Dual Protection of Wood Surface Treated with Melamine-Modified Urea-Formaldehyde Resin Mixed with Ammonium Polyphosphate against Both Fire and Decay

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Abstract

Surface coatings of melamine-modified urea-formaldehyde resins (MUFs) containing ammonium polyphosphate (APP) have been shown to significantly improve the fire retardancy of wood by prolonging the ignition time and reducing the heat release rate, total heat released, and mass loss rate. Dual protection of wood against both decay and fire has been proposed for remedial situations and interior construction. In this study, the fire retardant MUF resin type 3 (MUF3)/APP mixture system showed strong activity against wood decay fungi via an activity inhibition test. Two species of wood were subjected to steeping with the fire retardants MUF3/APP. The treatments were evaluated for fire and decay resistance using cone calorimetry and fungal decay resistance tests. The results showed that MUF3/APP surface treatment can provide dual protection to wood against degradation by decay fungi and fire.

Wood biodeterioration and combustibility represent two major obstacles that routinely affect the service life of wood and wood-based products (Zabel and Morrell 1992). Dual protection of wood against decay and fire, if achievable, is desirable (Chen 2008). Several approaches are used to produce a combined fire retardant–wood preservative treatment system aimed at dual protection (Marney and Russell 2008). One of these is combinations of fire retardants and preservatives that may be beneficial in improving performance of wood against both fire and decay (Terzi et al. 2011). White and Sweet (1992) evaluated preservatives that are compatible with leach-resistant fire retardants. LeVan and DeGroot (1992) used a one-step process for imparting both decay resistance and fire retardancy to wood and cellulosic materials by impregnating the products with a treatment solution composed of a water-soluble mixture of tertiary and quaternary ammonium preservative compounds and an organic phosphate fire retardant compound. Marney et al. (2008) found that the performance of the preservative copper naphthenate–permethrin enhanced protection against fungal and termite attack when coformulated with a synthetic polymer-based fire retardant. Terzi et al. (2011) studied the fire performance and decay resistance of wood treated with the quaternary ammonia compounds didecyl dimethyl ammonium chloride (DDAC) and didecyl dimethyl ammonium tetrafluoroborate (DBF), both independently and paired with the common fire retardants monoammonium phosphate (MAP), diammonium phosphate (DAP), and ammonium sulfate (AS), to determine if the preservatives showed fire retardancy or showed decay-resistant properties by them-

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selves. However, their findings indicated that MAP, DAP, and AS were not effective against decay fungi.

Previous reports of the chemical impregnation of wood using conventional fire retardants demonstrate effective biocidal properties (Marney and Russell 2008). Kajita and Imamura (1991) found that particleboards impregnated with phenol-formaldehyde resin exhibited enhanced resistance to decay and termites. Lee et al. (2004a, 2004b) found that treatment with a phosphorus pentoxide–amine system could protect wood from fungal decay and thermal degradation. However, many conventional fire retardants are not suitable for exterior use because of their tendency to leach when in contact with moisture or liquid water.

Melamine-modified urea-formaldehyde resins mixed with ammonium polyphosphate (MUFs/APP) have been found to significantly improve the fire retardancy of medium-density fiberboard (MDF; Ma et al. 2013b). In that study, MUFs containing APP could significantly improve the fire retardancy of MDF by prolonging ignition time and reducing the heat release rate, total heat released, and mass loss rate. The MUFs also had good water resistance, low formaldehyde emission, low cost, and a long storage period (Zhu et al. 2013).

The objective of this study was to assess the antifungal activity of the fire retardant MUF resin type 3 (MUF3)/APP mixture system via fungal inhibition plate assays. Two species of wood (softwood species *Pinus radiata* and hardwood species *Populus deltoides*) surface treated with a fire retardant MUF3/APP system were subjected to cone calorimeter and fungal decay resistance tests to evaluate fire and decay dual resistance.

Materials and Methods

MUF/APP preparation

The MUF3 resin was prepared according to the method used by Tohmura et al. (2001). The final molar ratio was 1.5 and 1.0 for F/(M+U) and M/U, respectively. Melamine content to MUF resin was 46 percent. The MUF3 was mixed with APP with a mass ratio of 100:60.

