CHEMICAL MODIFICATION OF WOOD TO IMPROVE DECAY AND THERMAL RESISTANCE
Hong-lin Lee 1; George C. Chen 2; Roger M. Rowell 2
1 Taiwan Forestry Research Institute, 53 Nan-hai Road, Taipei, Taiwan
2 USDA, FS, Forest Products Laboratory, 1 Gifford Pinchot Dr, Madison, WI, USA

ABSTRACT
Wood reacted with phosphoramides produced in situ by reacting phosphorus pentoxide with amines resisted fungal and thermal degradation. Moisture sorption study at 90% relative humidity for 4 weeks showed that wood reacted with phosphoramides absorbed moisture similar to or higher than untreated wood. This indicated that the decay protection of the modified wood was not based on hydrophobicity but was attributed to the release of fungicidal groups from the reacted wood.

Thermal analysis by DSC in nitrogen of wood reacted with phosphoramides showed that the mechanism of fire retardancy was attributed to dehydration.

Keywords: Chemical modification, wood, phosphoramides, fungal and thermal resistance

INTRODUCTION
The degradation of wood by decay, fire and UV constitutes the three major losses of wood products in use. Commercial wood preservatives including chromated copper arsenate (CCA) and pentachlorophenol (penta) were developed to only protect wood from decay. Dual protections of wood against decay and fire are desirable. Many phosphorus and boron compounds possess fire retardant and decay resistant properties (Grassie, 1990). The aim of this research was to investigate the possibility of dual protections of wood by reacting wood with phosphoramides. Phosphoramides have been shown to have good fire retardant properties (Hendrix et al., 1970a, 1970b, 1972a, 1972b; Langley et al. 1980; Kaur et al. 1986). In our preliminary study, phosphoramides produced in situ by reacting phosphorus pentoxide with butylamine were able to react with wood and the resultant modified wood has fire and decay protecting properties. Another aim of this research was to investigate the influence of functional groups of phosphoramides including alkyl, aryl and halogens on fire retardancy and decay resistance.

MATERIALS AND METHODS
Characterization: Bond formation between wood and phosphoramides was identified by FTIR using KBr on a Wattson Model 5000 FTIR spectrophotometer. The distribution of chemicals in cell walls of wood was determined by energy dispersive X-ray analysis using a Tracor Northern 5500 energy dispersive spectrometer. The distribution of chemicals in wood cells was detected by X-ray maps. Elemental analysis was performed by the Galbraith Laboratories.

Fungal Decay Evaluation: Eighteen loblolly pine or sweetgum blocks (1.9 cubic cm in radial, tangential and longitudinal directions) in a reaction flask were vacuumed at 2.1-3.3 kPa for 30 min in a desiccator and then impregnated with DMF (900 ml) (dried over molecular sieve 4A more than 1 day). Phosphorus pentoxide:amine:wood (calculated as 1,4-anhydroglucopyranose equivalent) in a molar ratio of 1:3:1 were added to the flask. The amines used in the reaction with wood were listed in Table 1. The solution was maintained at 115°C. During the reaction, six blocks were withdrawn at 7, 8 and 10 h intervals for the pine blocks and 1, 2 and 4 h intervals for the sweetgum blocks. The blocks from each treatment were extracted with acetone (900 ml) in a Soxhlet extractor for 12 h, air dried for 1 day and then leached in distilled water (300 ml) daily for 2 weeks. After leaching, the blocks were heated in an oven at 60°C for 1 day. The blocks were conditioned at 26.7°C and 30% relative humidity for 3 weeks before decay test.

Soil-block fungal decay tests were conducted according to ASTM standard D1413 (ASTM 1990). Gloeophyllum trabeum (Pers.:Fr.) Murr., MAD-617, a brown rot fungus, was used with loblolly pine blocks, and Coriolus versicolor (L.:Fr.) Quel., MAD-697, a white rot fungus, was used with sweetgum blocks. Five replicate blocks from each treatment, five control, and five blocks treated with solvent alone were tested for decay resistance over a period of 12 weeks. The extent of decay was evaluated by the weight loss. Chemical retention that resulted in 2% weight loss by decay was generally considered the threshold retention.

