PHYTIC ACID FOR DUAL WOOD PROTECTION AGAINST FUNGI AND FIRE

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Abstract. Phytic acid (PA) is a natural compound derived from plant seeds and cereals with excellent antifungal properties and fire resistance. However, the potential of PA for dual wood protection is yet to be reported. This study investigated the antifungal properties and fire performance of PA for wood protection. The antifungal properties of PA against common wood-decaying fungi, including two white-rot fungi, *Trametes versicolor* (*T.v.*) and *Irpex lacteus* (*I.l.*), and two brown-rot fungi, *Gloeophyllum trabeum* (*G.t.*) and *Rhodonia placenta* (*R.p.*), were studied for both in vitro and in vivo tests. The thermal stability (pine and polar) and fire resistance (pine) of wood samples treated with different concentrations of PA by vacuum impregnation were also evaluated. For the in vitro test, PA almost fully inhibited the growth of three of the four fungi tested at a PA concentration of 0.25 wt% except for fungus *R.p.*, which was less sensitive to PA and could still grow at 4 wt% PA. The in vivo durability test results showed that PA significantly improved the fungal resistance of both pine and poplar wood blocks for the brown-rot and white-rot fungi, respectively, as shown by lower mass losses of 5-25% compared with the control group's 25-45%. The results from thermogravimetric analysis under both air and nitrogen indicated that PA increased the thermal stability of both pine and poplar samples, which was further confirmed by the results from the mass loss calorimeter. The peak heat release rate and the total heat release rate of 10 wt% PA-treated samples were decreased by 39% and 48%, respectively, at 148 kW/m^2 and 34.6 MJ/m^2 compared with the control, whereas the residual mass increased by 137% at 48.4%. Overall, this research demonstrates the potential of using PA to improve both fungal resistance and fire performance of wood products.

Keywords: Phytic acid, dual protection, durability, bio-based wood preservative, fire performance.

INTRODUCTION

As one of the oldest building materials, wood is used worldwide for construction and indoor decoration due to its aesthetics, strength, thermal protection, and environmental benefits. Moreover, the carbon storage potential of wood makes it a promising material to help achieve the carbon neutrality goal. However, wood is susceptible to both fungal deterioration and fire attack (USDA FPL 2021), which lead to structural failures and pose potential safety concerns. For example, fungal damage on wood can reduce its strength (Lepage et al 2022) while the inherent combustible

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nature of wood-based structures can contribute to fire growth (Thomas et al 2021). There is also an increased risk of wildfire events due to climate change in the wildland-urban interface area where fire retardant treatment of wood structures is needed. Therefore, it is imperative to develop approaches that provide dual protection against fungal decay and fire and extend the service life of wood.

There has been extensive research on imparting both durability and fire retardancy to wood for outdoor applications using combined treatments (Marney and Russell 2008). These technologies generally include modifying an existing preservative with a fire retardant (Baysal 2002), modifying wood using common fire retardants with biocidal activities (Lewin 1997; Lee et al 2000), fixing conventional preservatives that have good fire retardance into wood (Tsunoda 2001; Kartal et al 2004; Baysal et al 2006), and forming wood-inorganic composites (Yamaguchi 2003). Among these technologies, boron compounds have been most commonly used due to their dual functionalities but the leaching issue of boron remains (Marney and Russell 2008). A more recent study investigated the decay resistance and fire performance of two quaternary ammonia compounds, didecyl dimethyl ammonium chloride (DDAC) and didecyl dimethyl ammonium tetrafluoroborate (DBF), on both solid wood and plywood samples. Although DDAC- and DBF-treated samples showed resistance against the fungi tested, these samples were more flammable and had higher heat release rates (HRRs) than the controls (Terzi et al 2011). Similar results were also reported with lauric arginate-treated wood (Alorbu et al 2021) and laccase-assisted enzymatic grafting of wood with kraft lignin and sulfonated lignin (Bolaño et al 2021).

Phytic acid (PA) is a bio-based compound that can be found in grains and cereals (Kalali et al 2019). It has excellent metal-chelating properties (Zhang et al 2013) and a high phosphorus content (ca. 28 wt% to its molecular weight) (Costes et al 2017). These properties have allowed PA to be used for different applications, such as natural antimicrobials for food preservation and potential fire retardants in textiles or wood composites (Leng et al 2022; Zhang et al 2023). PA has been demonstrated to improve the bio-control efficacy of *Rhodotorula mucilaginosa* against postharvest gray mold spoilage and natural spoilage of strawberries (Zhang et al 2013) and inhibited the growth of pathogenic fungi, eg, *Fusarium oxysporum* (Li et al 2023). It also inhibited spore germination and vegetative cell growth of *Clostridium perfringens* (type A), which is one of the most widely distributed pathogenic microorganisms (Bloot et al 2022). In terms of fire retardancy, there has been extensive research on combining PA with metal ions or other chemicals to improve the fire performance of wood and wood composites. For example, PA chelating with metal ions, such as Cu, Fe, Zn, and Mg, has shown improved fire performance and reduced smoke release for loblolly pine (*Pinus taeda*) (Zhang et al 2022). Spraying PA solution along with sodium silicate on wood particles increased the fire retardance of wood composites without significantly affecting the key mechanical properties (Lin et al 2023). Moreover, unlike traditional halogenated fire retardants that can affect human health and the environment, PA could be a nontoxic and environmentally friendly alternative to improve the fire performance of wood while preventing fungal deterioration.

