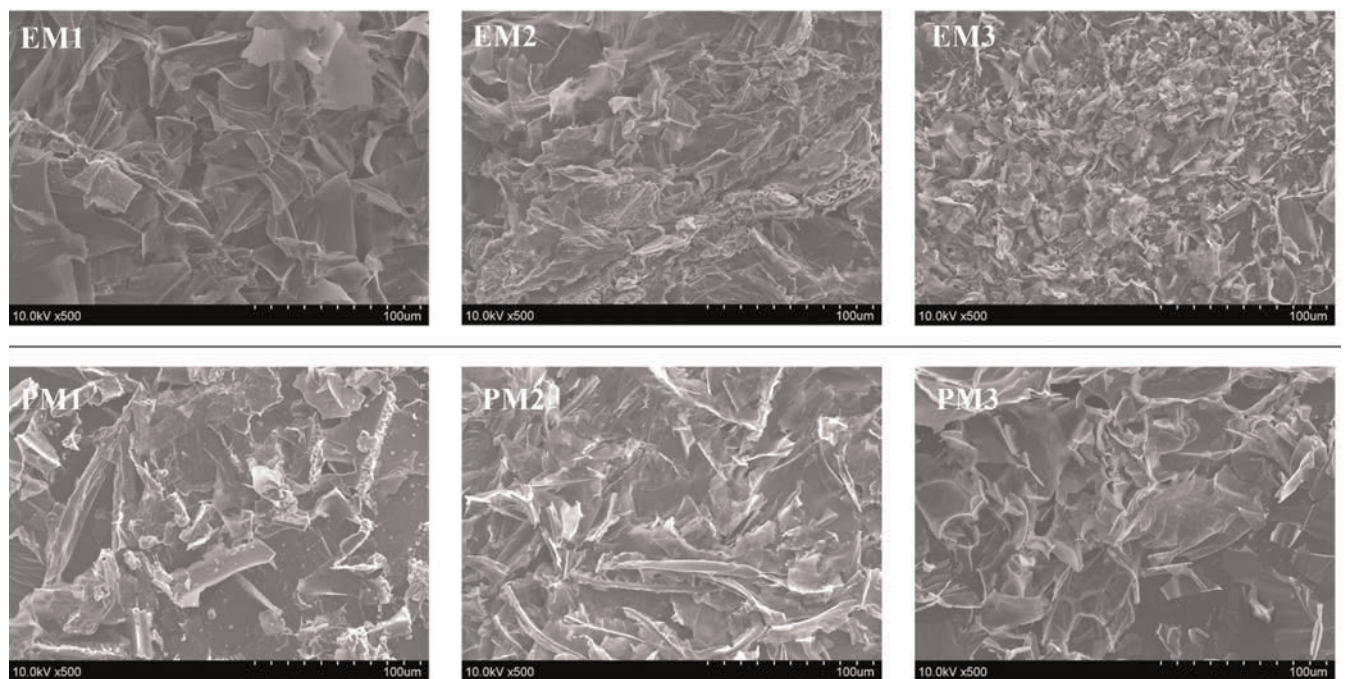
Fig. 1. Heat release profiles for different formulation coatings of EM series (EM1 with 15(binder resin)/35(carbonizing substance)/15 (foam producing substance)/35(dehydrating agent), EM2 with 15/35/25/25, and EM3 with 15/35/35/15) and PM series (PM1 with 15/35/15/35, PM2 with 15/35/25/25, and PM3 with 15/35/35/15) on 4-mm plywood panels under cone calorimeter tests, A) HRRav and THR, B) first and second PHRR, C) time to first and second PHRR, D) effective heat of combustion

layer. By contrast, other formulations demonstrated that the char layer structure was more compact and more homogeneous. These structures showed better flame retardancy. Therefore, the compact and spongy intumescent char layer have better heat insulation effect.

A comparison between the EM and PM series indicates that PVAc had a better flame retardancy performance relative to EVA. In our previous study (Chuang et al., 2013), different emulsion resins (i.e., vinyl acetate-acrylic copolymer) with the same formulations were tested using the cone calorimeter.



A)



B)

Fig. 2. Digital photographs (A) and (B) SEM micrographs (x 500). The different formulations of EM series (EM1 with 15(binder resin)/35(carbonizing substance)/15(foam producing substance)/35(dehydrating agent), EM2 with 15/35/25/25, and EM3 with 15/35/35/15) and PM series (PM1 with 15/35/15/35, PM2 with 15/35/25/25, and PM3 with 15/35/35/15) char residues of different formulations (EM series and PM series) obtained from cone calorimeter under the same test time

The HRRav, THR, and time to the second PHRR of FRV5 (with an improved result in varying the ratio of FPS/DA) were 28 kW m^{-2} , 23 MJ m^{-2} , and 327 s, respectively. These results indicated that the binder resin is crucial for flame retardancy. This observation is consistent with those reported by Pimenta et al. (2016) and Anna et al. (2001). A comparison of three vinyl acetate copolymer emulsion resins (i.e., ethylene vinyl acetate emulsion, polyvinyl acetate copolymer emulsion, and vinyl acetate acrylic emulsion resin) indicated that PVAc has better flame retardancy. This result indicates that PVAc maintains the completeness and continuity of the char layer and exhibits a better thermal insulation effect to retard the decomposition of the plywood material.