Thermal Properties Evaluations: 30 Loblolly pine samples (6.4 x 3.2 x 25.4 mm in radial, tangential and longitudinal directions) were dried in an oven at 60°C for 1 day. The samples in a reaction flask were vacuumed at 2.1-3.3 kPa for 30 min. and then impregnated with N,N-dimethylformamide (DMF)(20 ml, dried over molecular sieve 4A for more than 1 day). Phosphorus pentoxide, amine and wood (calculated as 1,4-anhydroglucopyranose equivalent) in a molar ratio of 1:3:1 were added to the flask (Table 1). The solution was maintained at 115°C for 24 h. During reaction, six samples were withdrawn at 2, 4, 8 and 12 h intervals. The samples in each treatment were extracted with acetone (600 ml) in a Soxhlet extractor and then leached in distilled water (600 ml) daily for 14 days. After leaching, the samples were used for DSC and TGA analysis.
RESULTS AND DISCUSSION

Characterization (bond formation and chemical distribution): Bond formation between wood and phosphoramides was evidenced by the IR absorptions of P-OH, P=O and P-N groups which were able to detect at chemical weight gain of 52% (Fig. 1). The absorptions at 2,480, 1,240 and 926 cm⁻¹ were attributed to P-OH stretching vibration, P=O vibration and asymmetric stretching vibration of P-N groups, respectively (Colthup et al., 1964).

The distribution of bromine and phosphorus in the cell walls of monobromophenyl phosphoramide reacted wood (Fig. 2) indicated that phosphoramides were able to bond to wood. At chemical weight gain of 12.8% (50 mmoles/100 g wood), the distribution of bromine in the middle lamella was higher than phosphorus. This indicated that other reactive chemicals containing bromine were also presented. These reactive chemicals were able to react preferably with lignin in wood. The distribution of bromine and phosphorus were the same in the S2 layer of cell walls.

Another evidence of bond formation between wood and butyl phosphoramide was provided by the high content of phosphorus(10%) and nitrogen(3.5%) of the reacted wood(52 % weight gain of chemical in wood)by the elemental analysis.

Fungal Decay Evaluation: Brown rot fungus: Threshold retentions with *G. trabeum* of wood reacted with alkyl phosphoramides including octyl, hexyl, butyl and propyl derivatives were 13, 13.3, 18.7 and 20.4 mmoles per 100 g wood(Table 2). This indicated that increased hydrophobicity of the modified wood increased decay resistance.

For wood reacted with halophenyl phosphoramides, threshold retentions with *G. trabeum* were 11.3, 12.7, 17.0 and 8.1 mmoles for fluoro, chloro and bromo and tribromo derivatives, respectively(Table 2). The results indicated that tribromo derivative was the most effective followed by fluoro, chloro and bromo derivatives. It indicated that the increase bromine substitution on the phenyl ring increased the efficacy of decay protection.

For wood reacted with phenyl phosphoramides, threshold retentions with *G. trabeum* were 9.3, 19.2 mmoles for nitro and 4-methyl derivatives, respectively, while anilino and anise derivatives were ineffective (Table 2). The increase in hydrophobicity on the aromatic ring may play a role in decay resistance.

White-rot fungus: Decay test of wood reacted with alkyl phosphoramides showed that threshold retentions with *C. versicolor* were 4.7, 5.9, 11.2 and 13.3 mmoles for octyl, hexyl, butyl and propyl derivatives, respectively (Table 3). The increase in hydrophobicity of the modified wood may contribute to decay resistance.

For wood reacted with monohalophenyl phosphoramides, threshold retentions with *C. versicolor* were 4.5, 5.6 and 6.3 mmoles for chloro, fluoro and bromo derivatives, respectively (Table 3). It was difficult to access that chloro was more effective than the fluoro derivative because only one concentration was used to determine the threshold value. For bromine derivatives, increased bromine substitution increased fungitoxicity. Threshold value for tribromo derivative was 3.5 mmoles while monobromo derivative was 6.3 mmoles.

