Thermochimica Acta, 188 (1991) 213–219
Elsevier Science Publishers B.V., Amsterdam

Thermogravimetry of wood reacted with hexamethylphosphorus triamide as a flame retardant treatment

W.D. Ellis

USDA Forest Service, Forest Products Laboratory [1], *One Gifford Pinchot Drive, Madison, WI 53705-2398 (USA)*

(Received 16 January 1991)

Abstract

Specimens of pine were reacted with hexamethylphosphorus triamide (HMPT) in dimethylformamide solutions. The specimens were evaluated using thermogravimetry for their potential fire resistance. Specimens reacted with HMPT had a temperature at maximum pyrolysis rate 113 °C lower than that of unreacted wood. There was 45.4% residual char after pyrolysis of reacted specimens that were water extracted, compared to 17.6% residual char from unreacted specimens. The amount of residual char and peak temperatures of HMPT-reacted specimens were indicative of an effective flame retardant and were essentially unchanged when specimens were extracted with water. Reacted specimens would not burn in a simple flame test.

INTRODUCTION

The use of inorganic salts to treat wood for flame retardancy can increase hygroscopicity and corrosivity of the treated wood [1–3]. Inorganic salts are not chemically bonded to the wood and are mostly water soluble; therefore, chemical blooming and chemical leaching can occur in wet conditions. Because of the characteristics of inorganic salts, their use as flame retardants has limitations. The amount of wood being treated for flame retardancy could be increased if more flame retardant treatments not adversely affected by moisture were available.

Some organophosphorus compounds have the potential of reacting with wood and thereby provide a flame retardant treatment that is not affected by moisture. These compounds would become a permanent part of the wood but would also be able to perform as flame retardants.

During pyrolysis wood will normally have the hemicellulose component decompose between 200 and 260 °C and the cellulose decompose from 240

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to 350 °C. Lignin decomposes over a broader temperature range, from 280 to 500 °C [4]. The presence of phosphorus changes the temperatures of decomposition of the constituents of wood. Phosphorus compounds are effective flame retardants because they change these thermal degradation processes in wood. They reduce the temperature at which pyrolysis occurs, reducing the amount of flammable volatiles formed and increasing the amount of residual char [5]. Phosphorus compounds also prevent glowing combustion of the wood [6]. Compounds that contain phosphorus have been used extensively for treating textiles, wood, and other materials for flame retardancy [7].

This research describes the potential of using hexamethylphosphorus triamide (HMPT), $[(CH_3)_2N]_3{-}P$, as a reactive flame retardant for wood. HMPT has been reacted with cotton cellulose to give a fabric containing up to 1.7% phosphorus and 0.5% nitrogen, with fair to excellent flame resistance [8]. Hexamethylphosphoramidate (HMPA), $[(CH_3)_2N]_3{-}P{=}O$, a compound very similar to HMPT, has also been reacted with cellulose to study the thermal degradation of the resulting cellulose phosphoramides [9]. This study with HMPA found that the temperature of maximum pyrolysis rate was 246 °C for specimens having 4.1% phosphorus (P) and 1.8% nitrogen (N) (N/P ratio 0.44) for a 24 h reaction at 80 °C.

EXPERIMENTAL METHODS

Specimens of pine were cut, 25 × 25 × 6 mm (radial by tangential by longitudinal), and oven-dried at 105 °C. Specimens were reacted in a 10% solution of HMPT in dimethylformamide (DMF) with 0.1% dimethylamine hydrochloride as a catalyst. The solution was put in a flask and maintained at 95 °C in a water bath. The reactants in the flask were protected with an atmosphere of nitrogen.

All specimens were put into the hot solution, then duplicate specimens were removed after 15, 30, 60, and 120 min. Immediately after reaction, specimens were rinsed with acetone, then water, followed by a final acetone rinse. Specimens were then oven-dried for 4 h at 105 °C and milled to pass a 40 mesh screen. Portions of the milled specimens were extracted for 24 h with water at room temperature. Specimens that were both extracted and not extracted were subjected to thermogravimetry, nitrogen analysis by a micro-Kjeldahl method, and phosphorus analysis by a modified vanadomolybdate method [10,11].

Thermogravimetry was chosen to investigate the effect of HMPT on pyrolysis, residual char formation, and the potential flame resistance of the reacted wood. A Perkin-Elmer TGS-2 [a] system was used. Specimens were

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TABLE 1

Phosphorus and nitrogen in water-extracted and non-extracted ponderosa pine reacted with HMPT

Reaction time (min)	Phosphorus (P) (%)		Nitrogen (N) (%)		N/P ratio	
	Not extracted	Extracted	Not extracted	Extracted	Not extracted	Extracted
15	4.76	4.14	2.13	1.50	0.48	0.36
30	5.45	4.90	2.39	1.87	0.44	0.38
60	5.68	5.39	2.42	1.92	0.43	0.36
120	7.21	6.28	2.86	2.20	0.40	0.35

pyrolyzed in a flow of nitrogen (40 ml min^{-1}). Pyrolysis temperatures were programmed from 40 to 600 °C at 20 °C min^{-1}. The weight remaining at 600 °C was measured and used to calculate the percentage of residual char. The temperatures at maximum rate of pyrolysis (peak temperatures) were recorded. Peak temperatures and amounts of residual char for specimens reacted with HMPT were compared to those of wood treated commercially with ammonium phosphate and an amino resin flame retardant.