However, no studies have been found investigating both the antimicrobial properties and fire resistance of PA-treated wood. Based on the encouraging results from our preliminary study (Liang et al 2023), this research first investigated the antifungal properties of PA against common wood-decaying fungi, including two white-rot fungi, *Trametes versicolor* (*T.v.*) and *Irpex lacteus* (*I.l.*), and two brown-rot fungi, *Gloeophyllum trabeum* (*G.t.*) and *Rhodonia placenta* (*R.p.*), using both in vitro and in vivo assays. Second, the fire resistance of wood blocks treated with different PA concentrations was evaluated using thermogravimetric analysis (TGA) and mass loss calorimeter (MLC).

MATERIALS AND METHODS

Materials

PA (50 wt% in water, Tokyo Chemical Industry Co., Ltd., Portland, OR), malt extract (Oxoid Ltd., Lowell, MA), yeast extract (Oxoid Ltd., Lowell, MA), and agar (Fisher Bioreagents, Pittsburgh, PA) were purchased from Thermo Fisher Scientific (Shelton, CT). Two white-rot fungi, *Trametes versicolor* (Linnaeus: Fries) *Lloyd*, (ATCC#42462, *T.v.*), and *Irpex lacteus (Fr.) Fr.* (ATCC#11245, *I.l.*), and two brown-rot fungi, *Gloeophyllum trabeum* (Madison 617/ATCC 11539, *G.t.*), and *Rhodonia placenta* (*Fr.*) (ATCC#11538, *R.p.*), were purchased from ATTC and used for both in vitro and in vivo tests.

Softwood (loblolly pine [denoted as Pine], *Pinus taeda* L., 488 ± 23 kg/m^3) was donated by Weyerhaeuser, Bruce, MS, and hardwood (yellow poplar [denoted as Poplar], *Liriodendron tulipifera* L., 484 ± 19 kg/m^3) was purchased from a local store, Moscow Building Supply, Moscow, ID. Wood blocks (14 mm × 14 mm × 14 mm, $L \times T \times R$) of both pine and poplar were used for PA treatment and durability test against the brown-rot and white-rot fungi, respectively. Pine wood blocks with dimensions of 100 mm × 100 mm × 10 mm ($L \times T \times R$) were further used for the fire performance test by MLC. All wood samples were defect-free and prepared based on standard AWPA E10 (AWPA 2017). The wood samples without treatments or with DI water treatments were used as controls, depending on the testing specified below.

In Vitro Antifungal Properties of PA

The in vitro antifungal properties of PA were studied by measuring the growth rates of four common wood-decaying fungi (*T.v.*, *I.l.*, *G.t.*, and *R.p.*) in PA-amended malt agar media and the results were compared with those of the control (Cai and Kuo 2022). Specifically, the growth medium of the control group was prepared by mixing and autoclaving 2.0 wt% malt extract, 1.2 wt% agar, and 0.2 wt% yeast in distilled water. PA-amended (0.125-4 wt%) malt agar media were obtained by adding different amounts of PA solutions into the sterilized control malt-agar solution. Subsequently, 20 mL of either the control or PA-amended culture media was cast into a Petri dish (90 mm diameter) and solidified in a biosafety hood. A 5 mm diameter mycelial plug was cut from the edge of an actively growing fungal colony and placed upside down at the center of the growth media. The inoculated plates were incubated at 25°C and 75% RH for 2 wk. Three replicates were prepared for each treatment. Finally, the growth of each fungus in the plates was observed and photographed every 2 d. The fungal growth area was captured using the ImageJ software and the fungal growth rate was calculated by Eq 1

$$Fungi\ growth\ rate\ (\%) = \frac{A_i - A_0}{A} \times 100 \quad (1)$$

where A_0, A_i, and A are the measured areas of the initial fungal plugs, the area where mycelium covered on the growth medium on Day i (i = 2, 4, 6, …, 14), and the area of the Petri dish used for the study, respectively.