For wood reacted with phenyl phosphoramides, threshold retentions with *C. versicolor* were 2.9, 5.0, 5.2 and 9.9 mmoles for nitro, anilino, 4-methyl and 4-methoxy derivatives, respectively (Table 3). The nitro derivative was the most effective, followed by anilino and methoxy derivatives while 4-methyl derivative was the least effective.

The results of decay tests indicated that wood reacted with phosphoramides was more effective to a white rot fungus than a brown-rot fungus. Threshold values were lower with a white rot fungus, & *versicolor* (ranging from 2.9 to 13.3 mmoles) while higher with a brown-rot fungus, *G. trabeum* (ranging from 8.1 to 20.4 mmoles). The decay resistance of wood reacted with phosphoramides was comparable to that of wood impregnated with known fungicides including pentachlorophenol and boric acid (Chen, 1994). The modified woods decayed by *G. trabeum* with threshold retentions ranging from 8.1 to 20.4 mmoles after leaching were slightly less effective than that of leached penta (3.2 mmoles) but were as effective as that of unleached boric acid (14 mmoles). The modified woods decayed by *C. versicolor* with threshold retentions ranging from 2.9 to 13.3 mmoles after leaching remained effective while that of leached penta was ineffective(9.8 mmoles of retention had 48% weight loss).

Thermal Properties Evaluations: DSC analysis: Pyrolysis of wood components and wood in nitrogen (Fig.3) showed that active pyrolysis took place after 150°C. Xylan pyrolyzed at lower temperature(150°C) and gradually increased exothermic reaction (peak at 190°C) followed by steep increase in exothermic reaction.
Pyrolysis of wood reacted with phosphoramides can be explained by the dehydration and depolymerization mechanisms (Kaur et al., 1986). Pyrolysis of wood reacted with alkyl, halophenyl phosphoramides including monosubstituted fluoro, bromo and chloro derivatives were dominant by dehydration reaction (Fig. 4-7, Table 4.5). The mechanism was similar to that of wood impregnated with diammonium phosphate. However, the pyrolysis of iodo and nitro derivatives were dominant by depolymerization reaction. The advantages of pyrolysis proceeded by dehydration reaction were to decrease volatiles and increase char formation (Hirata et al., 1991; LeVan, 1984; Shafiizadeh, 1984). The rate of char oxidation was also decreased.

Thermal decomposition in air of wood reacted with phosphoramides showed that active combustion took place at 200°C and ended at 520°C with two major peaks (Table 5). The first peak at 339°C was attributed largely to flamming combustion of volatiles and the second peak at 496°C was attributed to char oxidation (Sekiguchi et al., 1984). For alkyl derivatives, increased alkyl chain increase flamming combustion. Among the halophenyl derivatives, bromine derivatives reduced the flamming combustion the most, and the tribromo derivative reduced flaming combustion and char oxidation even further. The anisole derivative also reduced flaming and char oxidation.

Heat of combustion obtained from DSC thermograms of wood reacted with phosphoramides in air showed that heat release from first exothermic peak attributed to flaming combustion was reduced significantly (489.5-674.8 mcal/mg) compared to that of wood (693.5 mcal/mg) (Table 6). In particular, the halophenyl derivatives have smaller heat release (ranging from 489.5 to 579.9 mcal/mg). Trapping radicals by bromine compounds in the gas phase may be attributed to these reductions. The 2nd exothermic peak attributed to char oxidation was smaller for alkyl derivatives but halogen and phenyl derivatives were larger. The reasons for this difference were not clear. The char formed by alkyl derivatives may be more oxygenated resulting in low heat content while that of halophenyl and phenyl derivatives are less oxygenated.

TGA analysis: TGA in nitrogen at 600°C of phosphoramidated wood showed that most of them have higher char yields (ranging from 40.4 to 44.7%) than that of wood impregnated with diammonium phosphate (40.4%) while wood has only 20.1% char (Table 7). The iodo and phenylene diamine derivatives have low char yields 33.9% and 32.0%, respectively. TGA in air at 600°C of wood reacted with phosphoramides also showed that most of them (ranging from 11.1% to 17.7%) have higher char than that of wood impregnated with diammonium phosphate while wood has only 2.7% char yield (Table 8). Char yields of iodo and phenylene diamine derivatives were low, 7.7% and 8.5%, respectively.

