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Impact of wetting and drying cycle treatment of intumescent coatings on the fire performance of thin painted red lauan (*Parashorea* sp.) plywood

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Abstract Emulsion resins are widely used in wood-based materials for indoor furnishings. Previous studies have demonstrated that the ability of a material to retard flame arises from the interactions between four major components: i.e., binder resin (BR); carbonizing substrate (CS); foam-producing substance (FPS); and dehydrating agent (DA). Fire performance as influenced by wetting and drying cycle (WDC) treatment has not yet been reported. This study aimed to compare the fire performance of materials coated with EVAc (ethylene vinyl acetate copolymer) and PVAc (polyvinyl acetate copolymer) emulsion resins of differing BR/CS ratios, subjected to investigation by cone calorimeter. Intumescent formulation significantly enhanced the fire retardancy of painted plywood by exhibiting lower peak heat release rates (PHRR) and longer time to reach peak release rates. Additionally, lower BR content in the fire retardant systems further enhanced flame retardancy. The fire retardancy decreases with increasing the WDC treatment, caused by the weight loss of the coating materials. Infrared (FT-IR) analysis demonstrated that lower BR content extends the survival duration of the phosphor-carbonaceous structure of chars. The findings in this study enhance the state-of-the-art understanding of the effect of the intumescent.

Key words Ethylene vinyl acetate copolymer (EVAc) · Polyvinyl acetate copolymer (PVAc) · Cone calorimeter · Intumescent · Red lauan plywood

Introduction

Ethylene vinyl acetate copolymer (EVAc) and polyvinyl acetate copolymer (PVAc) emulsion resins are widely used in wood and wood-based materials for indoor furnishings. Wood and wood-based materials are of great importance in residential, commercial, and industrial building construction. Wood and resins are particularly flammable and emit a large amount of smoke while burning; thus, employing flame retardants becomes important. Plywood materials can be used more widely in public construction decorations after fire retardant treatment, and such materials are safer than those without fire retardant treatment. Due to an increasing requirement for public safety, flame retardant treatment of wood-based materials has experienced increased demand.^{1,2} Fire retardants are defined as chemical compounds that modify the pyrolysis mechanisms of the oxidation reaction and subsequently retard the process of combustion.³ Many types of flame retardants are currently used for consumer products.^{4,5}

In research for halogen-free flame retardants, intumescent flame retardant (IFR) has received considerable attention recently because it provide fire protection with minimum overall health hazards,⁶ and IFR is also the fastest and most convenient way to enhance the fire performance of wood-based materials. Under the heat of the earlier stage of a fire, intumescent paints achieve flame retardancy by forming a charred layer that acts as a physical barrier to deter heat and mass transfer between the gas and the condensed phases.⁷ The charred layers, with low thermal conductivity, then form a carbonaceous layer by cyclization and cross-linking with phosphate ester.⁸

The IFR system is composed of four components: (1) binder resin (BR), (2) a carbonizing substance (CS) to form the carbonized layer, such as polyols, (3) a foam-producing

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substance (FPS) to release inert gases NH_3 , CO_2 , and H_2O as well as to support intumescent action and char formation to further retard heat and mass transfer, and (4) a dehydrating agent (DA) to lower the decomposition temperature and accelerate the formation of a carbonized layer, such as ammonium phosphate, boric acid, and borax.⁹ The impact of intumescent formulation on the fire performance of coated plywood has been demonstrated.¹⁰ In our previous study, the results indicated that lower BR content increase the fire retardancy of coated plywood. However, the flammability of coating films after wetting and drying cycles (WDC) is rarely elucidated.

In this study, different formulations using these four major components were systematically investigated to provide a fundamental understanding of the influence of intumescent gradients, and the coating films treated by different WDC were also evaluated. The components used were (1) EVAc emulsion resin and PVAc emulsion resin as a BR, (2) pentaerythritol as a CS, (3) melamine as a FPS, and (4) ammonium polyphosphate (APP) as a DA. A cone calorimeter was employed to investigate the change in fire performance of plywood painted with the different formulations. This study also especially evaluated the different WDC affecting the weight loss related to fire retardancy. Chars of fire retardant paints exhibiting better flame retardancy were collected after exposure to heat and analyzed by Fourier-transform infrared (FT-IR) spectroscopy. Relationships between the char chemical structure and fire performance were also investigated.