PA Treatment on Wood Samples

The wood samples for the fungal resistance and fire performance tests were conditioned at 60°C for 48 h or until the consistent mass was recorded ($m_{trt.1}$). For the durability test, the wood blocks were vacuum impregnated with either DI water (as a control group) or PA solutions (2.5-10 wt% at an interval of 2.5 wt%) for 30 min and were kept in treating solutions for 12 h. The samples were reconditioned at 60°C until consistent weight ($m_{trt.2}$) was recorded. The mass gain after treatment was obtained following Eq 2:

$$\text{Mass gain}\ (\%) = \frac{m_{trt.2} - m_{trt.1}}{m_{trt.1}} \times 100 \quad (2)$$

where $m_{trt.1.}$ and $m_{trt.2}$ are the mass of the conditioned wood blocks before and after vacuum (or vacuum-pressure) impregnation, respectively.

Similarly, PA-treated samples for the fire performance test were vacuum-impregnated with 5 wt% and 10 wt% PA aqueous solutions for 2 h, followed by pressure treatment (827 kPa) for 1 h, whereas samples without treatment were used as the control group in the MLC test.

The treated samples were then conditioned at 60°C until a consistent weight before TGA and MLC tests. The mass gain of the samples was also calculated using Eq 2.

In Vivo Antifungal Properties of PA

The decay resistance of PA-treated wood was evaluated using the soil block method described in standard AWPA E10-16 (AWPA 2017). Before exposure, both treated and untreated wood samples were sterilized by spraying 70% ethanol solution on the surface and drying in the biosafety hood for 1 h. This process was repeated at least twice. Two wood blocks per bottle were placed on the top of the feeder strips containing the actively growing test fungus. At the end of inoculation, all the culture bottles were placed in the environment chamber at 25°C and 75% RH for 8 wk. Pine samples were only exposed to brown-rot fungi, whereas the poplar samples were only exposed to white-rot fungi. Six replicate blocks were prepared for each treatment level for all the testing fungi. The mass loss of the decayed wood was calculated by Eq 3

$$\text{Mass loss } (\%) = \frac{m_{\text{unexpo}} - m_{\text{expo}}}{m_{\text{unexpo}}} \times 100\% \quad (3)$$

where m_{unexpo} and m_{expo} are the mass of wood blocks conditioned at 60°C before and after fungal exposure, respectively.

TGA Analysis

The thermal degradation behaviors of PA-treated wood blocks and control water-treated wood blocks were studied by TGA on a PerkinElmer TGA-7 instrument (Shelton, CT) under both N_2 and air conditions. The samples (around 5-6 mg for each treatment) were heated from 38 to 850°C at a heating rate of 20°C/min under the gas flow of 30 mL/min. Three replicates were tested for each treatment.

Fire Performance Test

The fire resistance of PA-treated wood was evaluated using an MLC (Fire Testing Technology Ltd., East Grinstead, UK) at an irradiance of 50 kW/m^2. The HRR, total heat release (THR), mass changes, and time-to-ignition (TTI) were recorded and analyzed. Samples without treatment were used as a control group. Two replicates were tested for each treatment.

Statistical Analysis

Data (mass gain and mass loss) were statistically analyzed using SAS (9.4, SAS Institute Inc., Cary, NC), which included a normality test, homogeneity of variance test (unequal for all the data in this study) and a nonparametric post hoc analysis approach (Games-Howell test) for the group differences comparison. The results from the analysis were interpreted at a 5% significance level.

RESULTS AND DISCUSSION

In Vitro Antifungal Properties of PA

The growth rates of two white rot, *T.v.* and *I.l.*, and two brown rot, *G.t.* and *R.p.*, in PA-amended malt agar substrates over the 14-d incubation period are shown in Tables 1-4, respectively, and the photos of their overall growing status in the Petri dishes on day 14 are displayed in Fig 1. Overall, the growth of these four fungi was significantly inhibited as the concentration of PA increased and their growth was different across the fungal species. Specifically, in the control

Table 1. Average growth rates of four wood-decaying fungi *T.v.* exposed to different concentrations of phytic acid (PA)-amended malt agar medium over a 14-d incubation period.

Average growth rate of *T.v.* (%)					
	Concentration (wt% PA)				
Day	0	0.125	0.25	0.375	0.5
0	0	0	0	0	0
2	10.59 ± 2.00	1.94 ± 0.07	0	0	0
4	55.25 ± 6.43	3.92 ± 0.80	0	0	0
6	98.65 ± 0.01	6.89 ± 2.41	0	0	0
8	98.65 ± 0.01	9.82 ± 2.84	0	0	0
10	98.65 ± 0.01	13.15 ± 2.92	0	0	0
12	98.65 ± 0.01	16.42 ± 2.54	0	0	0
14	98.65 ± 0.01	18.93 ± 2.96	0	0	0

Table 2. Average growth rates of four wood-decaying fungi *I.l.* exposed to different concentrations of phytic acid (PA)-amended malt agar medium over a 14-d incubation period.