CONCLUSION

Phosphoramides prepared in situ by reacting phosphorus pentoxide with amines were able to react with wood. Evidences of bond formation between wood and phosphoramides were provided by FTIR, energy disperse x-ray and elemental analysis.

Moisture sorption study at high humidity (90% relative humidity for 4 weeks) showed that wood reacted with phosphoramides absorbed moisture similar to or higher than untreated wood. This indicated that the decay resistant of the modified wood was not based on hydrophobicity but attributed to the release of fungicidal groups from the reacted wood. The efficacy of decay resistant of wood reacted with phosphoramides was comparable to that of wood impregnated with penta or boric acid. Threshold retentions ranged from 8 to 19 mmoles for G. trabeum and 2.9 to 13 mmoles for C. versicolor.

Thermal analysis by DSC in nitrogen of wood reacted with phosphoramides showed that the mechanism Of fire retardancy was attributed to dehydration. Pyrolysis of the modified wood by dehydration reaction leads to decrease in production of volatiles and increase char formation. The rate of char oxidation was also decreased.

TGA in nitrogen or air showed that the modified woods have higher char yields than that of wood impregnated with diammonium phosphate. Heat of combustion of wood reacted with phosphoramides in air showed that heat release from halophenyl derivatives were less compared to the unreacted wood. The decrease in heat release may be attributed to the trapping of free radicals by halogen compounds in the gas phase. Heat release from 2nd peak attributed to char oxidation was more for halophenyl and phenyl derivatives but was less for alkyl
derivatives. Chars formed from alkyl derivatives may be more oxygenated which was low in heat content while char formed from halopheny and phenyl derivatives may be less oxygenated.

REFERENCES


Table 1. Chemicals reacted with wood through phosphorus pentoxide and amines system