3.2 Thermogravimetric Analysis

Thermogravimetric analysis results can assist in analyzing mechanisms of different formulations of the intumescent coating. The main reaction of intumescent paint is the formation of a phosphor-carbonaceous structure which is created by APP-PER-Melamine. In this study, we changed the ratio of melamine (FPS)/ammonium polyphosphate (DA) to examine the effect of DA on the phosphor-carbonaceous structure. Table 2 and Figs. 3 and 4 illustrate the thermogravimetric analysis data of a sole polymer and the EM and PM series. The sole

EVA and PVAc coating films exhibited two primary degradation peaks at approximately 340°C and 460°C , respectively (Figs. 3A, B and Table 2). The first stage was due to the vinyl acetate group of EVA which loses acetic acid. Rimez et al. (2008) reported that PVAc and EVA have two degradation stages under N_2 environment. In PVAc resin, the first degradation step, between 300 and 400°C , was identified as the deacetylation step. In the second stage polyene fully degrades in a subsequent degradation between 400 and 500°C . The decomposition of PVAc has an unsaturated material and aromatic residue or polyene during deacetylation. A similar degradation was also observed in EVA resin. However, the EVA resin with low content of vinyl acetate groups does not form a stabilized aromatic structure or char as was observed for PVAc. Therefore, our experimental results are in good agreement with those of Rimez et al. (2008).

Figure 4 shows three clear degradation stages in intumescent coatings of the EM and PM series. In this study, flame-retardant chemicals in the first stage of degradation were due to the decomposition of the APP (dehydrating agent), whereas the second stage was due to the degradation of the melamine (foam producing substance) and phosphate ester. Several reports pointed out that the degradation of ammonium polyphosphate formed the phosphor-carbonaceous structure and reacted with the hydroxyl groups of polyols between 280 and 330°C (Camino et al., 1989; Kandola and Horrocks, 1996).

No.	Stage I		Stage II		Stage III		Stage IV		Residue
	Weight loss %	Temp. $^\circ\text{C}$	Weight loss %	Temp. $^\circ\text{C}$	Weight loss %	Temp. $^\circ\text{C}$	Weight loss %	Temp. $^\circ\text{C}$	Weight %
EVA	–	–	36.8	340	–	–	47.4	460	1.5
EM1	21.8	240	27.7	340	–	–	16.1	430	20.5
EM2	14.8	230	29.9	330	–	–	22.9	440	22.4
EM3	22.8	240	33.9	340	–	–	18.4	450	17.1
PVAc	–	–	51.9	340	–	–	35.4	460	6.7
PM1	15.8	270	23.2	330	14.3	380	10.5	430	23.4
PM2	14.9	270	18.4	340	–	–	23.4	460	30.9
PM3	14.0	270	23.1	330	–	–	19.0	410	22.5

Table 2. Weight loss and temperature degradation of sole emulsion resin and intumescent painting by thermogravimetric analysis

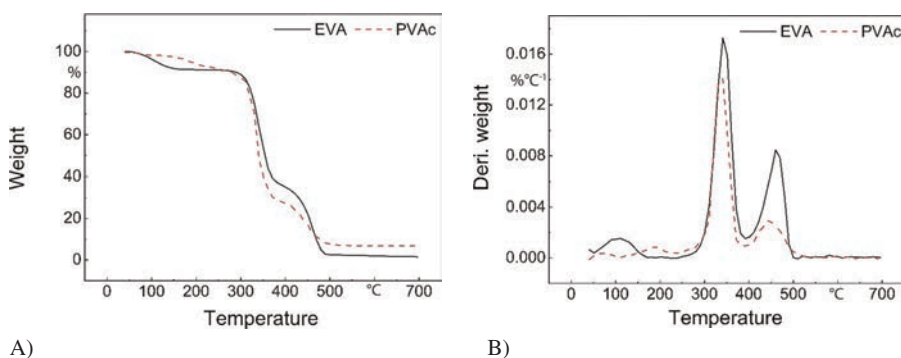


Fig. 3. Thermogravimetric analysis (A) TG curves and (B) DTG curves for sole ethylene vinyl acetate copolymer, EVA, and polyvinyl acetate copolymer, PVAc emulsion resin

According to the sole EVA and PVAc decomposition curve, the extension of the char layer was attributed to the generation of the polymers in the third stage. In this stage, the phosphoric acid and resin reacted to extend the char layer. Therefore the intumescent char layer can protect underlying material for a long period under heat combustion. The results are consistent with those of Pimenta et al. (2016).