Average growth rate of *I.l.* (%)					
	Concentration (wt% PA)				
Day	0	0.125	0.25	0.375	0.5
0	0	0	0	0	0
2	19.40 ± 1.45	10.56 ± 1.26	0	0	0
4	84.70 ± 3.06	37.33 ± 2.71	0	0	0
6	98.58 ± 0.14	73.47 ± 7.39	0	0	0
8	98.58 ± 0.14	98.56 ± 0.04	0	0	0
10	98.58 ± 0.14	98.56 ± 0.04	0	0	0
12	98.58 ± 0.14	98.56 ± 0.04	0	0	0
14	98.58 ± 0.14	98.56 ± 0.04	0	0	0

group, the mycelium of the two white-rot fungi (*T.v.* and *I.l.*) fully occupied the whole Petri dishes on day 6, whereas those of the two brown rot of *G.t.* and *R.p.* were significantly delayed to days 14 and 10, respectively, which were consistent with previous reports (Alorbu and Cai 2022; Cai and Kuo 2022). In comparison, at a PA concentration of 0.125 wt%, the growth of *T.v.* and *G.t.* was significantly inhibited with growth rates of 19% and 30%, respectively, on day 14. Although this concentration did not significantly change the growth of *I.l.* and *R.p.*, their growth rates were almost completely inhibited as the concentration of PA concentration increased to 0.25 and 4 wt%, respectively. Further increasing of PA concentration to 0.25 wt% also led to little growth

Table 3. Average growth rates of four wood-decaying fungi *G.t.* exposed to different concentrations of phytic acid (PA)-amended malt agar medium over a 14-d incubation period.

Average growth rate of *G.t.* (%)					
	Concentration (wt% PA)				
Day	0	0.125	0.25	0.375	0.5
0	0	0	0	0	0
2	3.70 ± 0.03	1.63 ± 0.27	0	0	0
4	14.49 ± 2.13	5.40 ± 0.88	0	0	0
6	28.60 ± 4.54	8.57 ± 0.31	0.38 ± 0.66	0	0
8	42.66 ± 7.23	12.74 ± 0.62	0.94 ± 1.06	0	0
10	61.47 ± 7.97	18.56 ± 0.95	2.62 ± 2.02	0	0
12	74.78 ± 6.99	24.67 ± 1.13	2.39 ± 2.12	0	0
14	88.80 ± 7.08	30.46 ± 2.22	4.15 ± 4.39	0	0

Table 4. Average growth rates of four wood-decaying fungi *R.p.* exposed to different concentrations of phytic acid (PA)-amended malt agar medium over a 14-d incubation period.

Average growth rate of *R.p.* (%)																	
	Concentration (wt% PA)																
Day	0		0.125		0.25		0.375		0.5		0.625		0.75		1		1.5		2		3		4	
0	0		0		0		0		0		0		0		0		0		0		0	
2	4.64	± 0.31	6.65	± 0.21	6.14	± 0.39	5.20	± 0.40	5.09	± 0.89	4.80	± 0.88	5.96	± 0.25	5.31	± 0.28	3.24	± 0.47	2.70	± 0.14	0		0	
4	30.69	± 1.14	35.69	± 0.56	28.02	± 0.02	21.81	± 2.06	18.57	± 1.43	17.26	± 0.46	17.03	± 0.87	13.07	± 0.66	10.65	± 3.14	8.49	± 1.48	2.83	± 0.44	0.11	± 0.19
6	60.17	± 3.27	64.30	± 3.97	59.63	± 5.10	49.78	± 5.41	42.76	± 1.35	36.94	± 1.58	29.18	± 0.76	24.41	± 1.16	19.67	± 4.28	15.21	± 5.09	4.52	± 0.07	0.60	± 0.52
8	71.58	± 5.12	81.45	± 0.67	76.82	± 5.78	71.10	± 6.75	65.72	± 2.02	58.74	± 3.36	46.99	± 0.56	34.64	± 3.11	29.02	± 7.80	19.44	± 5.14	5.33	± 0.15	0.83	± 0.33
10	95.39	± 5.57	98.69	± 0.06	98.64	± 0.04	98.62	± 0.01	93.01	± 9.54	75.41	± 2.37	64.85	± 5.40	47.50	± 4.66	36.70	± 6.34	32.88	± 7.82	7.83	± 0.55	1.79	± 0.13
12	98.59	± 0.09	98.69	± 0.06	98.64	± 0.04	98.62	± 0.01	98.55	± 0.08	98.64	± 0.05	80.75	± 7.61	64.73	± 2.45	46.29	± 5.84	38.17	± 6.20	10.37	± 0.37	2.19	± 0.21
14	98.59	± 0.09	98.69	± 0.06	98.64	± 0.04	98.62	± 0.01	98.55	± 0.08	98.64	± 0.05	98.61	± 0.05	78.98	± 4.11	55.40	± 4.86	43.50	± 5.92	14.60	± 1.30	2.54	± 0.31