<table>
<thead>
<tr>
<th>Chemical Structure</th>
<th>Molecular Weight</th>
<th>Symbol</th>
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<tbody>
<tr>
<td>Phosphorus pentoxide</td>
<td>P₂O₅</td>
<td>141.94</td>
</tr>
<tr>
<td>Diammoniumphosphate</td>
<td>(NH₄)₂HPO₄</td>
<td>132.06</td>
</tr>
<tr>
<td>Propylamine</td>
<td>C₃H₇NH₂</td>
<td>59.11</td>
</tr>
<tr>
<td>Butylamine</td>
<td>C₄H₉NH₂</td>
<td>73.14</td>
</tr>
<tr>
<td>Hexylamine</td>
<td>C₆H₁₃NH₂</td>
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</tr>
<tr>
<td>Octylamine</td>
<td>C₈H₁₇NH₂</td>
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</tr>
<tr>
<td>4-Fluoroaniline</td>
<td>C₆H₄F NH₂</td>
<td>111.12</td>
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<tr>
<td>4-Chloroaniline</td>
<td>C₆H₄Cl NH₂</td>
<td>127.57</td>
</tr>
<tr>
<td>4-Bromoaniline</td>
<td>C₆H₄Br NH₂</td>
<td>172.03</td>
</tr>
<tr>
<td>4-Iodoaniline</td>
<td>C₆H₄I NH₂</td>
<td>219.03</td>
</tr>
<tr>
<td>2,4-Dibromoaniline</td>
<td>C₆H₃Br₂NH₂</td>
<td>250.93</td>
</tr>
<tr>
<td>2,4,6-Trisbromoaniline</td>
<td>C₆H₃Br₃NH₂</td>
<td>329.83</td>
</tr>
<tr>
<td>Aniline</td>
<td>C₆H₅NH₂</td>
<td>93.13</td>
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<tr>
<td>p-Anisidine</td>
<td>C₆H₄OCH₂NH₂</td>
<td>123.16</td>
</tr>
<tr>
<td>p-Toludine</td>
<td>C₆H₄CH₂NH₂</td>
<td>107.16</td>
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<tr>
<td>4-Nitroaniline</td>
<td>C₆H₄NO₂NH₂</td>
<td>146.10</td>
</tr>
<tr>
<td>N,N,Dimethyl</td>
<td>C₆H₄N(CH₃)₂</td>
<td>136.20</td>
</tr>
<tr>
<td>1,4-Phenylenediamine</td>
<td>C₆H₄N₂H₂</td>
<td>108.14</td>
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</table>
Table 2. Soil-block decay test (12 weeks) of southern pine reacted with phosphoramides and inoculated with *Gloeophyllum trabeum* \(^a\)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Weight retention (^b) (%)</th>
<th>Weight loss (^c) (%)</th>
</tr>
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<tbody>
<tr>
<td>Control</td>
<td>46.8 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>DMF</td>
<td>30.3 ± 5.2</td>
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</tr>
<tr>
<td>PPAM</td>
<td>9.7 (20.4)</td>
<td>12.0 ± 1.0</td>
</tr>
<tr>
<td>PBAM</td>
<td>10.0 (18.7)</td>
<td>2.6 ± 0.5</td>
</tr>
<tr>
<td>PHAM</td>
<td>8.4 (13.3)</td>
<td>1.2 ± 0.3</td>
</tr>
<tr>
<td>POAM</td>
<td>9.9 (13.0)</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>PFAN</td>
<td>7.2 (11.3)</td>
<td>1.7 ± 0.5</td>
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<tr>
<td>PCAN</td>
<td>8.7 (12.7)</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>PBAN</td>
<td>14.5 (17.0)</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>PTBAN</td>
<td>11.5 (8.1)</td>
<td>1.7 ± 0.8</td>
</tr>
<tr>
<td>PAN</td>
<td>12.2 (22.5)</td>
<td>3.0 ± 0.2</td>
</tr>
<tr>
<td>PASD</td>
<td>16.9 (24.8)</td>
<td>5.9 ± 1.5</td>
</tr>
<tr>
<td>PTLD</td>
<td>11.8 (19.3)</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>PNAN</td>
<td>6.8 (9.3)</td>
<td>1.4 ± 0.5</td>
</tr>
</tbody>
</table>

\(^a\) Specimens leached with acetone in Soxhlet extractor for 12 hours and then leached for 14 days with distilled water before subjected to decay test. Values are means of five specimens.

\(^b\) Values in parentheses are mmol/100g wood.

\(^c\) Values are means of five specimens ± standard error.

Table 3. Soil-block decay test (12 weeks) of sweetgum reacted with phosphoramides and inoculated with *Coriolus versicolor* \(^a\)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Weight retention (^b) (%)</th>
<th>Weight loss (^c) (%)</th>
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<tbody>
<tr>
<td>Control</td>
<td>37.5 ± 3.5</td>
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</tr>
<tr>
<td>DMF</td>
<td>32.0 ± 11.7</td>
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<tr>
<td>PPAM</td>
<td>6.3 (13.3)</td>
<td>2.4 ± 0.7</td>
</tr>
<tr>
<td>PBAM</td>
<td>6.0 (11.2)</td>
<td>2.0 ± 0.1</td>
</tr>
<tr>
<td>PHAM</td>
<td>3.8 (5.9)</td>
<td>2.0 ± 0.1</td>
</tr>
<tr>
<td>POAM</td>
<td>3.5 (4.7)</td>
<td>2.1 ± 0.1</td>
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<tr>
<td>PFAN</td>
<td>3.6 (5.6)</td>
<td>2.1 ± 0.5</td>
</tr>
<tr>
<td>PCAN</td>
<td>3.1 (4.5)</td>
<td>1.9 ± 0.5</td>
</tr>
<tr>
<td>PBAN</td>
<td>5.2 (6.3)</td>
<td>2.1 ± 0.5</td>
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<td>PTBAN</td>
<td>4.8 (3.5)</td>
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<td>PAN</td>
<td>2.8 (5.0)</td>
<td>2.1 ± 0.6 (^*)</td>
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<td>PASD</td>
<td>6.6 (9.9)</td>
<td>0.4 ± 0.1</td>
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<td>3.3 (5.2)</td>
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<td>PNAN</td>
<td>2.1 (2.9)</td>
<td>1.9 ± 0.5</td>
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\(^a\) Specimens leached with acetone in Soxhlet extractor for 12 hours and then leached for 14 days with distilled water before subjected to decay test. Values are means of five specimens.