Materials and methods

Materials

The basic wood material is a 4-mm-thick red lauan (*Parashorea* sp.) plywood panel, 300 mm (L) \times 300 mm (W). The intumescent flame retardant (IFR) paint contained a commercial ethylene vinyl acetate (EVAc) copolymer emulsion resin and polyvinyl acetate copolymer (PVAc) emulsion resin, which served as binder resin (BR); the EVAc was supplied by Dairen Chemical (Taipei, Taiwan), with 2000 cps viscosity and a solid content of 55%, and the PVAc was supplied by Yeou Shuenn Products (Kaohsiung, Taiwan), with 15000 cps viscosity and a solid content of 44%. Pentaerythritol and melamine were purchased from Acros Organics (Phillipsburg, NJ, USA). Ammonium polyphosphate (APP) was purchased from U-Way C.E.T. (Taipei, Taiwan). The degree of polymerization (n) of ammonia polyphosphate in this study was approximately 1000.

Sample preparation

Two different sample groups were investigated, including the FRE and the FRP series. The ratio of formulation was in accordance with Chuang et al.¹⁰ The FRE (fire retardant paint with EVAc) and FRP (fire retardant paint with PVAc)

series had an identical solid weight ratio (w/w) of FPS and DA with changing ratios of BR and CS to investigate char-forming capability. The required weight of each of the four major components were combined and stirred at 600 rpm for 4 h.

The fire retardant paint was spread on the surface of the plywood panel using a brush and then air dried. The solid content of the fire retardant paint was approximately 60% during painting. The solid coating weight was 360 g m^{-2} (i.e., each plywood panel was coated with a total of 32.4 g paint after three equal coatings). Before flammability testing, air-dried specimens (i.e., coated plywood panels) were heated at 45°C in an oven for 48 h; the cooled specimens were then placed in a desiccator for 24 h. According to CNS 6532,¹¹ the moisture content for all specimens must be equal. Because the relative humidity of Taiwan is around 60%–80%, preconditioning is necessary. The preconditioning procedure for moisture content control is specified in ASTM E 1354-99.¹²

Wetting and drying cycle (WDC) treatments

WDC treatment was conducted for the coating samples, which were then evaluated for the effectiveness of fire-resistant performance. According to CNS 11728,¹³ the sample was placed vertically at $20^\circ \pm 3^\circ\text{C}$ and 90% relative humidity (RH) for 19 h. The sample was then placed in a 50°C oven for 5 h. The WDC treatments were done in triplicate. The weight of each WDC sample was recorded at each stage. The water absorption capability of different coatings was observed by weight. After the WDC treatment was repeated three times, the sample was placed into a sealed polyethylene plastic bag, to prevent it from adsorbing water, and then subjected to flammability tests by cone calorimeter.

Flammability tests by cone calorimeter

A cone calorimeter (Fire Testing Technology, East Grinstead, UK) was employed to evaluate the efficiency of the fire retardant, as specified using the ASTM E 1354 method.¹² Specimens were placed horizontally oriented with an external igniter, and the flux of the cone heater was set as 50 kW m^{-2} . The total test time was 1200 s, and all tests were conducted in triplicate. The following fire properties of the materials were determined: average heat release rate [HRR_{av} (kW m^{-2})] (within 1200 s); peak heat release rate [PHRR (kW m^{-2})]]; total heat release [THR (MJ m^{-2})]]; time to ignition [Tig (s)]; and time to PHRR (s). The PHRR and HRR_{av} values correspond to the acceleration of the thermal degradation of the materials, which is related to the spread of fire. Total heat release (THR) indicates the total heat capacity during the process of material combustion. THR with duration of 100, 200, 300, and 400 s were then integrated from the heat release profiles for additional analysis. PHRR was used to evaluate the fire retardancy of the intumescent char.

Fourier-transform infrared (FT-IR) analysis

The char of FRE and FRP samples, under 50 kW m^{-2} heat flux for 50 and 200 s, were collected, ground, and pelletized with KBr powder in 1:300 ratio (mg/mg). Then the pellets were scanned in the range of $500\text{--}4000 \text{ cm}^{-1}$, and as-synthesized manganese oxide samples were recorded on a Nicolet 380 spectrophotometer (Thermo Scientific, Waltham, MA, USA). The varied heating time of different compositions can be used to evaluate the functional groups of fire retardant chemical reaction.

Statistical analysis

SAS Institute software was employed for statistical analysis (SAS Institute, Cary, NC, USA). Statistical analysis of THR values was used to evaluate the correlation between different components and combustion time (i.e., 100, 200, 300, or 400 s). A linear regression analysis was applied and the goodness-of-fit was evaluated using r^2 (determination coefficient), level of significance (P value), and standard error (SE). Comparison of the different amounts of BR and FPS, correlated with combustion time, was performed using the least significant difference (LSD). The LSD values were calculated using SE and the t test at appropriate degrees of freedom and 95% confidence levels.

