

# Thermal Properties of Wood Reacted with a Phosphorus Pentoxide–Amine System

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Received 30 December 2002; accepted 23 July 2003

**ABSTRACT:** The objective of this research was to improve the fire-retardant properties of wood in one treatment using a phosphorus pentoxide–amine system. Phosphorus pentoxide and 16 amines including alkyl, halophenyl, and phenyl amines were compounded in *N,N*-dimethylformamide and the resulting solutions containing phosphoramides were reacted with wood. The characteristics of phosphoramide-reacted wood were analyzed by FTIR, energy-dispersive X-ray analysis, and elemental analysis. Fire retardancy of phosphoramide-reacted woods was evaluated by DSC and thermogravimetric analysis (TGA). DSC demonstrated that

the modification can lower the onset of an endotherm and decrease the heat of combustion and heat flow. TGA showed that most of the phosphoramide-reacted woods had higher char yields than that of wood impregnated with diammonium phosphate. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2465–2481, 2004

**Key words:** phosphoramide; fire retardancy; differential scanning calorimetry (DSC); char yield; thermogravimetric analysis (TGA)

## INTRODUCTION

Wood has many inherently good properties, such as wide availability, renewability, a high strength to weight ratio, thermal and sound insulation, and low cost, which make it a preferred building material. However, wood also possesses several undesirable properties that impair its performance and limit its application. Flammability of wood is one of the most severe problems, and is one source of huge loss of life and property.

The flammability of wood can be reduced by treating wood with certain chemicals. Organophosphorus compounds exhibit varying levels of effectiveness in fire retardancy depending on their chemical structures and offer an attractive combination of chemical, physical, and mechanical properties. Phosphorus-based compounds containing nitrogen increased the flame-resistance properties, and synergistically reduced the required additive level of the individual compounds.<sup>1,2</sup> Phosphoramides containing P–N groups are better dehydration agents as well as phosphorylation catalysts for improving fire retardancy compared to phosphates.<sup>3</sup> Many reports reported that phosphoramide compounds alter thermal degradation, promote retention of phosphorus in the char residue, and in-

crease char after pyrolysis.<sup>3–9</sup> However, very little was found in the literature about the properties of phosphoramide-reacted wood.

The aims of this research were to develop new fire retardants and to investigate the influence of functional groups of phosphoramides including alkyl, halophenyl, and phenyl on fire retardancy.

## EXPERIMENTAL

### Materials

Phosphorus pentoxide (P) and 16 amines including alkyl [propylamine (PAM); butylamine (BAM); hexylamine (HAM); and octylamine (OAM)], halophenyl [4-fluoroaniline (FAN); 4-chloroaniline (CAN); 4-bromoaniline (BAN); 4-iodoaniline (IAN); 2,4-dibromoaniline (DBAN); and 2,4,6-tribromoaniline (TBAN)], and phenyl [aniline (AN); *p*-anisidine (ASD); *p*-toluidine (TLD); 4-nitroaniline (NAN); *N,N*-dimethyl 1,4-phenylene diamine (DMPDA); and 1,4-phenylene diamine (PDAM)] amines were applied in this research (Table I).

### Chemical modification of wood

Twenty-four loblolly pine samples (6.4 × 3.2 × 25.4 mm in radial, tangential, and longitudinal directions, respectively) 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 a

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TABLE I  
Chemicals Reacted with Wood Through Phosphorus Pentoxide and Amines System