Thermal stability was also evaluated to understand the duration of the char layer. In this study, the temperature of 5% weight loss ($T_{5\%}$) was defined as an initial decomposition of the intumescent coating. $T_{50\%}$ indicated the forming of the phosphor-carbonaceous structure during heat combustion. $T_{5\%}$ of EM1 ~ 3 were 210, 210 and 200 °C respectively. The

$T_{50\%}$ of EM1 ~ 3 were 340, 340 and 310 °C, respectively. The experimental results indicated that the EM1 and EM2 have better thermal stability than EM3. The residual weight of char also indicated that the EM1 and EM2 have similar thermal resistance and phosphor-carbonaceous structure. On the other hand, $T_{5\%}$ and $T_{50\%}$ of PM series showed the same trend. The $T_{5\%}$ and $T_{50\%}$ of PM2 were 240 and 410 °C, respectively. The results showed that PM2 has better thermal stability than PM1 (230 and 360 °C) and PM3 (240 and 370 °C).

The data from the TGA and cone calorimeter test were compared, which indicated that coating films decomposed at lower temperatures, and thus had better flame retardancy. The low weight loss and decomposition temperature enhanced the

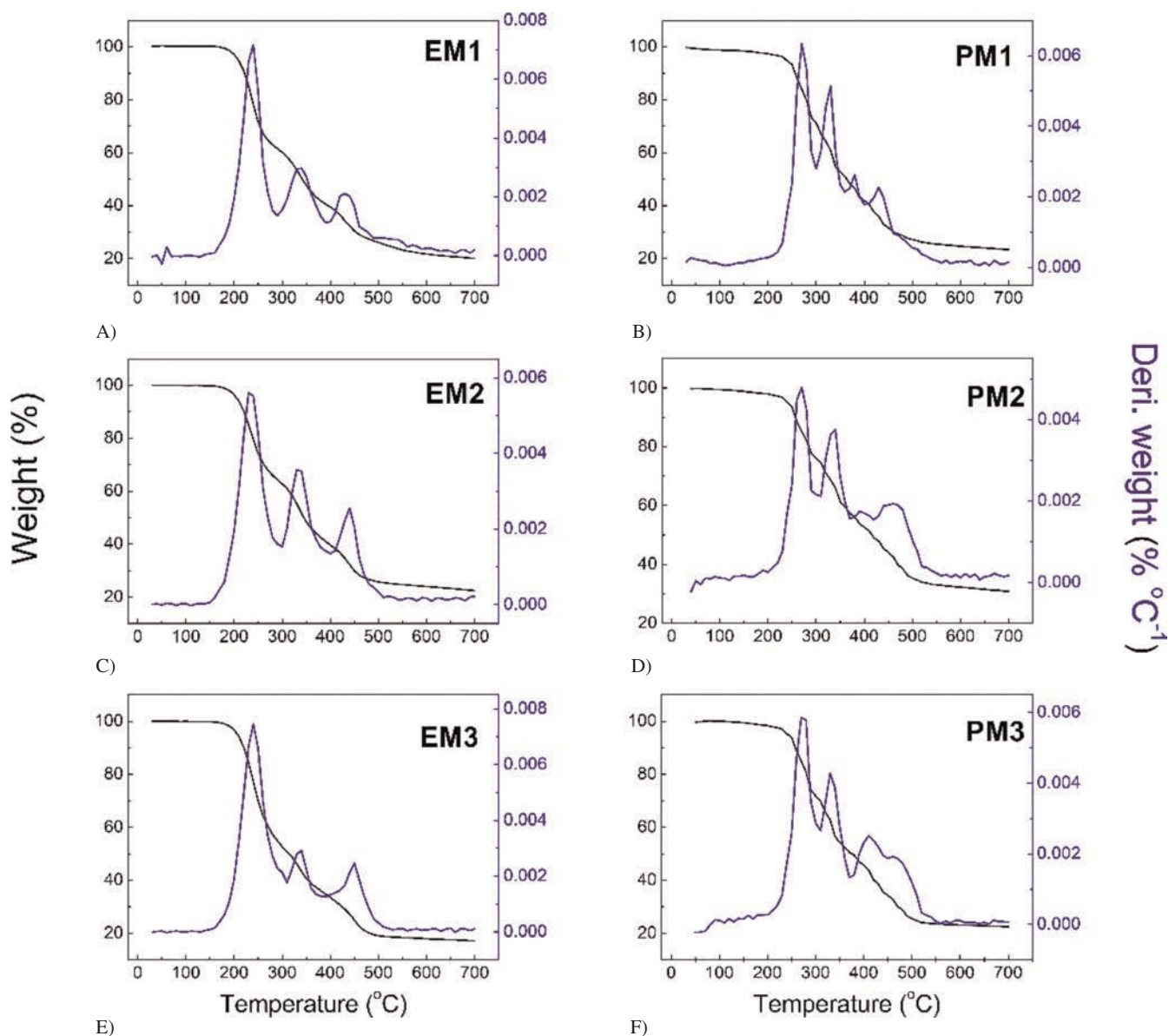


Fig. 4. Thermogravimetric analysis of TG and DTG curves of different formulations with EM series, A) EM1 with 15(binder resin)/35(carbonizing substance)/15(foam producing substance)/35(dehydrating agent), B) EM2 with 15/35/25/25, C) EM3 with 15/35/35/15 and PM series, D) PM1 with 15/35/15/35, E) PM2 with 15/35/25/25, F) PM3 with 15/35/35/15

flame retardancy of the plywood panel. In both the EM and PM series, the experiment exhibited the same trend, namely that high DA content enhanced flame retardancy performance.