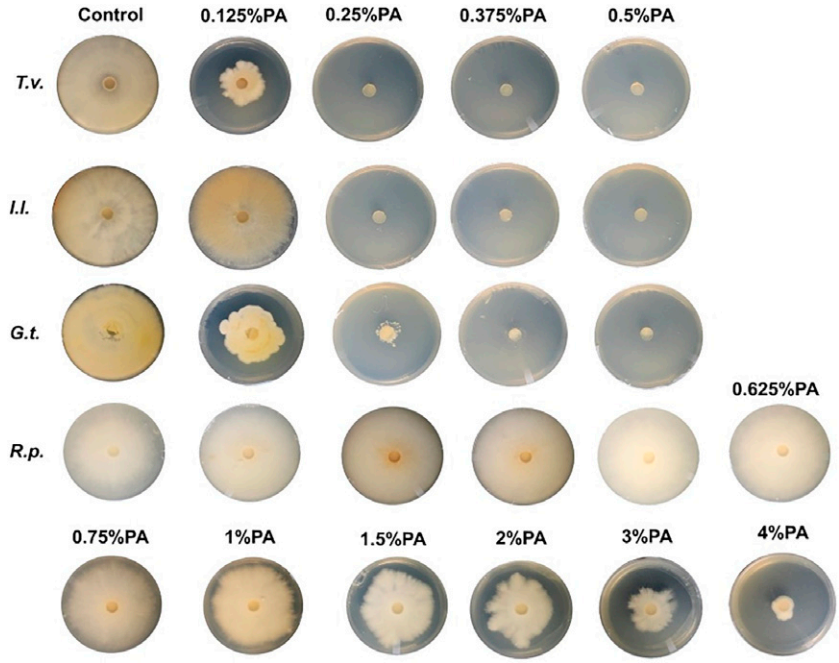

Figure 1. Photos of the wood-decaying fungi on PA amended and unamended plates on day 14.

of *T.v.* and *G.t.*, as shown in Tables 1 and 3, respectively. These results indicated that the white-rot fungi, *T.v.* and *I.l.*, and brown rot fungus *G.t.* used in this study were more sensitive to PA than brown rot fungus *R.p.* Moreover, fungus *R.p.* is the least sensitive to PA and could still grow at the PA concentration of 4 wt%, the highest concentration that the PA-amended malt agar media could solidify under the hood at room conditions.

Mass Gain of PA-Treated Wood Blocks

The mass gain of wood blocks after PA treatment is shown in Fig 2, which generally increases as PA concentration increases. The mass gain of poplar samples was significantly higher (p-value < 0.05) than those of pine samples at all treated concentrations, which is possibly related to the wood anatomical differences (Alorbu and Cai 2022). Moreover, the relatively simple structures of pine samples likely caused more leaching of the extractives in DI water-treated pine control samples than those of poplar samples.

In Vivo Antifungal Properties of PA

The mass loss of decayed samples with and without PA treatment is shown in Fig 3. In general, the PA-treated samples recorded significantly lower (p-value < 0.05) mass loss than those of

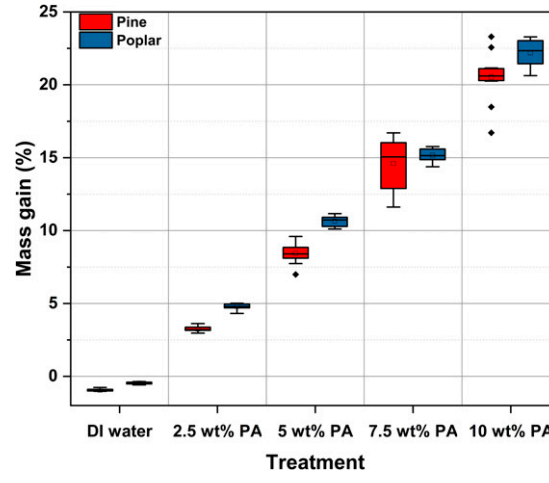

Figure 2. Mass gain of wood blocks after treatment.