Preservative preparation

The preservative copper azole type C (CA-C) was used in this test. The active ingredients of the preservatives and the treating solution concentrations are referenced in AWPA P5-10 (American Wood Protection Association 2011) and Ma et al. (2013a). The treating solution concentration was 0.4 percent (wt/wt).

Wood species preparation

P. radiata and *P. deltoides* were dried and sawed.

Inhibition zone test

The Oxford cup method was used to assess the antifungal activity of the test chemicals via modified filter paper discs (Ma et al. 2009). Four Oxford cups, with inner diameters of 6 mm and heights of 10 mm, were placed on the surface of potato dextrose agar petri dishes that had been inoculated with a fungal mycelial suspension created from actively growing cultures. The fungi used in the inhibition test were the white rot *Trametes versicolor* (L. ex Fr.) Pilat and the brown rot *Gloeophyllum trabeum* (Pers. ex Fr.). Three hundred microliters of the chemicals was added to each of three Oxford cups as treatment. An equal amount of water was added to a remaining cup as a control. The petri dishes were cultivated at 26°C to 28°C for 3 to 7 days until hyphae were visible, and then the diameters of the inhibition zones were measured with a Vernier caliper. Three replicates (petri dishes) were measured for each formulation.

Decay resistance tests

The size of the specimens for decay testing was 20 by 20 by 10 mm (radial by tangential by longitudinal). Thirty-six

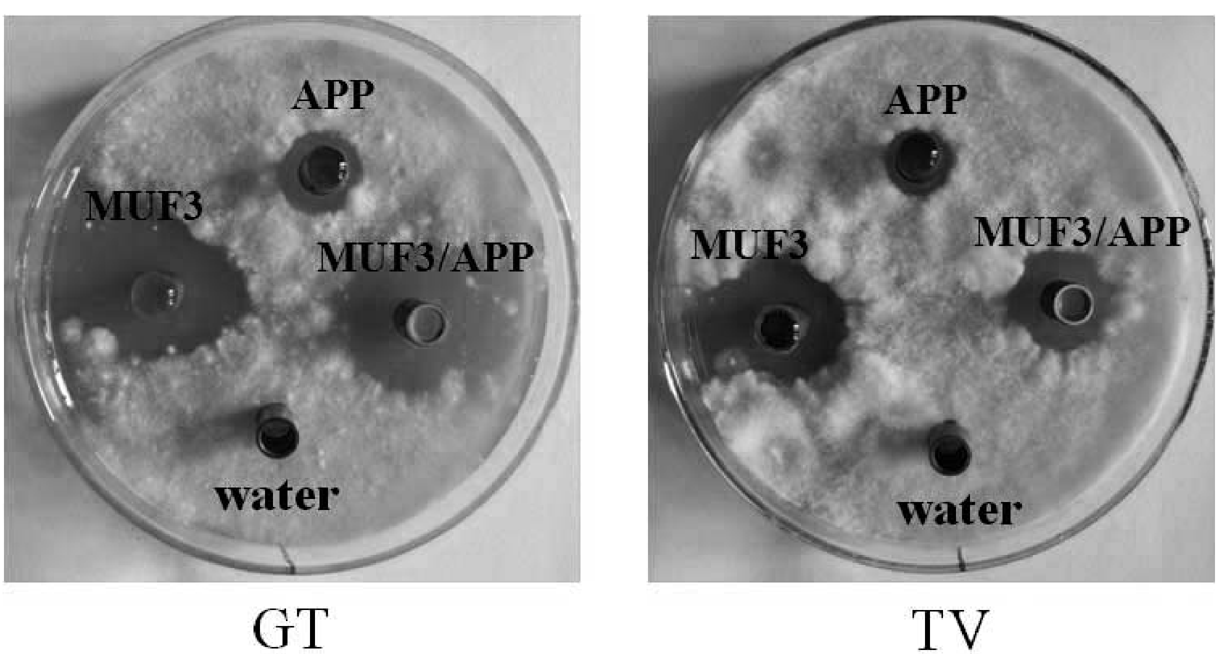

Figure 1.—The decay fungus inhibition test for melamine-modified urea-formaldehyde resin type 3 (MUF3), ammonium polyphosphate (APP), and MUF3 mixed with APP (MUF3/APP); GT = Gloeophyllum trabeum *(Pers. ex Fr.); TV =* Trametes versicolor *(L. ex Fr.).*