3.3 CO/CO₂ Emission of Different Coatings and Analysis

Asphyxiant gases, such as CO and CO₂, are toxic gases that are produced in a fire. In this study, the flame retardancy of different intumescent formulations was examined using a cone calorimeter. In terms of safety, the flame retardancy and gas emissions of intumescent coatings are crucial in fire protection. Therefore, CO and CO₂ emissions were detected for specimens with different formulations. Figure 1D demonstrated that the effective heat of combustion of EM3 and PM3 was 8.8 and 7.4 MJ kg⁻¹, respectively. EM1, PM1 and PM2 had lower effective heat of combustion than other intumescent formulations. Figure 5 shows the CO₂ emissions and the total quantity of CO₂ during the cone calorimeter test. The trend of CO₂ emissions was similar to that of heat release as depicted in Fig. 5A. Figures 5B and C show the total CO₂ emission of the EM and PM series, respectively. Further, EM3 and PM3 generated the highest CO₂ emissions of 3917 and 7963 ppm, respectively. In the EM series, EM1 generated the lowest total CO₂ emissions. When the amount of the FPS was changed from 15 to 35, the CO₂ emissions also increased. Therefore, the intumescent coating not only protected the plywood but also reduced CO₂ emissions. This observation is consistent with those reported by Siat et al. (1998) and Almeras et al. (2003).

In Fig. 5C, the total amount of CO₂ emission increased with an increasing amount of FPS in the PM series. These findings indicate that decomposition of the FPS generates CO₂. Previous studies (Camino et al., 1989; Władysław-Przybylak and Kozłowski, 1999) have reported that FPS, such as melamine, generate CO₂ during their decomposition in the intumescent system. A comparison of the EM and PM series indicated that the CO₂ emissions of the EM series were lower than those of the PM series at the same formulation. A comparison of the CO₂ emissions of each binder, which contained the vinyl acetate monomer, revealed that ethylene vinyl acetate emulsion resin as a binder resin is better than vinyl acetate acrylic emulsion or polyvinyl acetate copolymer emulsion resin.

Figure 6 shows the CO emission and total quantity of CO emissions produced in the cone calorimeter test. CO emissions occur at a low temperature in the early stages of a fire, mainly as a result of incomplete combustion. In Fig. 6A, three emission stages of CO were observed. The first and second stages were attributed to the coating and plywood, respectively. In the third stage, plywood specimens were smoldering. A comparison of the FPS content formulation indicated that a high FPS content resulted in high CO emissions. The EM and PM series had the same trend, and Siat et al. (1998) reported similar results. Based on a comparison of the HRR and CO emissions data, an increase in the FPS content increased the production of CO as given in Figs. 6B and C. Although CO blocked oxygen access, it did not enhance the fire retardancy of the plywood. According to the results of the cone calorimeter test, as shown in Figs. 6B and C, EM1 and PM1 exhibited better flame retardancy and emitted the lowest amount of CO (1.1 × 10⁵ and 1.3 × 10⁵ ppm, respectively). Moreover, a comparison of HRR

and CO and CO₂ emissions data indicates that the better content of FPS was approximately 15% to 25%. The PVAc series emitted higher amounts of CO and CO₂ than the EVA or VAc series. However, the PVAc series had a long time to PHRR and higher THR and HRR_{av} than did the EVA and VAc series.

To evaluate the flame retardancy and CO and CO₂ emissions at different FPS/DA ratios, the THR300 was used as an index according to the CNS 14705-1 regulation. In this study, this