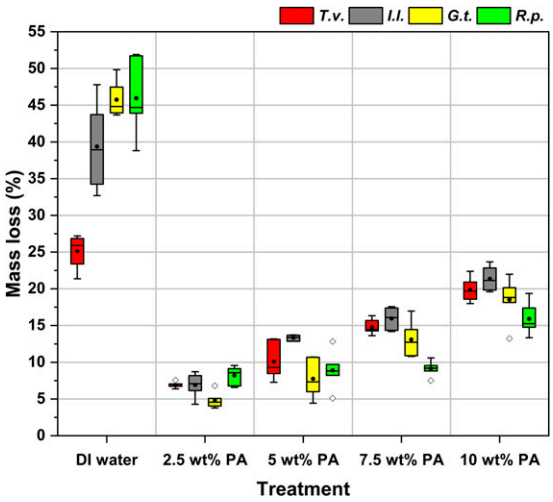

Figure 3. Mass loss of untreated and PA-treated wood blocks without leaching test after 8-wk exposure to white-rot and brown-rot fungi.

DI water-treated samples. For example, the average mass loss of the DI water-treated samples ranges from 25 to 50%, depending on fungal species, whereas the average mass loss of all PA-treated samples is below 25%, indicating PA's promising effectiveness against the common brown-rot and white-rot fungi. Among the PA-treated groups, the mass loss due to decay for each fungus generally increased with an increasing PA concentration (p-value < 0.05) except for fungus *R.p.* This is probably due to the leaching of PA from treated wood blocks during the fungal exposure period. The mass loss of the wood blocks due to fungi exposure was influenced by various factors, including the sample size, fungal exposure time, and chemicals used for the treatment. The results show that the growth of both brown-rot and white-rot fungi on wood has been significantly inhibited by PA treatments. The antifungal mechanism of PA against these four decaying fungi remains unclear but possible reasons could include the disruption of the fungal cell membrane, and inhibits the activity of pathogenesis-related enzymes (Li et al 2023).

TGA Analysis

The pyrolysis and thermal degradation behaviors of the tested wood samples under N_2 and air conditions, respectively, were studied using TGA, as shown in Fig 4, and their average onset temperatures and residues are summarized in Table 5. The TGA thermograms of pine and poplar samples showed no significant differences and generally involved three main stages, including dehydration, active pyrolysis (N_2) or oxidative degradation (air), and passive pyrolysis (N_2) or burnout (air).

Specifically, the dehydration of all the tested wood samples under both N_2 and air was observed below 170°C with less than 5% mass loss. As the temperature increased, all the samples under N_2 experienced active pyrolysis with significant Derivative thermogravimetry (DTG) peaks (Fig 4[a] and [c]). However, the active pyrolysis process for PA-treated samples was advanced (170-450°C) with onset temperatures at ~189-195°C, as compared with that of DI water-treated controls (~300-500°C) at around 310-320°C. Moreover, the onset temperatures of 10% PA-treated wood samples were significantly lower than those of 5% PA-treated, indicating a higher amount of acid could lead to an accelerated pyrolysis process of wood samples (Fu et al 2008). Further increasing of temperature to 800°C resulted in passive pyrolysis of both PA-treated and DI-water-treated controls, which were associated with the decomposition of lignin into cross-linked aromatic charcoal (Yang et al 2006). This observation was also consistent with the nearly zero mass loss rate in their DTG curves (Fig 4[c]). The residues of PA-treated samples were 33-39%, which were significantly higher than those of DI water-treated controls of ~10%.

The weight percentage changes of the samples under air were similar to those of under N_2 conditions before 450°C (Fig 4[b]). As the temperature increased, the samples under air were further oxidized and decomposed, which is evidenced by DTG peaks at ~480°C and above (Fig 4[d]). This process also led to significantly lower residues of the samples as compared with those under N_2 pyrolysis. For example, the residues for DI water-treated pine and poplar controls were nearly 0% (~10% under N_2) while the residues of 5% and 10% PA-treated wood samples were 5% and 10%