Pine specimens, $7 \times 3 \times 140$ mm^3 (radial by tangential by longitudinal), were reacted for 2 h at 95 °C with HMPT. These specimens were used in a simple flame test. They were extracted for 4 days with continuously running water, oven-dried, and conditioned at 27 °C and 30% relative humidity before being tested. The specimens were held vertically above the flame of a small burner. After 30 s, the specimens were removed from the flame, and the time it continued to flame was measured.

These experimental methods were used to evaluate potential flame resistance. Larger tests such as the standard ASTM E 84 flame spread test [12] are not practical for early exploratory work because of the high cost of time, chemicals, and other materials involved.

RESULTS AND DISCUSSION

Phosphorus and nitrogen

Specimens not extracted had phosphorus contents from 4.8% to 7.2% for reaction times of 15–120 min. After extraction, the phosphorus content was 4.1–6.3% (Table 1). The amount of nitrogen in specimens not extracted was 2.1–2.9% for reaction times from 15 to 120 min. After extraction, these specimens had 1.5–2.2% nitrogen.

An N/P ratio of 0.45 on a weight basis represents one nitrogen per phosphorus, a situation that would exist if two of the dimethylamino groups were removed from the HMPT molecule during the reaction. This 0.45 ratio is close to the N/P ratios found in specimens not extracted. The ratios of extracted specimens indicate less than one nitrogen atom per phosphorus atom on the average in the wood. It seems that on the average more than two dimethylamino groups but not all three were removed during the

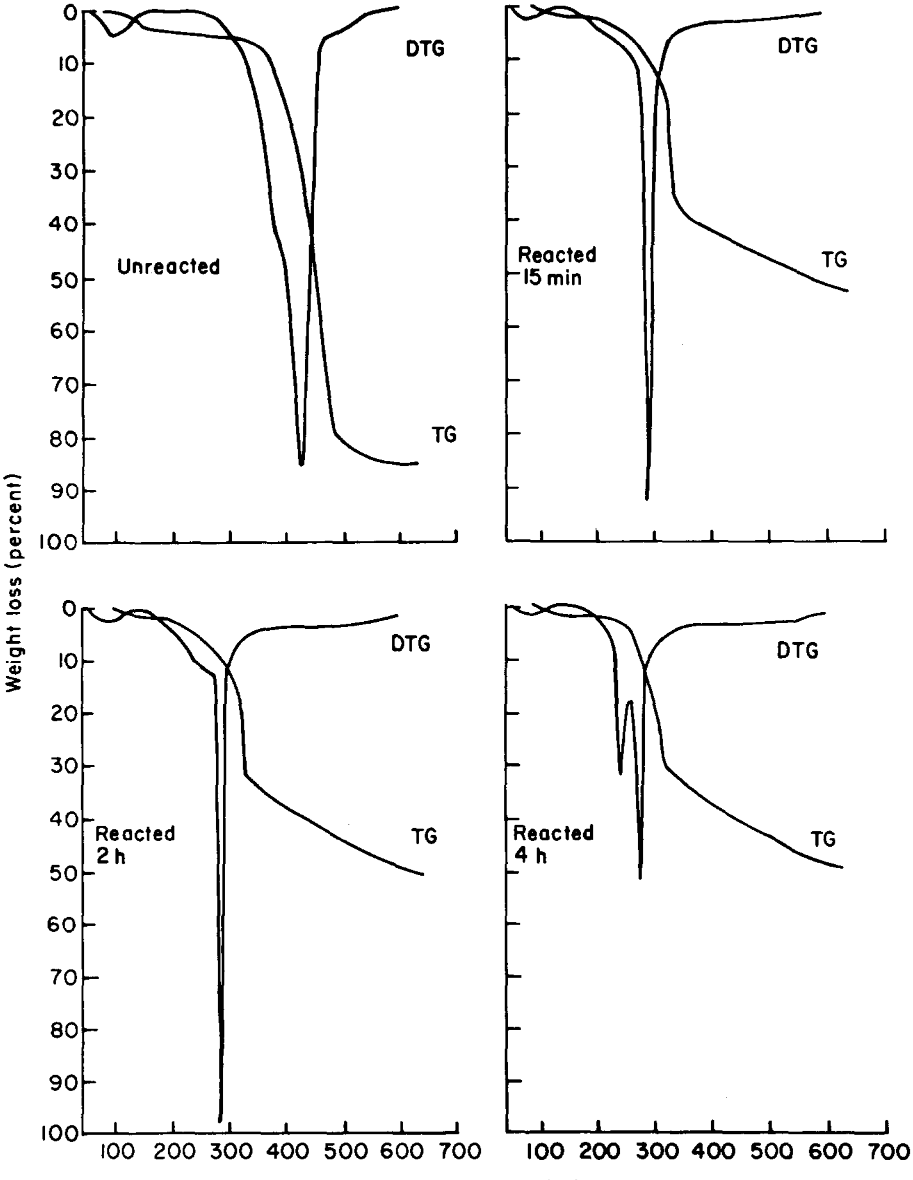

Fig. 1. Thermogravimetry (TG) and derivative thermogravimetry (DTG) curves of pine reacted with HMPT (ML90 5300).