Chemical	Structure	Molecular weight	Abbreviation
Phosphorus pentoxide	$P_2O_5$	141.94	P
Diammonium phosphate	$(NH_4)_2HPO_4$	132.06	DAP
Propylamine	$C_3H_7NH_2$	59.11	PAM
Butylamine	$C_4H_9NH_2$	73.14	BAM
Hexylamine	$C_6H_{13}NH_2$	101.19	HAM
Octylamine	$C_8H_{17}NH_2$	129.25	OAM
4-Fluoroaniline	$C_6H_4FNH_2$	111.12	FAN
4-Chloroaniline	$C_6H_4ClNH_2$	127.57	CAN
4-Bromoaniline	$C_6H_4BrNH_2$	172.03	BAN
4-Iodoaniline	$C_6H_4INH_2$	219.03	IAN
2,4-Dibromoaniline	$C_6H_3Br_2NH_2$	250.93	DBAN
2,4,6-Tribromoaniline	$C_6H_2Br_3NH_2$	329.83	TBAN
Aniline	$C_6H_5NH_2$	93.13	AN
<i>p</i> -Anisidine	$C_6H_4OCH_3NH_2$	123.16	ASD
<i>p</i> -Toludine	$C_6H_4CH_3NH_2$	107.16	TLD
4-Nitroaniline	$C_6H_4NO_2NH_2$	138.13	NAN
<i>N,N</i> -Dimethyl	$C_6H_4NC_2H_5NH_2$	136.20	DMPDA
1,4-Phenylene diamine	$C_6H_4N_2H_4$	108.14	PDAM

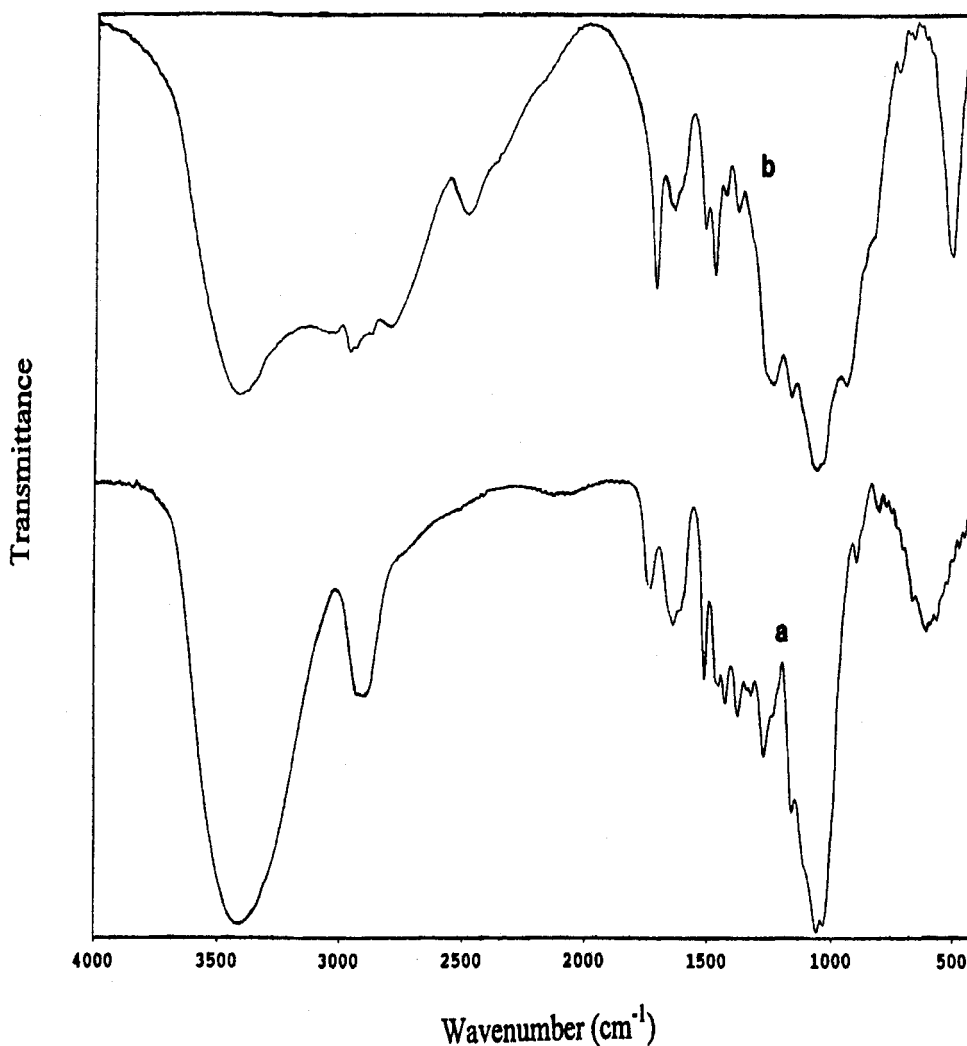
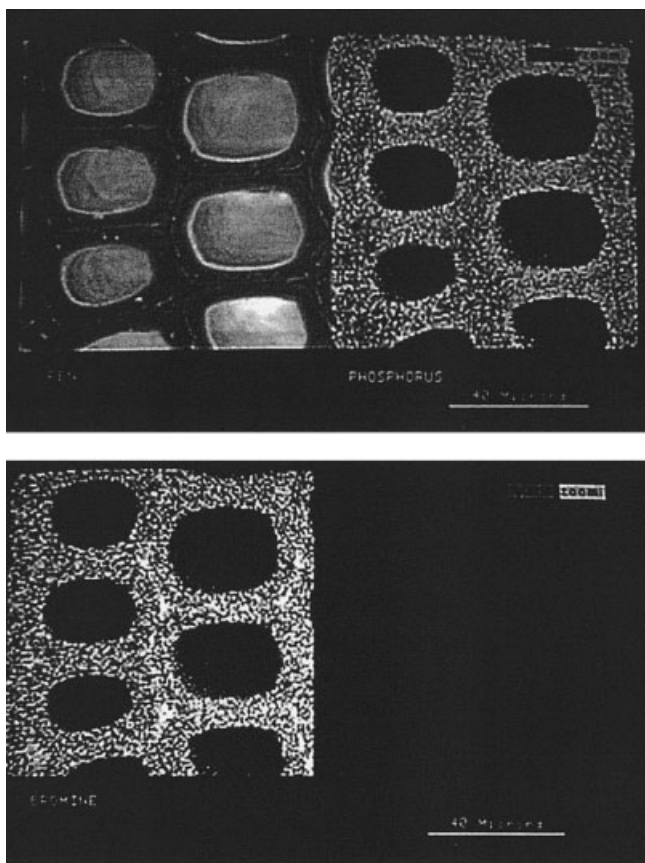


