Effects of added nanoclay for styrene-acrylic resin on intumescent fire retardancy and CO/CO$_2$ emission

Chih-Shen Chuang, Horn-Jiunn Sheen

Abstract Coating plywood with intumescent paint is an effective approach to ensure fire safety in materials. This study investigated the effects of applying an intumescent coating with nanoclay and different amounts of Cloisite 15A (1%, 3%, 5%, and 10%) on 4-mm plywood panels. The nanoclay coating had a lower total heat release and peak heat release rate than other approaches, and it significantly enhanced the fire retardancy of painted plywood. In addition, nanoclay treated with an organic modifier has better flame retardancy than unmodified nanoclay. Another critical parameter in this study was the concentration of organoclay added to the intumescent coating. Cloisite 15A at a concentration of 1% further enhanced the fire retardancy of plywood. A higher organoclay concentration can reduce CO emissions; however, it also increases CO$_2$ emissions during combustion. The intumescent char layers containing 1% and 3% organoclay had the most extensive phosphocarbonaceous structures according to Fourier-transform IR spectroscopy and ^{27}Al and ^{31}P nuclear magnetic resonance analyses. Regarding the mechanism of fire performance and CO/CO$_2$ emissions, the addition of 1% and 3% Cloisite 15A to intumescent coatings is recommended; it achieved superior performance to Cloisite 15A at a higher concentration (i.e., 10%).

Keywords Intumescent, Styrene-acrylic emulsion resin, CO/CO$_2$ emission, Plywood, Organoclay

Abbreviation

BR	Binder resin
CS	Carbonizing substance
FPS	Foam producing substance
DA	Dehydrating agent
FR1	Flame retardant with 5% montmorillonite without modification
FRD1	Flame retardant without organoclay
FR2	Flame retardant with 5% Cloisite 15A
FR3	Flame retardant with 1% Cloisite 15A
FR4	Flame retardant with 3% Cloisite 15A
FR5	Flame retardant with 10% Cloisite 15A
THR	Total heat release
THR300	Total heat release at 300 s
Time to PHRR	Time to peak heat release rate

C. -S. Chuang, H. -J. Sheen (✉)
Institute of Applied Mechanics, National Taiwan University, No. 1 Roosevelt Rd., Section 4, Taipei 10617, Taiwan, ROC
e-mail: sheenh@ntu.edu.tw

Introduction

Woods and polymers are frequently used in building decoration and finishing. Wood materials are extensively used in residential and public buildings to conserve energy and reduce carbon emissions. Polymer coatings are commonly used to protect wood material surfaces on indoor furnishings. However, polymer coatings used for indoor furnishings are generally flammable and emit a considerable amount of smoke as they burn; therefore, the use of these materials raises critical safety concerns. Because fire can cause human fatalities and economic losses, the use of fire retardants is essential and their demand is increasing.[1] Halogen-free intumescent fire retardants (IFRs) have

received considerable attention for their provision of fire protection with few health hazards.[2,3] Furthermore, organic materials generate fire and smoke when they are exposed to heat. These combustion products are highly toxic and the cause of most fire-related fatalities,[4–6] with CO and CO_2 being the primary toxic products.

Due to the considerable enhancements in mechanical, thermal, dimensional, and barrier performance properties, nanotechnology has become a promising new frontier technology in material science.[7–9] Nanoclay can reduce the peak heat release rate (PHRR) when it is mixed within a polymeric matrix. Nanomaterials are another alternative to conventional fire retardants; they also require further improvements to achieve lower levels of total heat release (THR). The effects of the intumescent formulation of a styrene-acrylic-based coating on flammability have been demonstrated in our previous study.[10] Several studies have determined that the fire retardancy of materials is based on their heat release behavior.[11] However, the mechanisms and CO/CO_2 emissions of intumescent materials with nanomaterials remain unclear, and the chemical structure of char has not yet been investigated in a styrene-acrylic emulsion with nanoclay.

In this study, ammonium polyphosphate (APP), melamine, and pentaerythritol were used in a standard formulation. The fire performance analysis of plywood painted with different amounts of unmodified clay and organoclay was performed using a cone calorimeter. The mechanism of CO/CO_2 emissions from different amounts of nanoclay was mainly evaluated. The intumescent chars produced by different heating periods were also collected to understand the chemical structure decomposition. Fourier-transform IR spectroscopy (FTIR), ^{27}Al, and ^{31}P solid-state nuclear magnetic resonance spectroscopy were employed to analyze the structural features of these chars.

Experimental

Materials

Red lauan (*Parashorea spp.*) plywood panels (4 mm thick) were used as the underlying material; they had an air-dried specific gravity of approximately 0.6–0.7. A commercial styrene-acrylic emulsion resin served as the binder resin (BR, Yeou Shuenn Products Co., Ltd., Taiwan). The viscosity and total solid content were 2000 cps and 48% w/v, respectively. The carbonizing substance (CS) was pentaerythritol (PER) and melamine served as the foam-producing substance (FPS); both were purchased from Sigma-Aldrich (Darmstadt, Germany). The decomposition temperature and melting point of melamine are 250 and 354°C, respectively. APP (U-Way C.E.T. Co., Taipei, Taiwan) was employed as a dehydrating agent (DA) in this study. The degree of polymerization (*n*) was 1000. Montmoril-lonite without modification was purchased from Sigma-Aldrich (Darmstadt, Germany). The organoclay used in this study was Cloisite 15A (montmorillonite modified by dimethyl dihydrogenated tallow, quaternary ammonium (2M2HT). The specification of the modifier (2M2HT) was approximately as follows: 65% C18, 30% C16, and 5% C14; this information was obtained from the supplier, Southern Clay Products, USA.