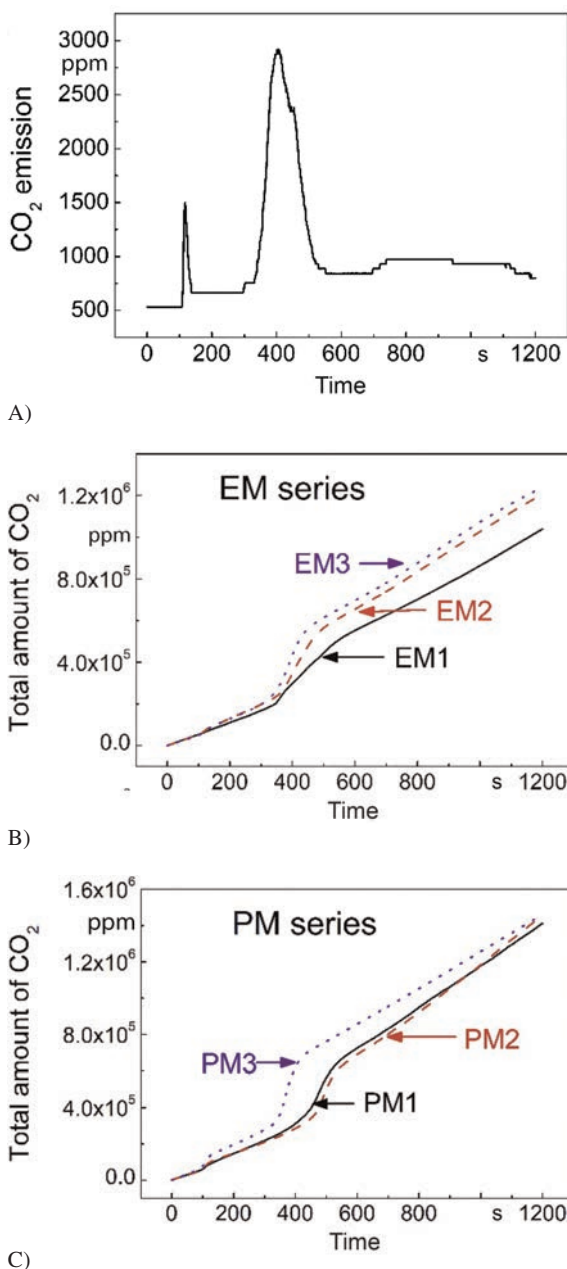
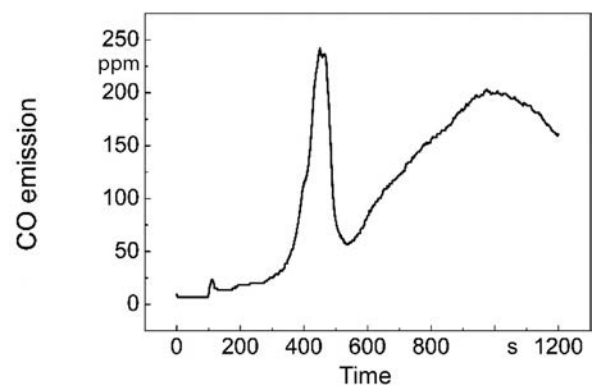


Fig. 5. CO₂ production (A) and total amount of CO₂ produced (B and C) with different formulations of EM series (EM1 with 15(binder resin)/35(carbonizing substance)/15(foam producing substance)/35(dehydrating agent), EM2 with 15/35/25/25, and EM3 with 15/35/35/15) and PM series (PM1 with 15/35/15/35, PM2 with 15/35/25/25, and PM3 with 15/35/35/15) on 4-mm plywood panels under cone calorimeter tests

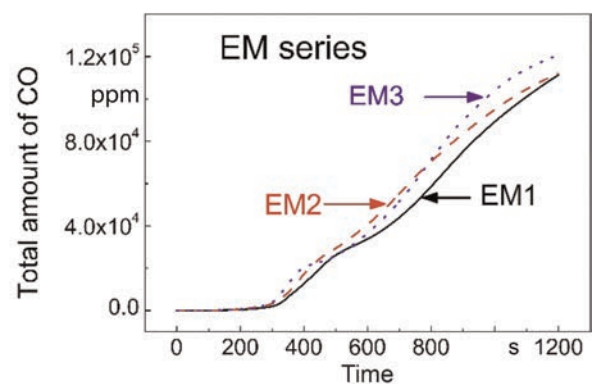
regulation was used to evaluate coating film durability, because the better durability of the intumescent char layer indicates that the char layer has a better structure. A better char layer structure can block heat transfer from the surface to the underlying material. As shown in Fig. 7A, the EM and PM series passed the CNS 14705-1 regulation (i.e., $\text{THR}_{300} < 8 \text{ MJ m}^{-2}$), indicating that the EM and PM series at different FPS/DA ratios became a flame-retardant material. In our pre-

vious study (Chuang et al., 2013), the THR_{300} of FRV4, 5, and 6 was 4, 3, and 17 MJ m^{-2} , respectively. The results indicated that FRV6 could not pass the CNS 14705-1 regulation, which means a higher DA content is required to facilitate the formation of phosphor-carbonaceous structures when VAC copolymer resin is used as a BR in intumescent coatings. Therefore, the intumescent coatings of the EM and PM series could protect the 4-mm plywood material. The binder comprising vinyl acetate monomer can enhance fire retardancy performance. This observation is consistent with that reported by Pimenta et al. (2016).

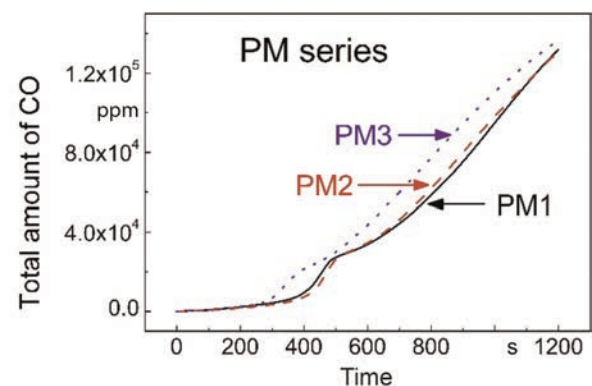
After ensuring the flame retardancy of the EM and PM series, the toxic products of combustion are another evaluation parameter for choosing the intumescent formulation. Figure 7B presents the evaluation results of $\text{CO}_{\text{av}300}$ and $\text{CO}_{2\text{av}300}$, which are toxic products of intumescent coatings produced in fire combustion. In the EM series, EM1 emitted lower amounts of CO (8.6 ppm) and CO_2 (564 ppm). By contrast, PM1 emitted a lower amount of CO_2 (584 ppm), and PM2 emitted a lower amount of CO (12 ppm). Furthermore, $\text{CO}_{\text{av}300}$ emissions in FRV4 and 5 were 21 and 15 ppm, respectively, and $\text{CO}_{2\text{av}300}$ emissions in FRV4 and 5 were 551 and 567 ppm, re-