Results and discussion

Cone calorimeter test results of different coatings on plywood panels without WDC treatment

Figure 1 shows the heat release rate (HRR) curves of all specimens without WDC treatment in the cone calorimeter tests. Table 1 lists the data of Tig, HRR_{av} , PHRR, THR, and time to PHRR. Obviously, the first peak (stage I) can be attributed to the fire retardant paint, and the second (stage II) is accounted for by the plywood. The PHRR and time to PHRR data were expressed as two items, forming the peak values of the two stages just described. The PHRR was the most significant parameter when identifying the enhancement of flame retardancy for the samples. As shown in Table 1, comparison of PHRR, HRR_{av} , THR, and time to PHRR could partially assist in evaluation of the flame retardancy of samples coated by the various intumescent formulations. HRR_{av} values of uncoated plywood before and after WDC treatment were 57 kW m^{-2} and 48 kW m^{-2} , respectively, in the previous study.¹⁰

Due to the importance of formulation of the four components, tests for the FRE and FRP series were employed to study the impact of altering the ratio of binder resin (BR) and the carbonizing substance (CS) upon the fire retardancy of the painted plywood, setting the solid weight ratio

Fig. 1. Heat release profiles for different coatings without wetting and drying cycle (WDC) treatment on 4-mm plywood panel of (A) FRE (fire retardant paint with EVAc) series and (B) FRP (fire retardant paint with PVAc) series

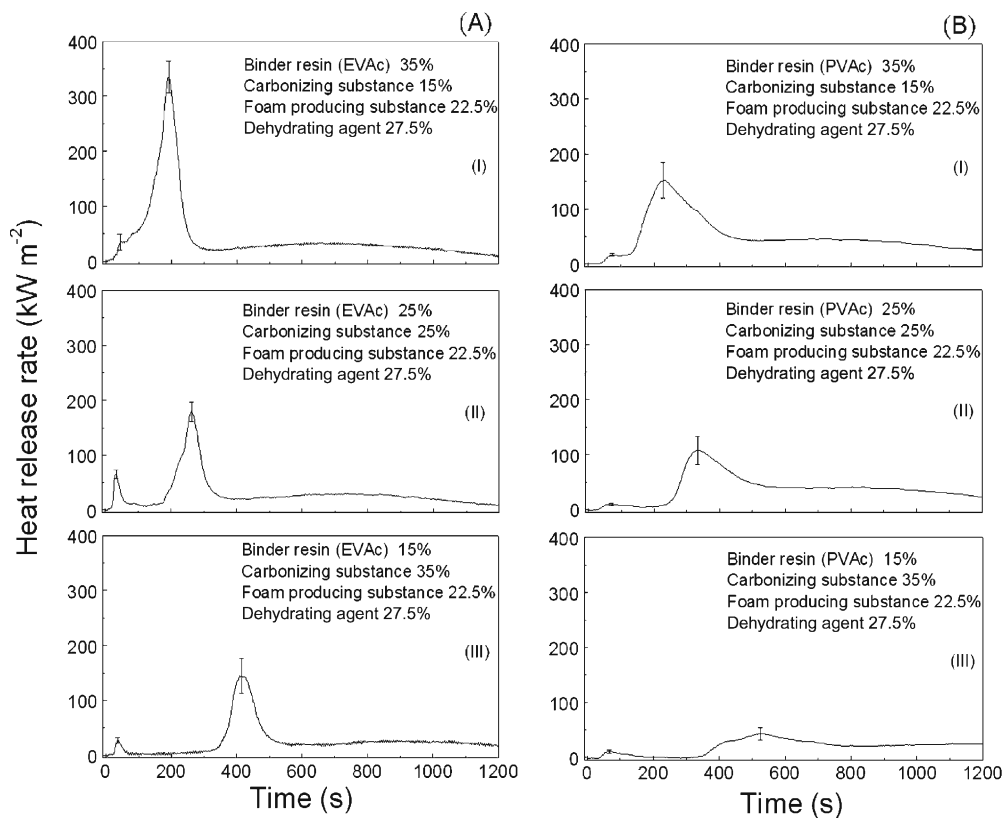


Table 1. Cone calorimeter evaluation of plywood coated with various formulations without and with wetting and drying cycle (WDC) treatment