replicates of each wood species were used. Twelve blocks were only surface treated with CA-C according to Ma et al. (2013b). Surface retention of *P. radiata* was approximately 3.3 g/m^2 and that of *P. deltoides* was approximately 3.8 g/m^2. Another 12 blocks were only brush treated with fire retardant (MUF3/APP) with a glue spread amount of 400 g/m^2 (Ma et al. 2013b). The resin was allowed to slowly solidify on the samples at room temperature. The remaining 12 blocks were nontreated controls. Samples were then prepared for decay resistance tests.

Decay testing was conducted according to Chinese standard LY/T 1283 (Standardization Administration of the People's Republic of China 2011) and Ma et al. (2013a). Two decay fungi, the white rot *T. versicolor* and the brown rot *G. trabeum,* were tested. Each specimen was weighed and recorded to an accuracy of 0.01 g before and after the decay test, and the percent mass loss was calculated. Decay resistance was rated on a scale of I to IV defined as mass losses: (I) highly resistant, mass loss from 0 to 10 percent; (II) resistant, mass loss from 11 to 24 percent; (III) moderately resistant, mass loss from 25 to 44 percent; (IV) slightly or nonresistant, mass loss more than 45 percent.

Fire retardant properties of the MUF3/APP test

The size of the specimens for cone calorimeter testing was 100 by 100 by 15 mm (radial by tangential by longitudinal). Three replicates were prepared for MUF3/APP surface treatment and the fire retardancy test. The fire retardancy test was conducted according to International Organization for Standardization (ISO) standard 5660-1 by using cone calorimeter (ISO 2002) and Ma et al. (2013b). All the tests were conducted at an irradiance level of 50 kW/m^2. The duration time of each individual test was 600 seconds. The average mass loss rate was calculated by followed formula: Average mass loss rate = (mass of the treated specimen before burning − mass of the treated specimen after burning for 600 s)/(600 s·0.1 m × 0.1 m).

Results and Discussion

Antifungal activity

The MUF3, APP, and MUF3/APP mixture systems were tested via inhibition activity to decay fungi (Fig. 1). Table 1 shows that the control was no inhibition and was recorded as 6 mm. APP had slight antifungal activity: only a 13.3-mm inhibition zone diameter was observed for *G. trabeum,* and an 11.6-mm zone diameter was observed for *T. versicolor*. The MUF3 showed strong activity against decay fungi, with a 28.2-mm inhibition zone for *G. trabeum* and a 22.5-mm inhibition zone for *T. versicolor*. The MUF3/APP mixture system showed strong activity against fungal growth, with inhibition zone diameters of 25.3 and 16.6 mm for *G. trabeum* and *T. versicolor,* respectively.

Decay resistance

Mass losses of wood specimens exposed to the two decay fungi are shown in Table 2. The mass losses of untreated *P. deltoides* specimens were 65.5 and 62.3 percent when exposed to *G. trabeum* and *T. versicolor,* respectively. Untreated *P. deltoides* were nonresistant against decay fungi (class IV). The CA-C–treated *P. deltoides* had no mass loss, showing high decay resistance (class I).

The mass losses of untreated *P. radiata* exposed to *G. trabeum* and *T. versicolor* were 31.0 and 42.2 percent, respectively. Untreated *P. radiata* were moderately resistant against decay fungi (class III). The mass losses of CA-C–treated *P. radiata* were 1.7 percent in tests with the white-rot fungus, and no mass loss was observed with the brown-rot fungus, showing high decay resistance (class I).

Mass losses of MUF3/APP-treated *P. deltoides* and *P. radiata* exposed to *G. trabeum* were 2.1 and 0.9 percent, respectively. Mass losses for these two wood species exposed to *T. versicolor* were 7.5 and 5.5 percent,

Table 1.—Comparison of the inhibition zone between chemicals.