A)

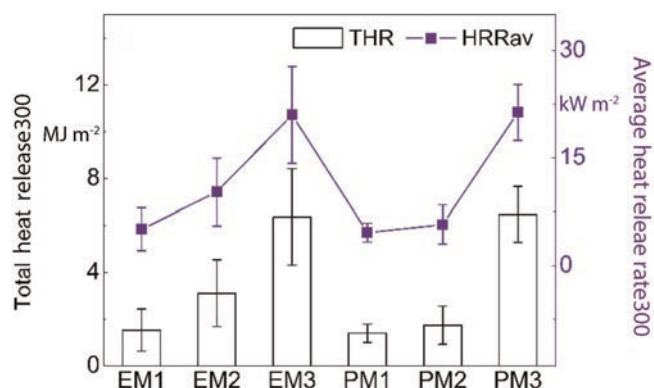


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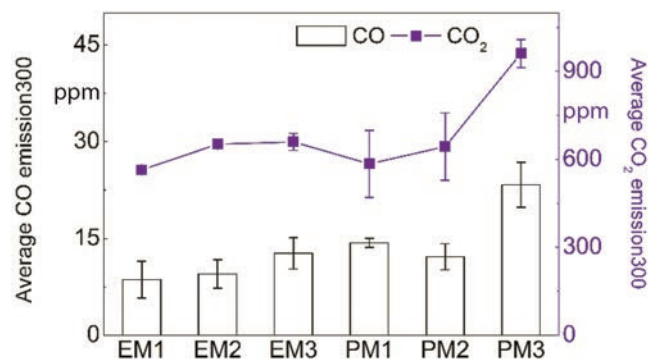


C)

Fig. 6. CO production (A) and total amount of CO produced (B and C) with different formulations of EM series (EM1 with 15(binder resin)/35(carbonizing substance)/15(foam producing substance)/35(dehydrating agent), EM2 with 15/35/25/25, and EM3 with 15/35/35/15) and PM series (PM1 with 15/35/15/35, PM2 with 15/35/25/25, and PM3 with 15/35/35/15) on 4-mm plywood panels under cone calorimeter test



A)



B)

Fig. 7. Combustion profiles and CO/ CO_2 production for different formulation coatings of EM series (EM1 with 15(binder resin)/35(carbonizing substance)/15(foam producing substance)/35(dehydrating agent), EM2 with 15/35/25/25, and EM3 with 15/35/35/15) and PM series (PM1 with 15/35/15/35, PM2 with 15/35/25/25, and PM3 with 15/35/35/15) on 4-mm plywood panels, A) total heat released at 300 s (THR_{300}), B) and the average heat release rate at 300 s ($\text{HRR}_{\text{av}300}$) average CO at 300 s ($\text{CO}_{\text{av}300}$) and average CO_2 at 300 s ($\text{CO}_{2\text{av}300}$)

spectively. These results indicated that EM1 emitted a lower amount of CO among the three different vinyl acetate copolymer emulsion resins and that FRV4 emitted a lower amount of CO₂. Although PVAc as a BR in intumescent coatings exhibited better flame retardancy in the cone calorimeter test results, its CO and CO₂ emissions were high during combustion.

3.4 Statistical Analysis of Different Formulations

To investigate the impact of intumescent formulations on flame retardancy, the THR values obtained at different heating durations were correlated with FPS contents in the EM and PM series. The values of statistical parameters (r^2 , P, and SE) for both series are summarized in Table 3. The r^2 values were 0.97, 0.95, 0.93 and 0.96 for the THR values of the EM series, indicating a good correlation between the THR and FPS content. The THR value decreased with decreasing FPS content in the EM series. The PM series showed the same trend. The r^2 values were 0.99, 0.99, 0.87, and 0.81 for the THR values of the PM series. The THR values decreased in the earlier stage of combustion. The normalized r^2 value is an effective criterion

for evaluating the FPS content because it is related to the formulation of each series.

Table 3 indicates that the trend was observed for CO₂ emissions. The r^2 values of the EM series for CO₂ emissions were 0.88, 0.93, 0.94, and 0.97, indicating a good correlation between the CO₂ and FPS content. The r^2 values of the PM series for CO₂ emissions were 0.96, 0.95, 0.99, and 0.98. The CO₂ values decreased in the earlier stage of combustion. The FPS content had the most effect on the samples in the EM and PM series. In particular, the trends of SE and P values for the EM and PM series were consistent in the earlier stage of combustion. Results of CO emissions also showed the same trend. These findings indicate that the intumescent formulation controlled the THR and CO₂ and CO emissions values in the earlier stages of combustion. This phenomenon improves the flame retardancy of painted plywood.