Sample preparations

In this study, a high-speed mechanical stirrer was used to mix the styrene-acrylic resin and different amounts of organoclay. Each formulation had an identical weight ratio (w/w). In our previous study, the optimal formulation of styrene-acrylic emulsion resin was binder resin 15%, carbonizing substance 35%, foam-producing substance 15%, and dehydrating agent 35% (i.e., FRD1).[10] Therefore, the BR concentration was set at 15% (w/w), and it was mixed with various types and amounts of clay. The different formulation and pigment volume concentration values are shown in Table 1. The mixed resin and three other major components of the flame-retardant paint were stirred for 4 h at a stirring speed of 600 rpm.

The panel's plywood surface was coated using a fire-retardant paint. The solid content of the fire-retardant paint was approximately 60%. The coating amount (*C*) was calculated according to the following equation:

$$C = \Sigma(W_2 - W_1)/A \tag{1}$$

where W_2 is the plywood's weight after coating (g), W_1 is the uncoated plywood's weight (g), and *A* is the coating area (m^2). The fire-retardant paint was spread on the surface of a plywood panel using a brush and then air-dried. The amount of coating applied to the plywood panel surface was 360 g m^{-2}. Before flammability testing was conducted, the air-dried specimens were conditioned in a 45°C oven for 48 h. Then, the cooled specimens were placed in a desiccator for 24 h. Following CNS 6532 regulatory standards,[12] identical moisture content was assured for all specimens. The preconditioning procedure for moisture content control is specified in ISO-5660-1. The coating films were also prepared for thermogravimetric (TG) analysis.

Flammability tests

A cone calorimeter (Fire Testing Technology Ltd., East Grinstead, UK) was used to evaluate the flame retardancy of the samples. The method set forth in ISO 5660-1 was followed. Specimens were placed in a horizontal orientation with an external igniter. The total test time in this study was 1200 s, and the heater flux was set at 50 kW m^{-2}. The following fire-related properties of the materials were determined: average

Table 1: Different formulations and pigment volume concentration values of intumescent coatings in solid weight ratio (w/w)

No.	BR (%)		CS (%)	FPS (%)	DA (%)	Pigment volume concentration value (%)
	Clay	Resin				
FRD1	**0**	15	35	15	35	77.9
FR1	5 (Mt)					78.1
FR2	5 (15A)					78.1
FR3	1 (15A)					78.0
FR4	3 (15A)					78.0
FR5	10 (15A)					78.3

Mt, montmorillonite; 15A, Cloisite 15A

heat release rate [HRRav (kW m^{-2}) (within 1200 s)], PHRR (kW m^{-2}), THR (MJ m^{-2}), time to ignition [Tig (s)], and time to PHRR (s). PHRR and HRRav correspond to the acceleration of the material's thermal degradation, which is related to the spread of fire. THR denotes the total heat capacity during the material combustion process. Analysis of all cone calorimeter experiment samples was performed in triplicate. The THR times were calculated using the following equation:

$$THR = \int_{t=0}^{t_{end}} Heat\ release\ rate \tag{2}$$

where t_{end} was 300 or 1200 s; the THR times were denoted as THR300 and THR, respectively. When the THR300 value is less than 8 MJ m^{-2}, the intumescent coating becomes a flame-retardant material and passes the CNS 14705-1 regulatory standards.[13] CO and CO$_2$ were also evaluated using specialized analytical equipment (Siemens Ultramat 23). The gas analyzer was calibrated with nitrogen as the zero level gas and CO/CO$_2$ as the span gas (0.96/9.1%). The total concentrations of CO and CO$_2$ at 300 s were also evaluated in this study.

Thermogravimetric analysis

The thermal properties of the intumescent coating films were tested through thermogravimetric analysis (TGA) using a TA-2950 analyzer (TA Instruments, New Castle, DE). For the TGA, different intumescent paints were coated onto the aluminum foil. After the samples were air-dried, the coating films were collected and placed into a sealed plastic bag to prevent water adsorption. Flame-retardant coating films were placed in a ceramic sample pan. The sample weight was 5.0 mg. The gas flow and heating rates were set at 60 mL min^{-1} and 10°C min^{-1}, respectively. The heating experiment was conducted at temperatures ranging from 40 to 700°C under nitrogen gas. All TGA experiments were performed in triplicate. The TGA

was performed to calculate mass loss and obtain the derivative thermogravimetric (DTG) curves.

Fourier-transform IR (FTIR) analysis

In this study, FTIR was used to evaluate the length of time of the phosphocarbonaceous char structure and the functional groups of fire-retardant chemical reaction. The char of the FR2, FR3, and FR4 samples was collected. The heat flux was 50 kW m^{-2}, and the heat time was 40 and 120 s, respectively. Two stages related to intumescent coating were analyzed in this study. The combustion time of 40 s was after the first PHRR, and 120 s was the time at which the underlying material began to burn. The samples and KBr powders were pelletized at a ratio of 1:300 (mg mg^{-1}). The infrared (IR) spectra were tested using a Nicolet 380 spectrophotometer (Thermo Scientific, Inc., Waltham, MA) at a scanned range of 4000–500 cm^{-1}.

Spectroscopy analysis of ^{27}Al and ^{31}P solid-state nuclear magnetic resonance

^{27}Al and ^{31}P solid-state nuclear magnetic resonance (NMR) spectroscopy was used to further comprehend the chemical reactions of intumescent coatings with organoclay. The samples were also analyzed using a cone calorimeter; the heating times were 40 and 120 s at a heat flux of 50 kW m^{-2}. Solid-state NMR spectroscopy was employed to analyze the different residuals. ^{27}Al NMR measurement was performed on a Bruker DSX 400WB at 24.5 MHz (9.4 T) with magic angle spinning (MAS) using a 4-mm probe. A repetition time of 10 s was used for all samples. A saturated solution of Al(OH)$_3$ was used as a reference. Before a new experiment commenced, the chemical shift reference was always verified and calibrated within $\pm$ 0.2 ppm.