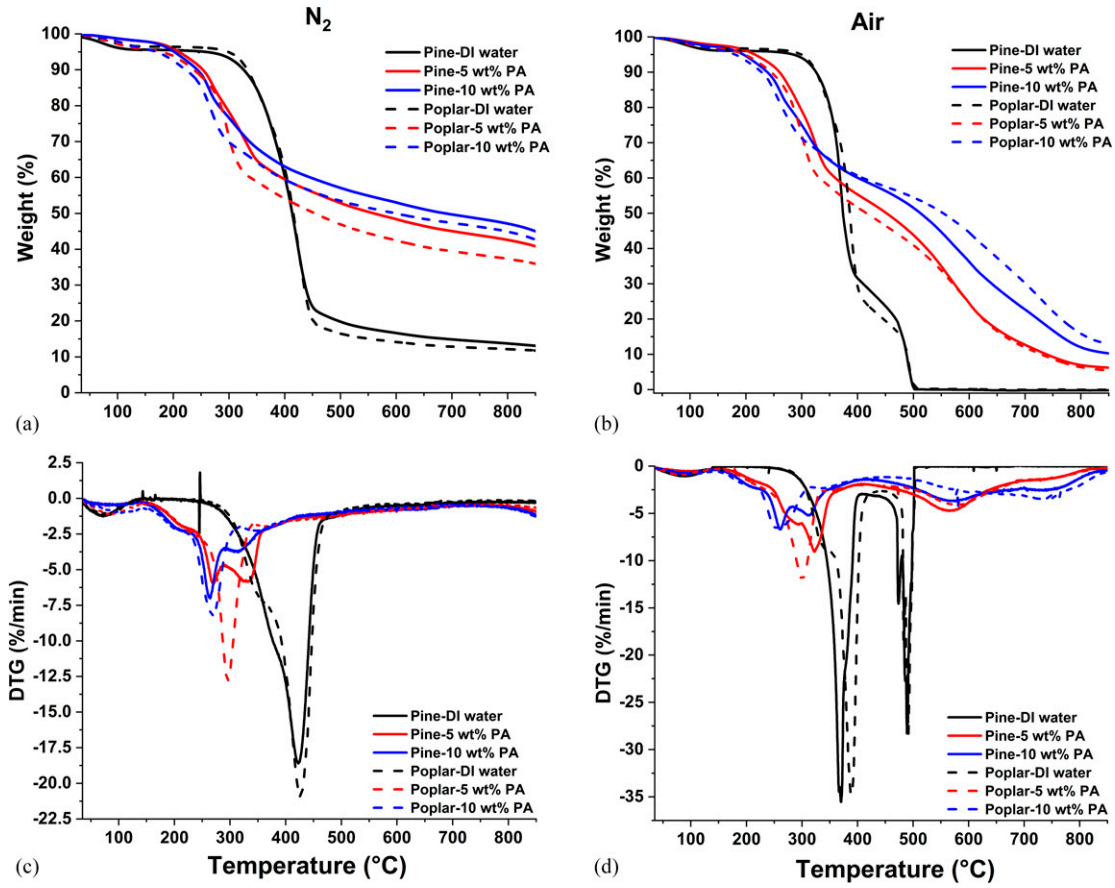

Figure 4. TGA curves of testing samples under (a) N_2 and (b) air; DTG curves of testing samples under (c) N_2 and (d) air.

(~36% under N_2), respectively. Regardless of the purge gas used, PA-treated samples have significantly lower onset temperatures (p-value < 0.05) than those of DI water-treated controls. The improved thermal stability of PA-treated wood samples is likely related to the increased char formation promoted by phosphoric acid from PA, which is less thermally stable and decomposes earlier than cellulose (Daneluti and Matos 2013; Yuan et al 2021). The formation of residual char

Table 5. Onset temperature and residue of pine and poplar samples of the TGA test.

	N_2		Air[a]		
Sample	Onset (°C)	Residue (%)	1st onset (°C)	2nd onset (°C)	Residue (%)
Pine-water control	317 ± 1	12 ± 1	309 ± 5	478 ± 8	0 ± 0
Pine-5 wt% PA	188 ± 5	38 ± 1	192 ± 2	488 ± 13	6 ± 2
Pine-10 wt% PA	178 ± 3	41 ± 1	180 ± 6	479 ± 14	10 ± 4
Poplar-water control	309 ± 3	11 ± 1	307 ± 5	485 ± 5	0 ± 0
Poplar-5 wt% PA	195 ± 4	34 ± 1	201 ± 9	518 ± 5	5 ± 2
Poplar-10 wt% PA	178 ± 3	38 ± 1	187 ± 5	537 ± 18	13 ± 4

[a]For samples exposed to the air, 1st and 2nd onset refers to the initial and 2nd temperatures testing samples start breaking down.