reaction. The remaining dimethylamino groups apparently were not replaced during the water extraction of the specimens. There was some loss of nitrogen; the N/P ratio was 0.35–0.38 for all extracted specimens compared to 0.40–0.48 before extraction. The amounts of both phosphorus and nitrogen increased as the reaction times increased, and the amounts of each element were reduced by water extraction. However, this reduction of phosphorus and nitrogen was not sufficient to affect significantly the peak temperatures or the amounts of residual char found using thermogravimetry.

Thermogravimetry

Thermogravimetric (TG) curves of unreacted pine, and pine reacted for 15 min or 120 min are shown in Fig. 1. After the initial loss of moisture from 40 to 150 ° C, the unreacted specimen began to degrade and lose weight at about 240 ° C. The derivative thermogravimetric (DTG) curve was broad and showed a gradual loss of weight with a shoulder between 380 and 400 ° C with the rate of weight loss peaking at 405 ° C. The temperature exceeded 520 ° C before the weight loss of unreacted specimens neared completion.

Specimens reacted with HMPT showed differences in thermal degradation when compared to unreacted wood. Wood reacted for 15 min with HMPT showed initial loss of moisture in the same temperature range as unreacted wood; however, weight loss from the degradation of wood components began at about 140 ° C. This is 100 ° C lower than the initial temperature for degradation of unreacted wood. The thermal degradation of wood reacted for 15 min with HMPT was rapid and peaked at 292 ° C, 113 ° C lower than the peak temperature for unreacted wood. The peak temperature was lowered 8 ° C by increasing the reaction time from 15 to 120 min. More than 75% of the weight loss had occurred before the temperature reached 350 ° C. In contrast, unreacted wood had less than 25% of its weight loss occur before the temperature reached 350 ° C. A shoulder between 225 and 275 ° C was evident on the DTG curves of specimens reacted with HMPT. This shoulder became more distinct as reaction times increased. The nature of the thermal degradation of the wood changed as more HMPT reacted with the specimens. The degradation shifted to a lower temperature more notably for one or more constituents of the wood than for other constituents. Wood reacted for 4 h with HMPT had a DTG curve showing two distinct peaks rather than just a shoulder and a peak.

Unreacted wood specimens had 17.6% residual char compared to 48.6% residual char for specimens reacted for 120 min with HMPT. The amount of residual char found for extracted specimens went from 45.4% for a 15 min reaction to 50.1% for a 120 min reaction. Water extraction of milled specimens did not change the amount of residual char or the peak temperatures for HMPT-reacted specimens (Table 2).

TABLE 2

Residual char and temperature at maximum rate of pyrolysis (peak temperature) for pine reacted with HMPT

Reaction time (min)	Weight gain (%)	Residual char (%)		Peak temperature (° C)	
		Not extracted	Extracted [a]	Not extracted	Extracted
0	0	17.6	15.7	405	410
15	17.3	45.2	45.4	292	294
30	21.6	47.0	47.7	289	292
60	22.6	47.6	48.0	286	289
120	29.6	48.6	50.1	282	286

[a] Milled specimens extracted for 24 h with water at 24° C.

The increase in the amount of residual char and other changes in thermal degradation caused by HMPT are indicative of effective flame resistance for reacted specimens. Results indicate that short reaction times may give sufficient flame resistance, especially if wood flakes or fibers for reconstituted wood products are being treated. Wood treated with commercial flame retardants of ammonium phosphate or amino resin had comparable peak temperatures and amounts of residual char (Table 3).

Flame test

The small-scale flame test resulted in unreacted pine specimens ($7 \times 3 \times 140$ mm^3) burning until only a small amount of ash remained. Specimens reacted with HMPT and extracted for four days with running water did not continue to flame or have glowing combustion when removed from the burner flame. After burning the reacted specimens consisted of hard black char. Although the results of this simple flame test are encouraging, they do not necessarily reflect the behavior of a material in the standard ASTM E 84 flame spread test [12] used for regulation of building materials.

CONCLUSIONS

HMPT reacted with wood under the conditions used in these experiments, and the reacted wood had lower pyrolysis temperatures and increased amounts of residual char compared to unreacted wood. These changes in

TABLE 3

Comparison of HMPT-reacted wood to wood treated with commercial fire retardants

Treatment	Residual char (%)	Peak temperature (° C)
None	17.6	405
HMPT	48.6	282
Ammonium phosphate	48.4	285
Amino resin	46.1	289

thermal degradation indicate HMPT has potential as a reactive flame retardant for wood. Wood reacted with HMPT did not burn in a simple flame test, and this flame resistance was not lost when the wood was extracted with water. The HMPT compound may prove to be an effective flame retardant compound for use with wood. Further research is planned.

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