High-resolution ^{31}P NMR spectroscopy of the solids was performed using a Bruker DSX 400WB NMR instrument. Bruker probe heads equipped with MAS components were used. The measurements were per-

formed at 40.5 MHz (2.35 T) using MAS (5 kHz) with or without 1H dipolar decoupling. A repetition time of 450 s was used for all samples. H_3PO_4 in an aqueous solution (85%) was used as a reference, and before a new experiment commenced, the chemical shift reference was always verified and calibrated within $\pm$ 0.2 ppm.

Results and discussion

Cone calorimeter test results for clay and organoclay

To understand the flame combustion effects of adding clay to an intumescent coating, modified and nonmodified clay samples were tested in this study. The heat release rate curves of different specimens were tested using a cone calorimeter (Fig. 1). Figure 2 shows the experimental data (i.e., HRRav, THR, THR300, and time to PHRR) related to all samples. The PHRR was the most useful parameter for indentifying the flame retardancy of the samples. The THR and HRRav of the original coating (FRD1) were 47 MJ m^{-2} and 40 kW m^{-2}, respectively.[10] The first stage of heat release peak and time of PHRR were 65 kW m^{-2} and 36 s, respectively (Figs. 2a and 2b). The second stage of heat release peak and time of PHRR were 248 kW m^{-2} and 303 s, respectively.[10] In the FR1 (with 5% montmorillonite, without modification) test, the first-stage PHRR decreased to 42 kW m^{-2}. Moreover, the second-stage PHRR decreased (Fig. 1). The experimental results related to FR1 showed that adding clay can enhance the flame retardancy and reduce the PHRR of this sample. The same trend is also shown in Fig. 2. Therefore, adding clay to an intumescent coating increases its flame retardancy.
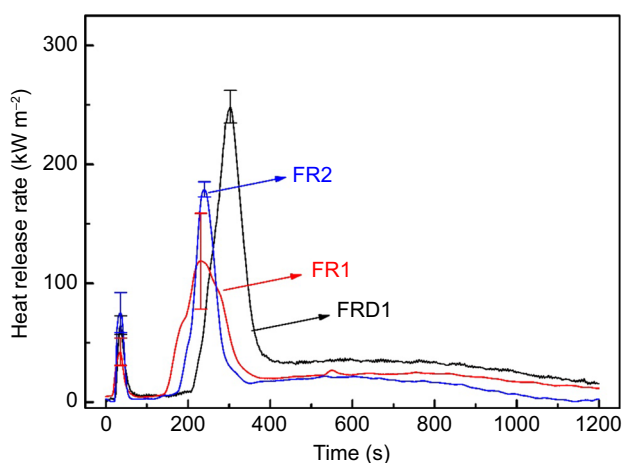

Fig. 1: Heat release profiles for different coatings on the 4-mm plywood panels of the FRD1 (original coating without organoclay, Chuang et al.[10]), FR1 (5% montmorillonite without modification), and FR2 (5% Cloisite 15A) samples under cone calorimeter tests

Furthermore, the same trend of fire performance was shown for FR2 (5% Cloisite 15A). Two HRR peaks were observed in FR2 (Fig. 1), and the THR and HRRav of FR2 were 25 MJ m^{-2} and 21 kW m^{-2}, respectively (Fig. 2a). Therefore, the intumescent coating with the added organoclay (i.e., Cloisite 15A) could decrease 45% THR than the original coating without organoclay. The THR value of the intumescent coating added with an organoclay was 22% lower than that of the same amount of unmodified clay. Therefore, the flame retardancy of the intumescent coating can be improved by intercalating this organic modifier into the coating; the results are consistent with those of Chuang et al.[14]

The THR value can also be used to evaluate flame retardancy, as described in CNS 14705-1.[13] Therefore, the THR300 values of all the intumescent coatings
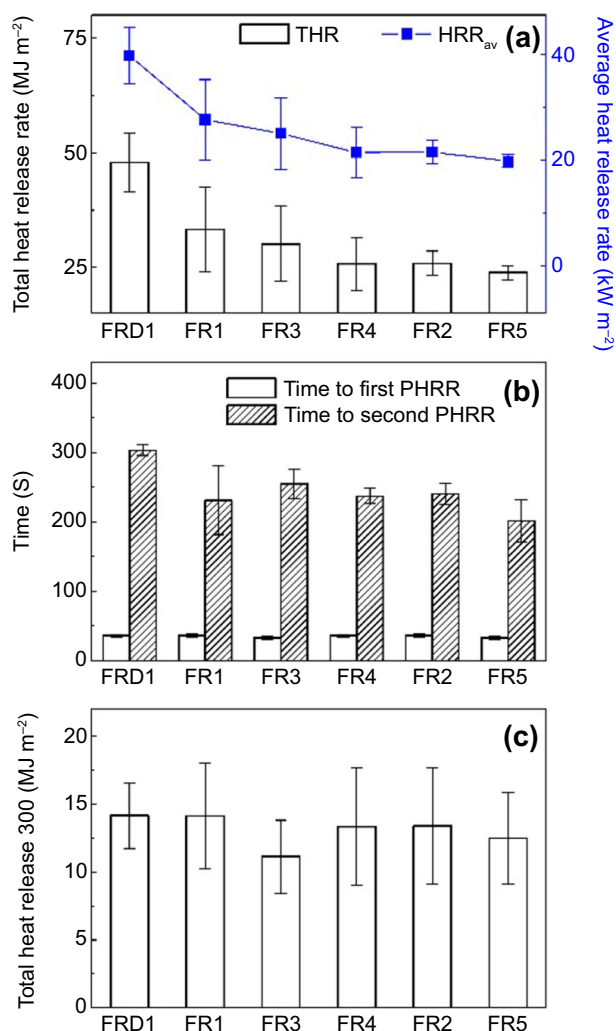