Without WDC treatment									
	Weight (g)		Tig (s)	HRR _{av} (kW m ⁻²)	PHRR (kW m ⁻²)		Time to PHRR (s)		THR (MJ m ⁻²)
	Before	After			Stage I	Stage II	Stage I	Stage II	
FRE1	31 ± 0.4	–	21 ± 3.0	43 ± 2.2	35 ± 14.2	334 ± 29.2	42 ± 2.1	192 ± 4.6	52 ± 2.6
FRE2	32 ± 0.7	–	18 ± 2.7	29 ± 3.1	65 ± 7.6	178 ± 17.4	33 ± 1.7	264 ± 3.0	35 ± 3.8
FRE3	30 ± 0.2	–	21 ± 1.7	28 ± 2.3	24 ± 5.1	144 ± 31.6	36 ± 3.0	414 ± 13.5	33 ± 2.7
FRP1	31 ± 1.5	–	36 ± 4.6	50 ± 5.2	16 ± 2.2	152 ± 32.5	75 ± 1.7	228 ± 7.5	60 ± 6.3
FRP2	31 ± 0.7	–	30 ± 4.6	38 ± 1.1	9 ± 1.5	107 ± 25.9	72 ± 3.0	333 ± 30.0	45 ± 1.3
FRP3	31 ± 0.5	–	30 ± 3.0	19 ± 4.7	11 ± 2.4	43 ± 11.2	66 ± 4.6	525 ± 9.2	23 ± 5.6

With WDC treatment									
	Weight (g)		Tig (s)	HRR _{av} (kW m ⁻²)	PHRR (kW m ⁻²)		Time to PHRR (s)		THR (MJ m ⁻²)
	Before	After			Stage I	Stage II	Stage I	Stage II	
FRE _w 1	31 ± 0.3	29 ± 0.6	36 ± 0.8	31 ± 2.7	99 ± 8.3	–	204 ± 10.7	–	37 ± 3.2
FRE _w 2	30 ± 3.1	28 ± 3.3	24 ± 4.6	34 ± 4.2	12 ± 2.3	101 ± 21.9	96 ± 7.5	327 ± 7.9	41 ± 4.9
FRE _w 3	30 ± 0.9	28 ± 0.2	21 ± 7.5	33 ± 6.9	14 ± 1.8	104 ± 19.4	51 ± 4.6	405 ± 13.5	40 ± 8.3
FRP _w 1	30 ± 2.1	29 ± 2.1	45 ± 4.6	31 ± 0.5	16 ± 12.2	124 ± 25.1	99 ± 3.0	258 ± 21.1	37 ± 0.6
FRP _w 2	29 ± 1.4	27 ± 1.5	18 ± 1.7	35 ± 5.1	15 ± 4.6	82 ± 31.3	54 ± 4.6	321 ± 31.8	42 ± 6.2
FRP _w 3	30 ± 3.2	28 ± 3.2	21 ± 3.0	26 ± 5.3	14 ± 5.4	58 ± 16.5	60 ± 14.8	438 ± 12.7	32 ± 6.4

Data are ± standard deviation ($n = 3$)

FRE, fire retardant paint with ethylene vinyl acetate copolymer (EVAc); FRP, fire retardant paint with polyvinyl acetate copolymer (PVAc); Tig, time to ignition; HRR_{av}, average heat release rate; PHRR, peak heat release rate; THR, total heat release; Before, before WDC treatment; After, after WDC treatment

of FPS and DA at 22.5% and 27.5%, respectively. The ratio of FRE1 was 35/15/22.5/27.5 (BR/CS/FPS/DA). The first and second stages of PHRR were 35 kW m⁻² and 334 kW m⁻² and THR was 52 MJ m⁻² (*I* in Fig. 1A; Table 1). The time to PHRR was 42 and 192 s for the FRE1 sample. The ratio of FRE2 was 25/25/22.5/27.5 (BR/CS/FPS/DA). The first-stage PHRR of FRE2 was 65 kW m⁻², and THR was reduced to 35 MJ m⁻². The second-stage PHRR was 178 kW m⁻² (*II* in Fig. 1A; Table 1). The time to PHRR of the first and second stages was 33 and 264 s, respectively. The ratio of FRE3 was 15/35/22.5/27.5 (BR/CS/FPS/DA). The first-stage PHRR of FRE3 was 24 kW m⁻² and THR was 33 MJ m⁻². The second-stage PHRR of FRE3 was 144 kW m⁻². Time to the first and second stages of peak heat release was 36 and 414 s, respectively (*III* in Fig. 1A). By showing lower rate values, larger intervals between peak heat release occurrence and longer times to peak heat release, the flame retardancy was ranked as FRE3 > FRE2 > FRE1. Lower PHRR and THR values demonstrated improved flame retardancy of painted plywood under combustion. The longer time between two PHRR appeared to translate into superior durability of formed char for FRE3 under heat. Excessive binder resin provided more combustibles, which contributed to higher PHRR and lesser thermal durability of the FRE1 char. Among the FRE series, the optimal BR/CS formulation was weight ratio of 15/35, as shown as FRE3.