4 Conclusions

In the intumescent formulation, different binder resins enhanced the fire performance of the painted plywood material.

THR						
	r^2		P		SE	
Time	EM	PM	EM	PM	EM	PM
100 s	0.97	0.99	1.4×10^{-2}	2.6×10^{-3}	0.2	0.2
200 s	0.95	0.99	2.4×10^{-2}	2.6×10^{-3}	0.3	0.2
300 s	0.93	0.87	3.2×10^{-2}	6.7×10^{-2}	1.5	1.7
400 s	0.96	0.81	1.9×10^{-2}	9.8×10^{-2}	2.8	5.2
CO ₂						
	r^2		P		SE	
Time	EM	PM	EM	PM	EM	PM
100 s	0.88	0.95	5.7×10^{-2}	2.5×10^{-2}	2.1×10^{-2}	1.8×10^{-2}
200 s	0.93	0.96	3.4×10^{-2}	2.0×10^{-2}	1.9×10^{-2}	2.0×10^{-2}
300 s	0.94	0.95	3.1×10^{-2}	2.5×10^{-2}	1.9×10^{-2}	2.2×10^{-2}
400 s	0.97	0.96	1.3×10^{-2}	1.9×10^{-2}	1.8×10^{-2}	2.6×10^{-2}
CO						
	r^2		p		SE	
Time	EM	PM	EM	PM	EM	PM
100 s	0.96	0.87	1.9×10^{-2}	6.5×10^{-2}	2.3×10^{-6}	2.7×10^{-4}
200 s	0.95	0.89	2.5×10^{-2}	5.3×10^{-2}	8.4×10^{-5}	4.1×10^{-4}
300 s	0.99	0.94	3.0×10^{-3}	2.5×10^{-2}	1.1×10^{-4}	4.6×10^{-4}
400 s	0.98	0.92	9.5×10^{-3}	3.8×10^{-2}	7.1×10^{-4}	1.2×10^{-3}

Table 3. Statistical analysis between the total heat released (THR), and CO₂ and CO values at 100, 200, 300, and 400 s and different resins of the EM (with ethylene vinyl acetate copolymer as the binding resin) and PM (with polyvinyl acetate copolymer as the binding resin) series

When the same binder was used, a low quantity of FPS enhanced the fire performance of the plywood panel. The THR analysis of the EM and PM series indicated that all samples in the EM and PM series satisfied Chinese National Standard (CNS) regulations for flame-retardant materials. Among the three vinyl acetate copolymer emulsion resins, PVAc exhibited better flame retardancy; however, it emitted high amounts of CO and CO₂. Therefore, the fire performance of intumescent coatings was affected by different BRs. High FPS content produces large quantities of noncombustible gas during combustion; the generation of considerable noncombustible gases did not provide an ideal phosphor-carbonaceous char layer. Therefore, EM3 and PM3 demonstrated higher THR, PHRR, and CO/CO₂ emissions in this study. Furthermore, TGA analyses also showed that EM3 and PM3 had lower thermal stability than other formulations such as EM1/EM2 and PM1/PM2. From the CO and CO₂ analysis, it was concluded that the formulation of EM1 (with a BR/CS/FPS/DA ratio of 15/35/15/35) and PM1 (with a BR/CS/FPS/DA ratio of 15/35/15/35) had better flame retardancy and emitted lower amounts of CO and CO₂. In summary, the EM1 formulation exhibited better THR and low CO and CO₂ emissions. In this study, the underlying mechanisms were studied; the results can assist in improving the fire performance of plywood with intumescent coatings.