	Inhibition zone diameter (mm)[a]	
	Gloeophyllum trabeum	*Trametes versicolor*
Control (no inhibition)	6	6
Melamine-modified urea-formaldehyde resin type 3 (MUF3)	28.2 (3.3)	22.5 (4.1)
Ammonium polyphosphate (APP)	13.3 (0.7)	11.6 (0.4)
MUF3/APP	25.3 (6.0)	16.6 (1.3)

[a] Values are means with standard deviations in parentheses.

Table 2.—Mass losses of surface-treated wood after being exposed to decay fungi.

		Mass loss[a] and decay resistance class						
		Untreated		Copper azole type C treatment			MUF3/APP[b] treatment	
Wood species	Fungus species	Mass loss (%)	Class	Surface retention ($g\ m^{-2}$)	Mass loss (%)	Class	Mass loss (%)	Class
Populus deltoides	*Gloeophyllum trabeum*	65.5 (13.9)	IV	3.8	0 (0.6)	I	2.1 (0.7)	I
	Trametes versicolor	62.3 (6.9)	IV	3.8	0 (0.7)	I	7.5 (2.5)	I
Pinus radiata	*G. trabeum*	31.0 (5.8)	III	3.3	0 (0.9)	I	0.9 (0.4)	I
	T. versicolor	42.2 (11.3)	III	3.3	1.7 (1.2)	I	5.5 (2.2)	I

[a] Values in parentheses are standard deviations.
[b] MUF3 = melamine-modified urea-formaldehyde resin type 3; APP = ammonium polyphosphate.

Table 3.—*Fire retardant properties of wood surface treated with melamine-modified urea-formaldehyde resin type 3 mixed with ammonium polyphosphate.*

Property	*Populus deltoides*		*Pinus radiata*	
	Untreated	Treated	Untreated	Treated
Time to ignition (s)	15.7	337.9	14.9	325.1
Delay of ignition time (s)	—	322.2	—	310.2
Total heat released for T600s (MJ/m^2)	54.3	5.5	70.4	6.5
Avg. mass loss rate ($g/s \cdot m^2$)	7.4	3.3	8.2	4.1

respectively. All mass loses were less than 10 percent, indicating high decay resistance (class I; Table 2). The results showed that surface treatment with MUF3/APP significantly enhanced the decay resistance of wood species.

Fire retardant properties of MUF3/APP-treated wood

Table 3 shows the fire retardant properties of *P. deltoides* and *P. radiata* surface treated with MUF3/APP. The ignition times of the untreated *P. deltoides* and *P. radiata* were 15.7 and 14.9 seconds; however, the specimens surface treated with MUF3/APP prolonged the ignition time significantly, up to 337.9 and 325.1 seconds, respectively. Delay of ignition time of 322.2 seconds for *P. deltoides* and 310.2 seconds for *P. radiata* indicated reduced flammability of treated specimens. The total heat released in 600 seconds from the untreated *P. deltoides* and *P. radiata* specimens were 54.3 and 70.4 MJ/m^2, respectively, but the total heat released from the MUF3/APP-treated wood decreased significantly, to 5.5 and 6.5 MJ/m^2, respectively. The average mass loss rate of the treated *P. deltoides* specimens decreased from 7.4 to 3.3 $g/s \cdot m^2$. The average mass loss rate of the treated *P. radiata* specimens decreased from 8.2 to 4.1 $g/s \cdot m^2$. Delay of ignition time, reduction of the total heat released, and the average mass loss rate means that the MUFs/APP-treated wood is more effective in retarding fire. It showed that treatment with MUF3/APP significantly enhanced the fire resistance of wood species.

Conclusions

The fire retardant MUF3/APP mixture system showed strong activity against wood decay fungi via an activity inhibition test. Decay testing showed that surface treatment with MUF3/APP significantly enhanced the decay resistance of wood species. Cone calorimeter testing showed that treatment with MUF3/APP significantly enhanced the fire resistance of wood species. This means that MUF3/APP surface treatment can provide dual protection for wood against degradation by rot fungi and fire.

Acknowledgments

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