The same trend was shown in the FRP series: FRP3 showed great flame retardancy of the intumescent layer (Table 1, Fig. 1B). In demonstrating lower peak heat release rates values, larger intervals between peak heat release

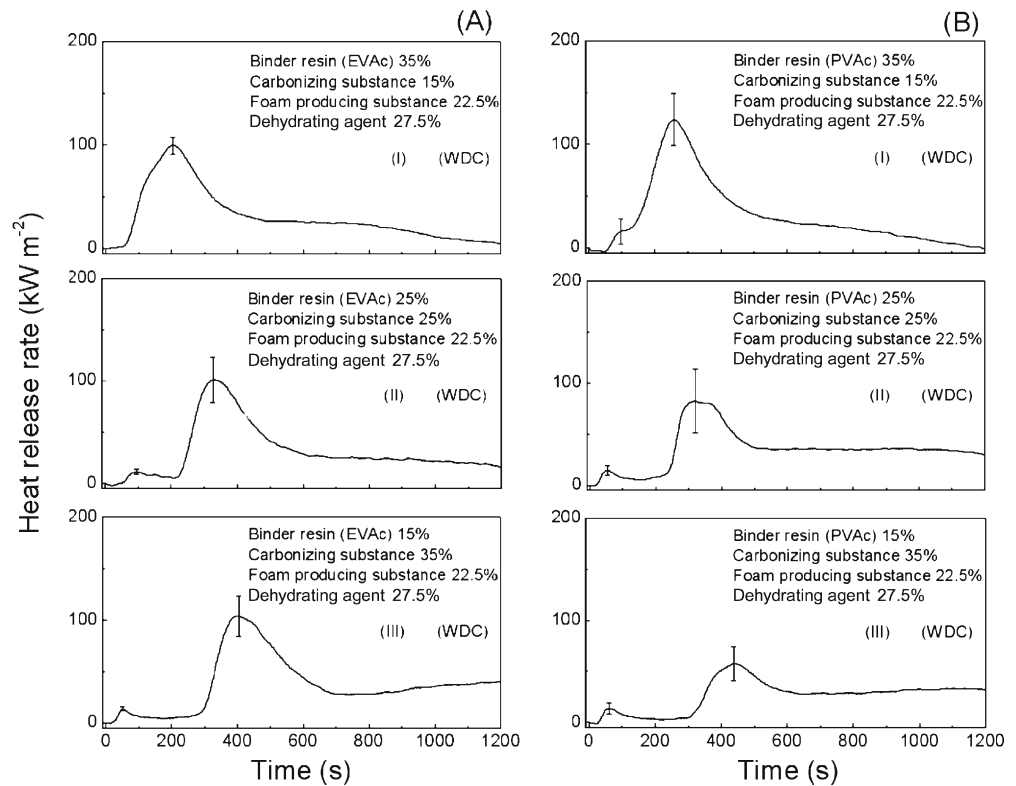
occurrence, and a longer time to peak heat release, the flame retardancy was ranked as FRP3 > FRP2 > FRP1. Excessive binder resin provided more combustible material and contributed to a higher PHRR and lowered thermal durability of the FRP1 char. Hence, lower BR content improved the fire performance and showed better protection of the underlying material (i.e., plywood). Among the FRP series, the optimal BR/CS formulation was at a weight ratio of 15/35, designated as FRP3. Similar observations were made by Chuang et al.¹⁰

Horrocks and Price⁸ pointed out that using a polyol compound as the carbonizing substance and phosphorus as a dehydrating agent may cause an esterification reaction under decomposition by heat. At the same time, the FPS (melamine) degraded and released incombustible gases. Wladyka-Przybylak and Kozłowski¹⁴ also concluded that a coating of fire retardant paint resulted in the production of incombustible gases, which blocked the access of oxygen. Comparison the FRE and FRP series, the PVAc as BR has better flame retardant performance than EVAc. This result indicated that PVAc maintains the completeness and continuity of char layer, and hence it can limit oxygen diffusion and/or can reduce heat transfer through the char layer.

Cone calorimeter test results of different coatings on plywood panels with WDC treatment

The FRE_w and FRP_w series with WDC treatment were conducted by the same ratios for FRE1, FRE2, and FRE3 samples and FRP1, FRP2, and FRP3 samples, respectively.

Fig. 2. Heat release profiles for different coatings with WDC treatment on 4-mm plywood panel combustion of (A) FRE_w series and (B) FRP_w series



The higher weight gain rate indicated the sample absorbed more water and weight loss in the oven was then higher. With WDC treatment, the weight gain and higher weight loss had more influence on coating flammability. In the IFR system, we inferred that the binder resin (BR) has the greatest influence of the four major compounds, because the BR wrapped the other three components. Thus, WDC treatment showed more influence on the binder resin than on the other three components. We infer that higher BR content absorbs more water during WDC treatment and causes the other three compounds to dissolve from the surface after oven drying. Thus, the fire retardant will decrease after WDC treatment. Moreover, the wettability of BR was a parameter of water absorption capability. From this point of view, EVAc has better water resistance than PVAc. According to the results, the higher weight increase rate indicated higher water absorption capability. Comparing weight change rate and flame retardant performance, the results show water absorption capability has a significant effect on the fire performance of different formulation coatings with WDC treatment.