Fig. 2: Heat profiles for FRD1 (original coating without organoclay), FR1 (5% montmorillonite without modification), FR2 (5% Cloisite 15A), FR3 (1% Cloisite 15A), FR4 (3% Cloisite 15A), and FR5 (10% Cloisite 15A) on the 4-mm plywood panels of (a) THR and HRRav (b) time to first and second PHRR (c) THR300

were calculated. As shown in Fig. 2c, the THR300 values of FRD1 and FR1 were 14.2 and 14.1, respectively. Although the THR value of FRD1 and FR1 decreased by almost 30% within 1200 s, they had almost the same THR300 value. The THR300 value of FR2 was 12 MJ m^{-2}. Regarding THR300 values, FR2 had a decrease of 12% compared with FRD1. Therefore, adding organoclay to an intumescent coating can improve the flame retardancy of wood material and provide it with superior protection. Regarding lower HRRav and THR values, the fire retardancy of these samples is presented in the following order: FR2 (Cloisite 15A) > FR1 (montmorillonite) > FRD1 (without clay). The results indicate that the chemical structure of the organic modifier and d value of clay were the two main factors influencing fire retardancy. The organic modifier can provide an additional carbon source during combustion and react with APP to form a phosphocarbonaceous structure. These results are consistent with those of Ribeiro et al.[15]

The results demonstrated that the intumescent coating added with organoclay could improve flame retardancy. The effects of different amounts of Cloisite 15A (FR2–FR5) on the fire retardance of the painted plywood were analyzed to understand the optimal formulations. The experimental data demonstrated that FR5 (10% Cloisite 15A) had lower HRRav and THR values than FR2 and FR4 within 1200 s (Fig. 2a). The thermal durability of the intumescent char layer can be evaluated based on the intervals between the first- and second-stage PHRR. The second-stage PHRR demonstrated that FR3 (1% Cloisite 15A) has a long interval between PHRR occurrences. FR3 also had lower THR300 values than other intumescent coatings (Fig. 2c). Furthermore, in a comparison of THR, THR300, PHRR, and time to PHRR, FR3 (1% Cloisite 15A) demonstrated the best fire retardancy. In this study, fire retardancy performance has the following order: FR3 (1% Cloisite 15A) > FR4 (3% Cloisite 15A) > FR2 (5% Cloisite 15A) > FR5 (10% Cloisite 15A). The experimental data showed that a higher concentration of Cloisite 15A (10%) did not enhance flame retardancy or protect the underlying material. In other words, a small amount of organoclay can significantly enhance fire retardancy.

Thermal property of intumescent coating with different amounts of organoclay

TGA results can assist in analyzing mechanisms of different formulations of intumescent coatings. In this study, the APP–PER reaction was the main reaction, and the coating films could form a phosphocarbonaceous structure under heat. Many studies have reported the mechanism of APP–PER.[16–18] In this study, we changed the amount of organoclay added to samples to examine the thermal stability of intumescent coatings. Figure 3 and Table 2 illustrate the TG and DTG data of FRD1 and the FR2–FR4 series,
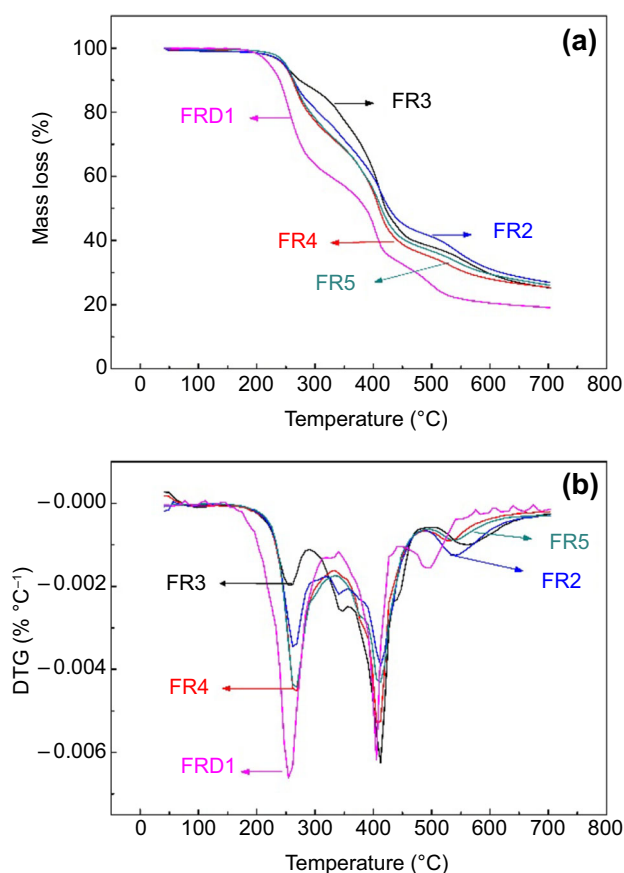