\(^b\) Values in parentheses are mmol/100g wood.

\(^c\) Values are means of five specimens ± standard error.
Table 4  Analysis of DSC responses of reacted wood with 50 m mole per 100g wood retention of fire retardants under flowing nitrogen

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Peak of temperature (°C)</th>
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<tr>
<td></td>
<td>Endo</td>
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<tr>
<td>Control</td>
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<tr>
<td>DAP</td>
<td>193,216</td>
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<td>PBN</td>
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<td>PIAN</td>
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<td>PDBAN</td>
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<td>PBTAN</td>
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Table 5  DSC results of reacted wood with 50 mmole/100 g wood retention of fire retardants in air

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Onset temp (°C)</th>
<th>Peak temp (°C) 1st</th>
<th>Peak temp (°C) 2nd</th>
<th>Heat flow at peak (mcal/sec) 1st</th>
<th>Heat flow at peak (mcal/sec) 2nd</th>
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<tbody>
<tr>
<td>Control</td>
<td>200</td>
<td>339</td>
<td>496</td>
<td>5.7</td>
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<tr>
<td>DAP</td>
<td>207</td>
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<td>500</td>
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<td>3.2</td>
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<td>PPAM</td>
<td>170</td>
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<td>500</td>
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<td>341</td>
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Table 6  Heat of combustion (mcal/mg) from DSC of reacted wood with 50mmole/100g wood retention of fire retardants in air

<table>
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<th>2nd area (%)</th>
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<tbody>
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</tr>
<tr>
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<tr>
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<td>440.1 (40.0)</td>
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<td>531.8 (48.7)</td>
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<td>512.8 (48.2)</td>
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<td>512.1 (46.9)</td>
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Table 7  Thermal and flammability data from TGA and DTG curves of reacted wood with 50 mmole/100 g wood retention of fire retardants in nitrogen

<table>
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<tr>
<th>Specimen</th>
<th>Ti (°C)</th>
<th>Tmax (°C)</th>
<th>Max. Weight loss rate (%)</th>
<th>Weight loss (°C) 5%</th>
<th>Weight loss (°C) 50%</th>
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</table>
Table 8  Thermal and flammability data from TGA and DTG curves of reacted wood with 50 mmole/100 g wood retention of fire retardants in air

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Ti  (°C)</th>
<th>Tmax (°C)</th>
<th>Max. weight loss rate (%)</th>
<th>Weight loss at (°C) 5%</th>
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<th>Char yields at 600 °C</th>
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Figure 1  FTIR spectra of control wood fiber and wood fiber reacted with PBAM at 52% weight gain: (a) control; (b) reacted fiber
Figure 2 EDXA distribution map of pine wood reacted with PBAN at 50 mmole/100g wood retention, leached (1000X)
Figure 3 DSC curves in nitrogen of wood components: (a) southern pine; (b) cellulose; (c) xylan; (d) lignin.

Figure 4 DSC curves in nitrogen of reacted wood with 50 mmole/100 g wood retention of (a) PPAM; (b) PBAM; (c) PHAM; (d) POAM.

Figure 5 DSC curves in nitrogen of reacted wood with 50 mmole/100 g wood retention of (a) PFAN; (b) PCAN; (c) PBAN; (d) PIAN.
Figure 6 DSC curves in nitrogen of reacted wood with 50 mmole/100 g wood retention of (a) PDBAN; (b) PTBAN; (c) PAN; (d) PNAN.

Figure 7 DSC curves in nitrogen of reacted wood with 50 mmole/100 g wood retention of (a) PASD; (b) PTLD; (c) PDMPDA (d) PPDAM.
Chemical and structural modifications of wood–based materials are required to improve properties and to maximize end use performance of bio–based composite materials.