References

- Almeras, X., Le Bras, M., Hornsby, P., Bourbigot, S., Marosi, G. Keszei, S. and Poutch, F., “Effects of Fillers on the Fire Retardancy of Intumescent Polypropylene Compounds”, *Polym. Degrad. Stab.*, **82**, 325–331 (2003), DOI:10.1016/S0141-3910(03)00187-3
- Alongi, J., Han, Z. and Bourbigot, S., “Intumescence: Tradition versus Novelty. A Comprehensive Review”, *Prog. Polym. Sci.*, **51**, 28–73 (2015), DOI:10.1016/j.progpolymsci.2015.04.010
- Anees, S. M., Dasari, A., “A Review on the Environmental Durability of Intumescent Coatings for Steel”, *J. Mater. Sci.*, **53**, 124–145 (2018), DOI:10.1007/s10853-017-1500-0
- Anna, P., Marosi, G., Csontos, I., Bourbigot, S., Le Bras, M. and Delobel, R., “Influence of Modified Rheology on the Efficiency of Intumescent Flame Retardant Systems”, *Polym. Degrad. Stab.*, **74**, 423–426 (2001), DOI:10.1016/S0141-3910(01)00180-X
- Biswas, B., Kandola, B. K., Horrocks, A. R. and Price, D., “A Quantitative Study of Carbon Monoxide and Carbon Dioxide Evolution during Thermal Degradation of Flame Retarded Epoxy Resins”, *Polym. Degrad. Stab.*, **92**, 765–776 (2007), DOI:10.1016/j.polymdegradstab.2007.02.006
- Bourbigot, S., Le Bras, M., Delobel, R., Decressaing, R. and Amoureux, J. P., “Synergistic Effect of Zeolite in an Intumescent Process: Study of the Carbonaceous Structures Using Solid-State NMR”, *J. Chem. Soc. Faraday Trans.*, **92**, 149–158 (1996), DOI:10.1039/FT9969200149
- Camino, G., Costa, L. and Martinasso, G., “Intumescent Fire-Retardant Systems”, *Polym. Degrad. Stab.*, **23**, 359–376 (1989), DOI:10.1016/0141-3910(89)90058-X
- Chuang, C. S., Tsai, K. C., Wang, Y. C., Wang, M. K. and Ko, C. H., “Impact of Wetting and Drying Cycle Treatment of Intumescent Coatings on the Fire Performance of Thin Painted Red Lauan (*Parashorea sp.*) Plywood”, *J. Wood Sci.*, **56**, 208–215 (2010), DOI:10.1007/s10086-009-1089-2
- Chuang, C. S., Yang, T. H., Tsai, K. C., Tseng, T. Y. and Wang, M. K., “Fire Retardancy and CO/CO₂ Emission of Intumescent Coatings on Thin Plywood Panel with Waterborne Vinyl Acetate-Acrylic Resin”, *Wood Sci. Technol.*, **47**, 353–367 (2013), DOI:10.1007/s00226-012-0491-x
- Demir, H., Arkis, E., Balköse, D. and Ülkü, S., “Synergistic Effect of Natural Zeolites on Flame Retardant Additives”, *Polym. Degrad. Stab.*, **89**, 478–483 (2005), DOI:10.1016/j.polymdegradstab.2005.01.028
- Gao, M., Sun, C. Y. and Wang, C. X., “Thermal Degradation of Wood Treated with Flame Retardants”, *J. Therm. Anal. Calorim.*, **85**, 765–769 (2006), DOI:10.1007/s10973-005-7225-3
- Girardin, B., Fontaine, G., Duquesne, S., Forsth, M. and Bourbigot, S., “Measurement of Kinetics and Thermodynamics of the Thermal Degradation for Flame Retarded Materials: Application to EVA/ATH/NC”, *J. Anal. Appl. Pyrol.*, **124**, 130–148 (2017), DOI:10.1016/j.jaap.2016.12.034
- Gu, J., Zhang, G., Dong, S., Zhang, Q. and Kong, J., “Study on Preparation and Fire-Retardant Mechanism Analysis of Intumescent Flame-Retardant Coatings”, *Surf. Coat. Technol.*, **201**, 7835–7841 (2007), DOI:10.1016/j.surfcoat.2007.03.020
- Kandola, B. K., Horrocks, A. R., “Complex Char Formation in Flame-Retarded Fire-Intumescent Combinations II-Thermal Analytical Studies”, *Polym. Degrad. Stab.*, **54**, 289–303 (1996), DOI:10.1177/004051759906900512
- Pimenta, J. T., Concalves, C., Hiliou, L., Coelho, J. F. J. and Magalhães, F. D., “Effect of Binder on Performance of Intumescent Coatings”, *J. Coat. Technol. Res.*, **13**, 227–238 (2016), DOI:10.1007/s11998-015-9737-5
- Qian, W., Li, X., Zhou, J., Liu, Y. and Wu, Z., “High Synergistic Effects of Natural-Based Tea Saponin in Intumescent Flame-Retardant Coatings for Enhancement of Flame Retardancy and Pyrolysis Performance”, *Prog. Org. Coat.*, **127**, 408–418 (2019), DOI:10.1016/j.porgcoat.2018.10.031
- Rimez, B., Rahier, H., Van Assche, G., Artoos, T., Biesemans, M. and Van Mele, B., “The Thermal Degradation of Poly(vinyl acetate) and Poly(ethylene-co-vinyl acetate), Part I: Experimental Study of the Degradation Mechanism”, *Polym. Degrad. Stab.*, **93**, 800–810 (2008), DOI:10.1016/j.polymdegradstab.2008.01.010
- Siat, C., Le Bras, M. and Bourbigot, S., “Combustion Behaviour of Ethylene Vinyl Acetate Copolymer-Based Intumescent Formulations Using Oxygen Consumption Calorimetry”, *Fire Mater.*, **22**, 119–128 (1998), DOI:10.1002/(SICI)1099-1018(199805)22:3<119::AID-FAM646>3.0.CO;2-2
- Wladyka-Przbylak, M., Kozłowski, R., “The Thermal Characteristics of Different Intumescent Coatings”, *Fire Mater.*, **23**, 33–43 (1999), DOI:10.1002/(SICI)1099-1018(199901/02)23:1<33::AID-FAM667>3.0

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