Fig. 3: TG and DTG curves for FRD1 (original coating without organoclay), FR2 (5% Cloisite 15A), FR3 (1% Cloisite 15A), FR4 (3% Cloisite 15A) and FR5 (10% Cloisite 15A)

respectively. As shown in Table 2, the pure styrene-acrylic emulsion resin had one main mass loss stage around 410°C, and its residual weight was 1.9%. This mass loss is related to direct decomposition by chain scission mechanisms into volatile monomers.[17] Figure 3 shows three clear degradation stages in intumescent coatings of FRD1 and FR2–FR4. Intumescent fire retardancy resulted from esterification, which started with APP and PER and formed a phosphocarbonaceous structure.[19] The initial degradation temperature of APP was 215°C and that of melamine (the FPS) was 330–410°C.[16] Ammonia and water were produced at temperatures higher than 400°C. Furthermore, Camino et al.[20] pointed out that the elimination of ammonia and a dehydration reaction occurred with APP (i.e., the DA), resulting in the crosslinking of phosphate chains, which also reacted with the hydroxyl groups of polyols (i.e., pentaerythritol) at temperatures between 280°C and 330°C. In addition to the APP–PER reaction, BR can provide a carbon source during esterification.[17,21] The final product of this reaction was polyol phosphate ester. Therefore, the first stage of degradation occurred due to the decomposition of DA and CS, and the

Table 2: Mass loss and temperature degradation of different formulations by thermogravimetric analysis

No.	Stage 1		Stage 2		Stage 3		Residual
	Mass loss (%)	Temperature (°C)	Mass loss (%)	Temperature (°C)	Mass loss (%)	Temperature (°C)	Weight (%)
Styrene-acrylic resin	–	–	77.0	410	–	–	1.9
FRD1	18.6	254	26.3	406	10.9	493	19.0
FR2	9.2	261	35.5	412	18.2	540	26.9
FR3	6.5	254	38.7	412	21.7	561	25.2
FR4	13.4	268	34.1	405	19.8	526	25.3
FR5	12.5	268	36.8	412	17.1	540	26.0

second stage was due to the degradation of the FPS and phosphate ester.

Thermal stability was also evaluated in this study. From FRD1 test results, 10% (T_{10}) and 40% (T_{40}) mass losses occurred at 239 and 319°C, respectively. After 5% organoclay was added to the intumescent coating (FR2), the degradation temperature of T_{10} and T_{40} increased to 261 and 398°C, respectively. The experimental results indicated that adding organoclay can enhance the thermal stability of the intumescent coating. The enhancement of thermal stability is due to the effect of nanoclay on the copolymer. This finding was consistent with that of Chozhan et al.[22] and Shiralizadeh et al.[23] The T_{10} values of FR3, FR4, and FR5 were 268, 261, and 261°C, respectively. The T_{40} values of FR3, FR4, and FR5 were 398, 390, and 383°C, respectively. The results indicate that using a higher concentration of organoclay does not increase the thermal stability of a coating. The data from the TGA and cone calorimeter testing were compared, revealing that coating films with organoclay decomposed at lower temperatures and thus had superior flame retardancy.

CO and CO₂ emission of intumescent coatings with different concentrations of organoclay

CO and CO_2 are toxic gases produced during a fire; they are also asphyxiants that can cause human fatalities. The fire retardancy and gas emission of intumescent coatings are crucial for fire safety. Therefore, CO and CO_2 emissions were detected for coatings with different formulations. Figure 4a displays the total quantity of CO emissions measured in the cone calorimeter test. CO emissions occur at low temperatures in the early stages of a fire, mainly as a result of incomplete combustion. They also occur at the end of combustion, in this case, because of plywood smoldering. The total concentration of CO in FRD1 at 1200 s was 1.8×10^5 ppm. After 5% of unmodified clay (FR1) was added, the CO emission reduced by 1.8% and reached 1.7×10^5 ppm. Moreover, FR2 resulted in a
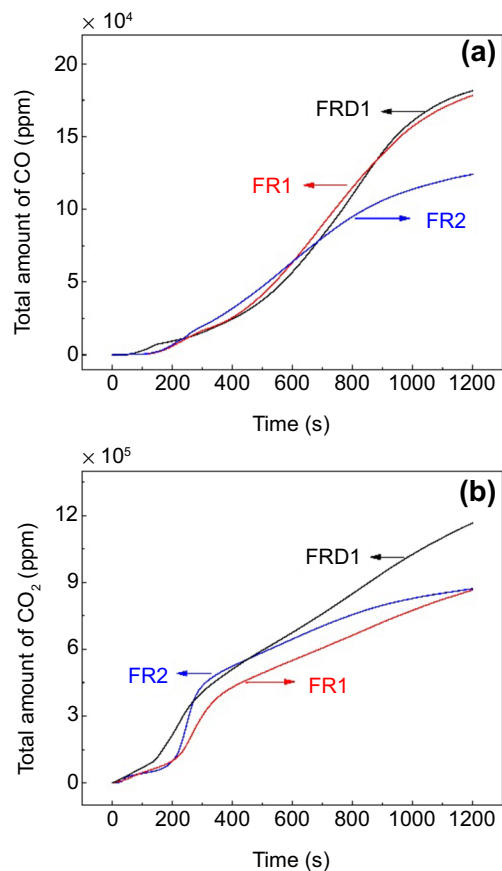

Fig. 4: The total quantity of CO (a) and CO₂ (b) produced of FRD1 (original coating without organoclay), FR1 (5% montmorillonite without modification), and FR2 (5% Cloisite 15A) under cone calorimeter tests

significant reduction in CO emission than FRD1 and FR1. The experimental data showed that with FR2, the CO emission reduced by 30% and reached 1.2×10^5 ppm. During combustion, organoclay combined with phosphoric acid and formed a protective barrier that may have insulated the underlying material and

induced smoke suppression. This result was in good agreement with those of Song et al.[24] and Liu et al.[25]