According to the WDC treatment results of the cone calorimeter tests summarized in Table 1, the PHRR was 99 kW m^{-2} and the THR was 37 MJ m^{-2} [Fig. 2A(I), Table 1]. The time to PHRR was 204 s for the FRE_{w1} sample. The result was close to that of untreated plywood,¹⁰ and the typical peak of the intumescent layer was delayed; this indicated the protective shield of the char layer has disappeared. The first-stage PHRR of FRE_{w2} was 12 kW m^{-2} , and THR was reduced to 41 MJ m^{-2} . The second-stage PHRR was 101 kW m^{-2} [Fig. 2A(II), Table 1]. The time to PHRR of the first and second stages was 96 and 327 s, respectively.

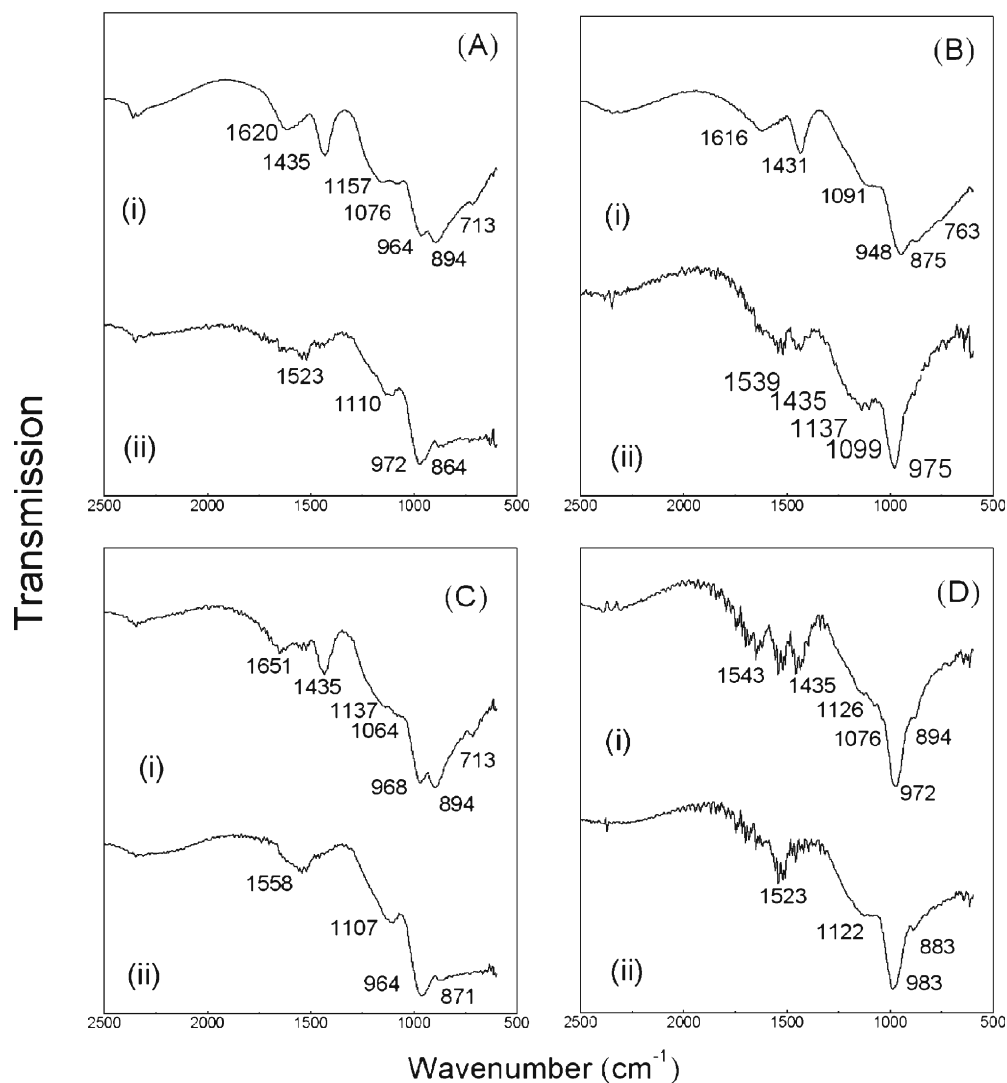
The first-stage PHRR of FRE_{w3} was 14 kW m^{-2} and THR was 40 MJ m^{-2} . The second-stage PHRR of FRE_{w3} was 104 kW m^{-2} . Time to the first and second stages of peak heat release was 51 and 405 s, respectively [Fig. 2A(III)]. In FRE_{w3}, about 5% weight loss led to THR decrease of 21%.