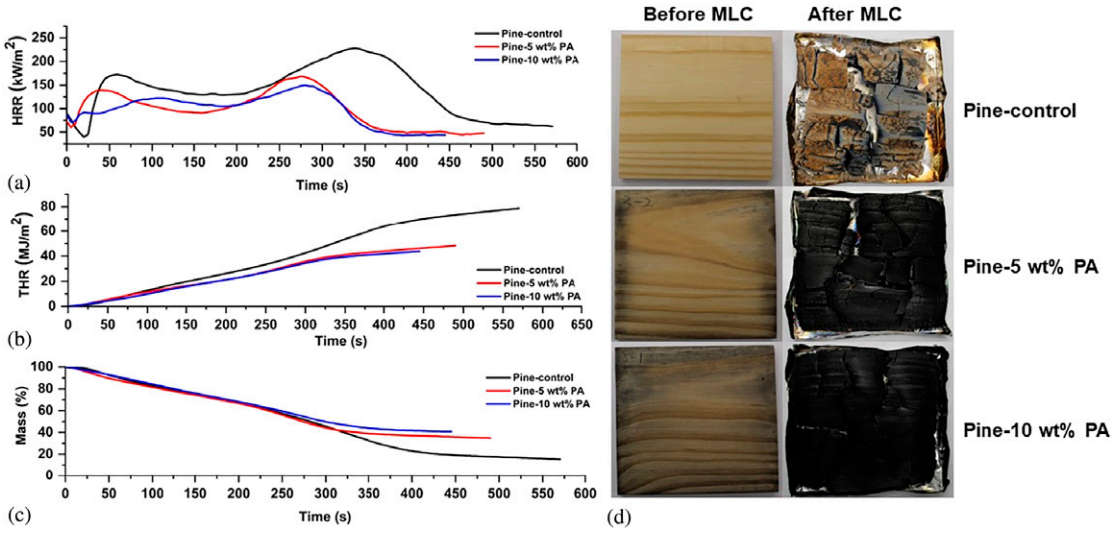

Figure 5. Representative (a) heat release rate (HRR) curves, (b) total heat release (THR) curves, (c) mass curves, and (d) pine samples with different treatment levels before and after the MLC test.

helped reduce the release of flammable gases and heat/mass transfer, contributing to significantly higher (p-value < 0.05) residue at 850°C.

Fire Performance Test

The combustion properties of control wood samples, 5 wt% and 10 wt% PA-treated wood samples were shown in Fig 5. Specifically, in the HRR curves (Fig 5[a]), two peaks were observed in all the testing samples. The first and second peaks correspond to the formation and breakdown of the char layer, respectively (White and Dietenberger 2004; Wang et al 2022). The latter also has a higher HRR value than the former and is noted as peak HRR (pHRR), which helps determine the maximum combustibility and flashover potential of a fire retardant-treated material. For example, the pHRR of the control group is the highest at 241 kW/m^2, whereas those of 5 wt% and 10 wt% PA-treated samples decreased by 26% and 39% to 178 and 148 kW/m^2, respectively. Similarly, the THR(Fig 5[b]) of 5 wt% and 10 wt% PA-treated samples are 47.7 and 34.6 MJ/m^2, respectively, 29% and 48% lower than that of the control at 66.8 MJ/m^2. Moreover, as shown in Fig 5(c), the 5 wt% and 10 wt% PA-treated samples recorded 80% and 137% higher mass residue (36.6% and 48.4%), respectively, than that of the control (20.4%). The increased mass residues of PA-treated wood samples were also evidenced by their improved char formation after burning (Fig 5[d]). In comparison, the residue in the control group was mainly ash. It is also worth noting that the TTI (Table 6) of control wood samples was 21.5 s whereas those of the 5 wt% and 10 wt% PA-treated wood samples were shortened to 7.0 and 5.5 s, respectively. The shortened TTI could be related to the changed chemical structure of PA-treated wood samples, which might have been degraded by the strong PA solution causing the darkening of the surface of wood samples (Shi et al 2018) (Fig 5[d]). Collectively, the shortened ignition time, together with the significantly reduced values in pHRR and THR, and increased

Table 6. Mass Loss Cone data (averaged) of pine-treated samples.

Sample	TTI (s)	pHRR (kW/m^2)	THR (MJ/m^2)	Residue (%)
Pine-control	21.5	241	66.8	20.4
Pine-5 wt% PA	7.0	178	47.7	36.6
Pine-10 wt% PA	5.5	148	34.6	48.4

pHRR refers to the peak HRR value. THR refers to heat release calculated from the start of the test to 2 min after flaming out.

mass residue after flame out indicate PA might help lower the onset decomposition temperature (as shown in TGA analysis above) and catalyze the carbonization of wood compounds, thus facilitating the formation of residual char as insulation and reducing the heat and mass transfer (Yuan et al 2021). Our findings are also consistent with the previous results found in the combined treatment of PA (6 wt%) and uracil on poplar wood samples (Zhang et al 2021).

CONCLUSIONS

The in vitro tests demonstrated the effectiveness of PA in inhibiting the growth of two white-rot fungi, *T.v.* and *I.l.*, and the brown-rot fungus, *G.t.* at a concentration of 0.25 wt%. However, fungus *R.p.* was the least sensitive to PA and continued to grow at a PA concentration of 4 wt%. Soil block tests further evidenced the improved resistance of PA-treated wood blocks to wood-decay fungi with around 5-25% mass loss, compared with the control group's 25-45%. Thermal stability of wood samples under both air and N_2 conditions was significantly improved with higher residue and lower DTG peak after PA treatment. The MLC tests of pine samples showed that PA treatment significantly reduced the pHRR and THR of wood samples from 241.0 and 66.8 kW/m^2 to 147.8 and 34.6 kW/m^2, respectively, and increased the charring from 20.4 to 48.4% during combustion. Our research findings indicated PA provides both antifungal properties and fire retardance to wood products.

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