Figure 4b displays the total CO_2 emissions of FRD1, FR1, and FR2. FRD1 generated the highest total CO_2 emissions at 1.1×10^6 ppm, whereas FR1 had the
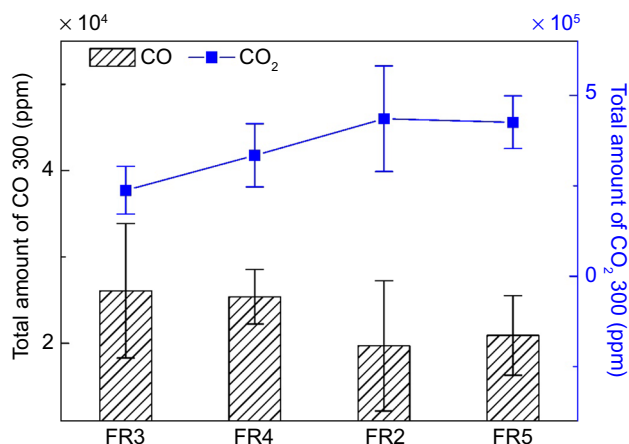

lowest amount at 8.6×10^5 ppm (Fig. 4b). Chen et al.[26] pointed out that metal hydroxide had a smoke-suppressing effect. Natural clay, such as montmorillonite, is composed of Mg, Al, and Si. During heat combustion, metal hydroxide can decompose gaseous products or dilute the combustible gases by generating a considerable amount of water vapor.[27] Therefore, FR1 (5% montmorillonite) can reduce CO_2 emissions by 21% compared with FRD1.

The CO and CO_2 emissions of FR2–FR5 were also evaluated in this study to further understand the effects of different amounts of organoclay on such emissions. Figure 5 shows CO and CO_2 emissions at 300 s. Regarding the total amount of CO 300 emissions, FR3 (1% 15A) had the largest and FR2 (5% 15A) had the lowest emissions. A comparison of FR2 and FR3 revealed that increased amount of organoclay can reduce CO emissions by 24%. These experimental data indicate that an increase in the concentration of nanoclay can decrease CO emissions. The results are in accordance with those of Gao et al.[28] By contrast, FR2 had the highest CO_2 emission levels in this study (Fig. 5). Studies have reported that intumescent coatings generate CO_2 during their decomposition and protect the underlying materials.[16,29] We inferred that the phosphocarbonaceous structure was decomposed and could not protect the plywood.

Fig. 5: The total amount of CO/CO_2 at 300 s production for FR2 (5% Cloisite 15A), FR3 (1% Cloisite 15A), FR4 (3% Cloisite 15A), and FR5 (10% Cloisite 15A) with different amounts of Cloisite 15A
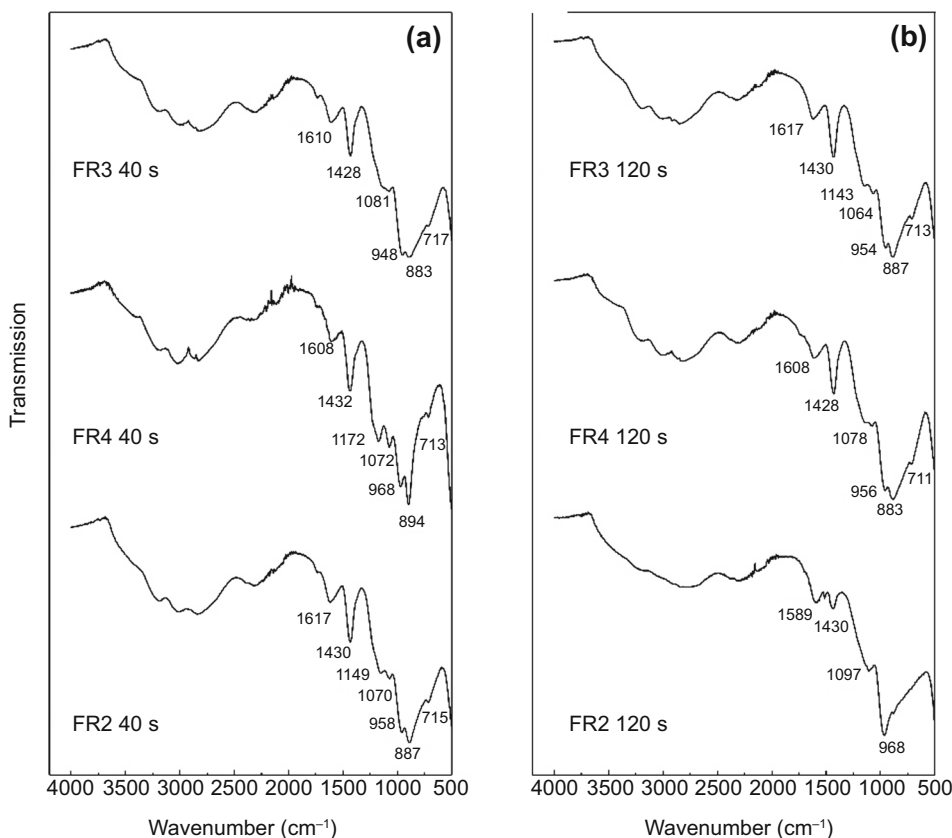