The same trend was demonstrated in the FRP series (Table 1, Fig. 2). After WDC treatment, delayed time of occurrence to stage I PHRR and earlier occurrence to stage II PHRR was observed, e.g., FRP_{w2} and FRP_{w3}. The delayed time of occurrence to stage I PHRR suggested the postponement of intumescent action. The earlier occurrence to stage II PHRR suggested the inferior heat endurance of the intumescent layer. Both findings indicated the decreased fire performance of intumescent coatings. Thus, WDC treatment decreased the performance of fire protection for wood. In FRP_{w3}, about 6% weight loss led to THR decrease of 39%. The WDC treatment demonstrated the binder resin characteristic has significant influence in weight variation. More weight variation in WDC treatment decreased the fire performance.

Fourier-transform infrared analysis (FT-IR) of FRE and FRP series

The reactions of the FRE and FRP series were further evaluated. The FTIR analysis of the chars heated for 50 and 200 s demonstrated the different functional groups after combustion (Fig. 3). In the FRE series, the deformation vibration of P-O was observed to be 713 cm^{-1} , and the P-O-P of IR bending vibration was observed to be $864\text{--}894 \text{ cm}^{-1}$

Fig. 3. Fourier transform-infrared (FT-IR) spectra at different heating times: (A) FRE1 (with BR/CS/FPS/DA ratio of 35/15/22.5/27.5) and (B) FRP1 (with BR/CS/FPS/DA ratio of 35/15/22.5/27.5), without WDC treatment; (C) FRE_w1 (with BR/CS/FPS/DA ratio of 35/15/22.5/27.5) and (D) FRP_w1 (with BR/CS/FPS/DA ratio of 35/15/22.5/27.5), with WDC treatment. *i*, heated for 50 s; *ii*, heated for 200 s



in different heating times. The additional broad bands about 964–972 cm⁻¹ were assigned to modes of symmetrical vibration of PO₂ and PO₃.¹⁶ The P-O-C bonds of IR vibration modes were observed at 1076–1100 cm⁻¹, which was the result of “phosphate-carbon” complexes and/or P-O in a vitreous structure.¹⁵ The P-O-C bond was formed by alcoholysis of the polyphosphate chain.¹⁶ The P = O of the IR vibration mode was found at 1157 cm⁻¹. The stretching mode of P-OH was observed at 1620 cm⁻¹. At 50 s, these IR absorption bands indicated that the interaction between phosphoric acid and alcohol had resulted in a phosphor-carbonaceous structure (Fig. 3A), this was the main product and its formation dictated the flame retardancy. At 200 s, there was no P-OH IR absorption band, P = O absorption band, or P-O absorption band in the IR spectra of FRE1. This result indicated that the phosphor-carbonaceous char was broken and there was no fire protection for the underlying material. Compared to the cone calorimeter experiment, the plywood coated with FRE1 burned at 21–300 s. The time to second PHRR was 192 s; thus, the phosphor-carbonaceous char was degraded and the plywood was exposed to the heat at 200 s.

The FRP series had the same trend in phosphor-carbonaceous char transformation. In Fig. 3B, there was only one P-O absorption band, which disappeared at 200 s. The FRP1 IR spectra also demonstrate the entire phosphor-carbonaceous char at 50 and 200 s (Fig. 3B). The results indicated that the fire retardancy of FRP1 was better than FRE1 at 200 s. Compared by the cone calorimeter test, the result also has the same trend. On the other hand, the IR absorption bands were shown to be NH₄⁺ at 1432–1523 cm⁻¹,¹⁵ which was derived from the melamine. The flame retardancy can be evaluated by the degree of esterification, with faster esterification corresponding to a more flame retardant char.^{17–20} Consistent trends, demonstrated by cone calorimeter tests and FT-IR analysis, indicated that lower BR content resulted in a more durable phosphor-carbonaceous char structure. Thus, different proportions of the four major compounds had significant impact on the fire performance of painted thin plywood.

The sample treated by WDC has the same trend in FT-IR analysis. In the FRE_w series, the deformation vibration of the P-O absorption band and the stretching mode of P-OH disappeared at 200 s (Fig. 3C,D). Comparing to the

Table 2. Statistical analysis between THR values at 100, 200, 300, and 400 s and binder resin (BR) content of FRE and FRP series without and with WDC treatment

Time	100 s	200 s	300 s	400 s
Without WDC treatment				
r^2				
FRE	0.99	0.83	0.99	0.96
FRP	0.85	0.79	0.87	0.99
P				
FRE	3×10^{-3}	2.7×10^{-2}	3×10^{-3}	1.2×10^{-2}
FRP	2.5×10^{-2}	3.1×10^{-2}	2.4×10^{-2}	4.0×10^{-3}
SE				
FRE	0.1	5.9	0.9	2.9
FRP	0.1	1.9	5.3	1.1
With WDC treatment				
r^2				
FRE	0.98	0.75	0.92	0.95
FRP	0.61	0.82	0.93	0.99
P				
FRE	8×10^{-3}	3.3×10^{-2}	1.8×10^{-2}	1.3×10^{-2}
FRP	4.3×10^{-2}	2.8×10^{-2}	1.7×10^{-2}	2.0×10^{-3}
SE				
FRE	0.1	3.1	3.1	2.1
FRP	0.3	0.8	2.6	0.4

FRE series and cone calorimeter test, the results indicated the WDC treatment accelerated the combustion of coating films and plywood as a consequence of the degradation of the phosphor-carbonaceous structure. The FRP_w series also show the same trend. With WDC treatment, the P-O-C bending disappeared in the FRP_w series. Compared to the cone calorimeter test, the results indicated the phosphor-carbonaceous char structure was broken after WDC treatment. Thus, the IR analysis also coincided with the results of cone calorimeter tests (Fig. 3C,D). Hence, the binder resin (BR) properties and WDC treatment have significant effects on fire performance.

Statistical analysis with and without WDC treatment

Without WDC treatment, the FRE and FRP series were evaluated using the cone calorimeter, and all fire retardant-painted plywood samples demonstrated two stages of peak heat release. The first-stage PHRR was char forming from the fire retardant formulation to protect the underlying plywood panel, and the second-stage PHRR was char decomposition and the burning of plywood. To investigate the impact of intumescent formulation on flame retardancy, THR values of different heating durations were correlated with binding resin content in the FRE and FRP series. Table 3 summarizes the values of statistical parameters (r^2 , P , and SE) for both series. The determination coefficient (r^2) was 0.99, 0.83, 0.99, and 0.96 for the THR values of the FRE series, indicating good correlation between THR and BR content. THR decreases with decreasing concentration of EVAc emulsion resin (i.e., BR) in the FRE series. On the other hand, THR also decreases with decreasing polyvinyl acetate copolymer emulsion resin content in the FRP series. The r^2 values were 0.85, 0.79, 0.87, and 0.99 in the FRP series. The THR value was also clearly affected by the

PVAc content in this series. The THR values were decreased in the earlier stage of combustion. It should be noted that the normalized r^2 value is an effective criterion for evaluating BR content because it is definitely related to the formulation of each series.

With WDC treatment, the results have the same trend. The r^2 was 0.98, 0.75, 0.92, and 0.95 for the THR values of the FRE_w series, indicating good correlation between THR and BR content. In the FRP_w series the r^2 values were 0.61, 0.82, 0.93, and 0.99. The THR values were also decreased in the earlier stage of combustion. Obviously, the BR content had the greatest influence in the samples with and without WDC treatment. In particular, the trends of SE and P values for both the FRE and FRP series were consistent in the earlier stage of combustion. The foregoing analysis indicates that the intumescent formulation controls the THR values in the earlier stages of combustion and improves the flame retardancy of painted plywood.

Conclusions

The fire performance of painted thin red lauan plywood can be changed after being coated with an intumescent with different concentrations of the four major compounds. According to the cone calorimeter tests, the formulations of FRE3 (with BR/CS/FPS/DA ratio of 15/35/22.5/27.5) and FRP3 (with BR/CS/FPS/DA ratio of 15/35/22.5/27.5) displayed superior flame retardancy. Additionally, from THR and PHRR statistical analysis, time to PHRR demonstrated that the FRP3 formulation was better than the FRE3 formulations. WDC treatment demonstrated that the BR characteristic has significant influence in weight variation. More weight variation after WDC treatment decreased fire performance. Moreover, by FT-IR analysis, lower BR content

facilitated the extension of phosphor-carbonaceous structures and promoted fire performance. After WDC treatment, the phosphor-carbonaceous structures were degraded quickly. As demonstrated by cone calorimeter and FT-IR analysis, the higher weight losses after WDC treatment reduced fire performance and accelerated degradation of the phosphor-carbonaceous char structure. Elucidation of the mechanism can assist further improvement of the fire performance of plywood with an intumescent coating.

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