Fig. 6: The FTIR spectra at different heating periods: (a) FR2 (5% Cloisite 15A), FR3 (1% Cloisite 15A), and FR4 (3% Cloisite 15A) at 40 s, (b) FR2, FR3, and FR4 at 120 s
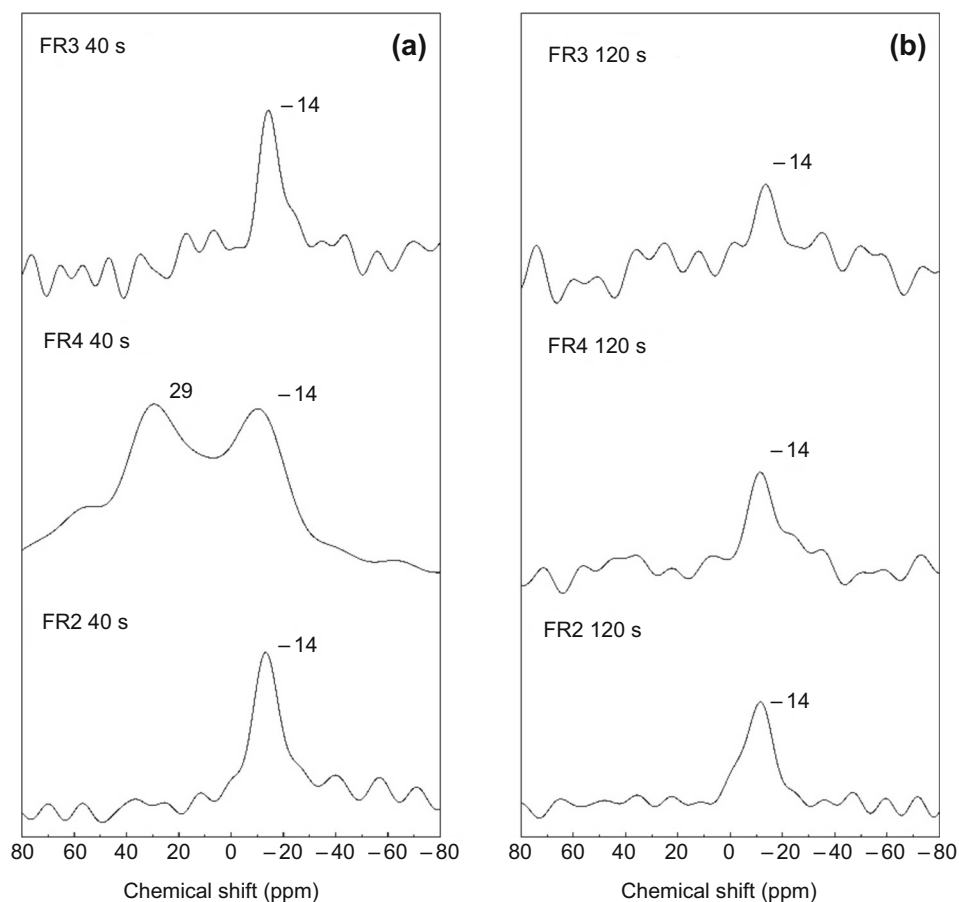
Fig. 7: The ^{27}Al NMR spectra at different heating periods: (a) FR2 (5% Cloisite 15A), FR3 (1% Cloisite 15A), and FR4 (3% Cloisite 15A) at 40 s, (b) FR2, FR3, and FR4 at 120 s

FTIR analysis of different coatings

To understand the decomposition of the phosphocarbonaceous structure and to evaluate the flame performance, FTIR analysis was used to evaluate the mechanism underlying the thermal degradation of FR2–FR4. The char of FR2–FR4 was heated for 40 and 120 s to demonstrate the different functional groups after combustion (Fig. 6). At 40 s, all test samples were observed to have P–O–P bonds at IR bending vibrations of 883–887 cm^{-1}, and the additional broadbands were assigned to modes of symmetrical vibration of PO_2 and PO_3 at about 948–968 cm^{-1}.[30] The P–O–C bonds of IR vibration modes were observed at 1070–1081 cm^{-1}, which was due to phosphate-carbon complexes or P–O in a vitreous structure.[30] The P–O–C bond was formed by alcoholysis of the polyphosphate chain.[20] The P=O absorption band in the IR vibration mode was found at 1149–1172 cm^{-1}. At 40 s, the phosphocarbonaceous structure was observed in these IR absorption bands. These bands indicate an interaction between phosphoric acid and alcohol (Fig. 6a). The main product of intumescent coating dictated the flame retardancy of the samples. No P=O IR absorption band (i.e., 1149 and 1172 cm^{-1})

was observed in the IR spectra of FR2 and FR4 (Fig. 6b) at 120 s. No P–O–P bond was observed at 120 s in FR2. The result was attributed to the degradation of the phosphocarbonaceous structure. At 120 s, the char of FR1 had a better flame-retardant duration under cone calorimeter testing. NH_4^+ and the symmetrical deformation of CH_2, CH_3 were observed at 1428–1432 and 1589–1617 cm^{-1}, respectively.[30] These IR absorption bands were observed due to the decomposition of melamine. Flame retardancy can be evaluated by the degree of esterification, with faster esterification corresponding to a more flame-retardant char.[31–34] According to the cone calorimeter tests and FTIR analysis of the samples, FR3 (1% 15A) had the longest interval time before the second-stage PHRR and was entirely phosphocarbonaceous at 120 s.

Solid-state ^{27}Al and ^{31}P NMR analyses of different coatings

According to the FTIR spectrum, the formation and duration of phosphocarbonaceous structures were discussed. Furthermore, the thermal degradation of organoclay and APP in mixtures with the other three

compounds was performed using ^{27}Al and ^{31}P NMR analyses. The Al in tetrahedral and octahedral coordinations was centered at 50 and 3 ppm, respectively, in ^{27}Al NMR spectra at room temperature. Another peak had a chemical shift centered around 30 ppm, which can be assigned to $[AlO_5]$.[35,36] The experimental data of ^{27}Al NMR spectra for FR2–FR4 were obtained after the samples were heated for 40 and 120 s (Fig. 7). The experimental data showed all the spectra had a band at − 14 ppm, which is assigned to be the octahedral $[AlO_6]$ unit.[35] AlOx units can react with phosphorous and form $Al[OP]_6$, indicating that the organoclay could react with APP after being heated. This result was consistent with that of Bourbigot et al.[35] The intumescent char layer, which contains this structure, can act as a protective barrier and prevent fire from coming into contact with the underlying material. The concentration of 29 ppm was shown in FR4 at 40 s, which can be assigned to $[AlO_5]$. This indicates that the reaction of APP and alumina was delayed in FR4 at 40 s.

The degradation of APP, pentaerythritol, and melamine in the mixture with styrene-acrylic resin was evaluated using ^{31}P NMR spectroscopy (Fig. 8). Several studies have demonstrated that the characteristic bands of APP are centered at − 22 and − 24 ppm.[30,35] In Fig. 8a, all samples show a band centered at 0 ppm, which can be assigned to the orthophosphate group linked to aliphatic groups or orthophosphoric acid.[37] Pyrophosphate species or diphenyl- or triphenyl orthophosphate groups were observed at − 11 ppm in ^{31}P NMR spectra at 40 s.[38] The ^{31}P NMR spectral peaks located at 0 and − 11 ppm indicate that the APP was decomposed and acted with a polyol to form a protective barrier against fire. Therefore, the painted plywood could be protected from fire damage by a phosphocarbonaceous char. These data are consistent with the results of the cone calorimeter tests and FTIR analyses. Under the above-mentioned condition, the intumescent shield can limit oxygen diffusion to the substrate. At 120 s, the ^{31}P NMR spectral peak at − 11 ppm, which was assigned to pyrophosphate species, disappeared in FR2 (Fig. 8b). This experimental result suggests that the phosphocarbonaceous structure was degraded at this time. Due to the low concentration of organoclays, the $Al[OP]_6$ signal was not observed in ^{31}P NMR spectra (− 25 and − 35 ppm). From comparisons using the cone calorimeter test and FTIR and NMR analyses, it was revealed that the intumescent system with the added organoclay can provide improved fire performance and form a longer and more effective protective barrier than coatings without organoclay.
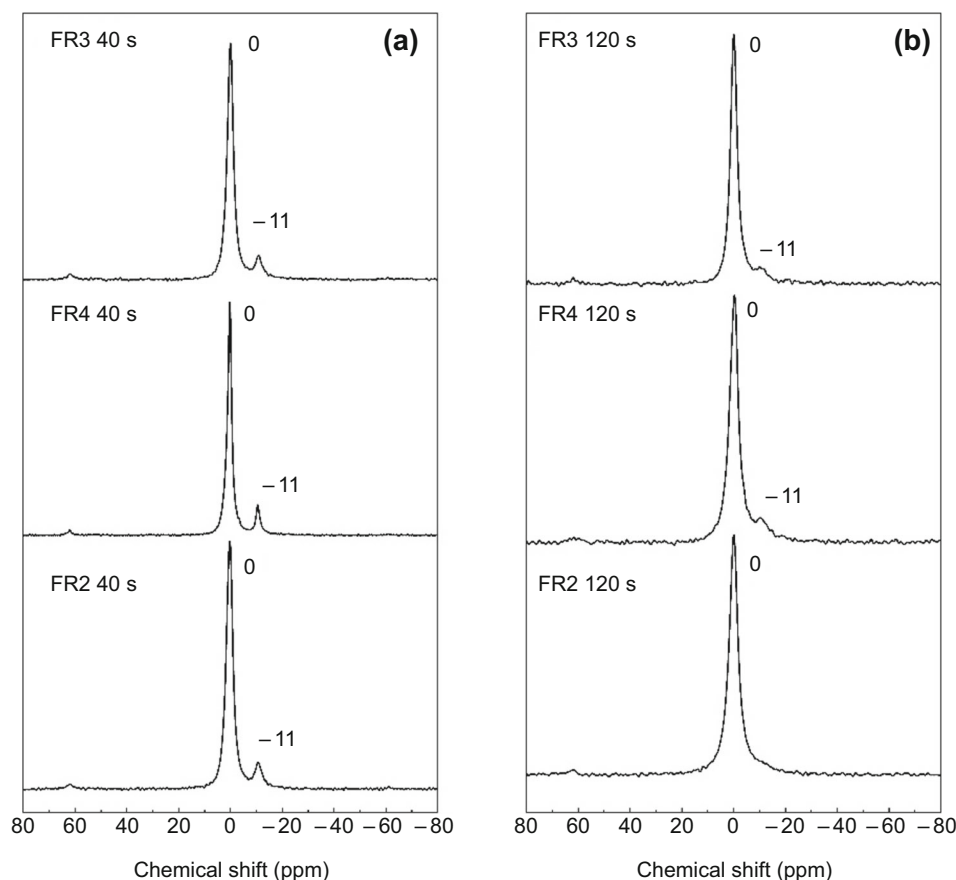

Fig. 8: The ^{31}P NMR spectra at different heating periods: (a) FR2 (5% Cloisite 15A), FR3 (1% Cloisite 15A), and FR4 (3% Cloisite 15A) at 40 s, (b) FR2, FR3, and FR4 at 120 s

Conclusions

Coating intumescent coatings with different concentrations of organoclay on thin red lauan plywood can improve its flame retardancy. According to the cone calorimeter test results, the modified clay (FR2, with 5% Cloisite 15A) has better flame retardancy than unmodified clay (FR1, with 5% montmorillonite). Additionally, a comparison of THR300, THR, PHRR, and time to PHRR values demonstrated that the formulation of FR1 (with 1% 15A) had the best flame retardancy of the samples. Furthermore, CO and CO_2 emission results indicated that higher amounts of organoclay (FR2, 5% 15A) resulted in the lowest CO emissions. FR2 had the highest CO_2 emissions during the 1200-s test in this study. The intumescent char layer demonstrated that more extensive phosphocarbonaceous structures enhanced fire performance according to FTIR, ^{27}Al, and ^{31}P NMR analyses. The fire performance of plywood with organoclay applied to the intumescent coating can be enhanced by gaining an understanding of the related mechanism. Regarding the mechanism of fire performance and CO/CO_2 emission, the addition of organoclay at concentrations of 1% and 3% in the intumescent coating is recommended due to its superior performance compared with higher concentrations (i.e., 10%).

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