Figure 1 FTIR spectra of control wood fiber and wood fiber reacted with PBAM at 52% weight gain: (a) control; (b) reacted fiber.



**Figure 2** EDXA distribution map of pine wood reacted with PBAN at 50 mmol/100 g wood retention, leached ( $\times 1000$ ).

4-Å molecular sieve for more than 1 day). Phosphorus pentoxide, amine, and wood (based on 1-4-anhydroglucopyranose equivalent) in a molar ratio of 1 : 3 : 1 were added to the flask. The solution was maintained at 115°C for 24 h. During the 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.

#### Characterization of phosphoramidate-reacted wood

Bond formation between wood and phosphoramidates 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 (EDXA) 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.

#### Thermal analysis

##### Differential scanning calorimetry (DSC)

Samples of reacted wood (5 mg) with retention at 50 mmol/100 g wood were taken for the DSC experiments. The calorimetry curves were obtained with the samples enclosed in covered aluminum pans with an empty covered pan as the reference. All DSC thermograms were run under either nitrogen or air at a flow rate of 20 mL/min with a heating rate of 10°C/min from 40 to 600°C. This instrument monitored the differential heat flow of the sample and reference and then the appropriate enthalpy  $\Delta H$  was measured by integration. The instrument was calibrated for temperature and enthalpy response according to the melting point and heat of fusion of a pure indium standard.

##### Thermogravimetric analysis (TGA)

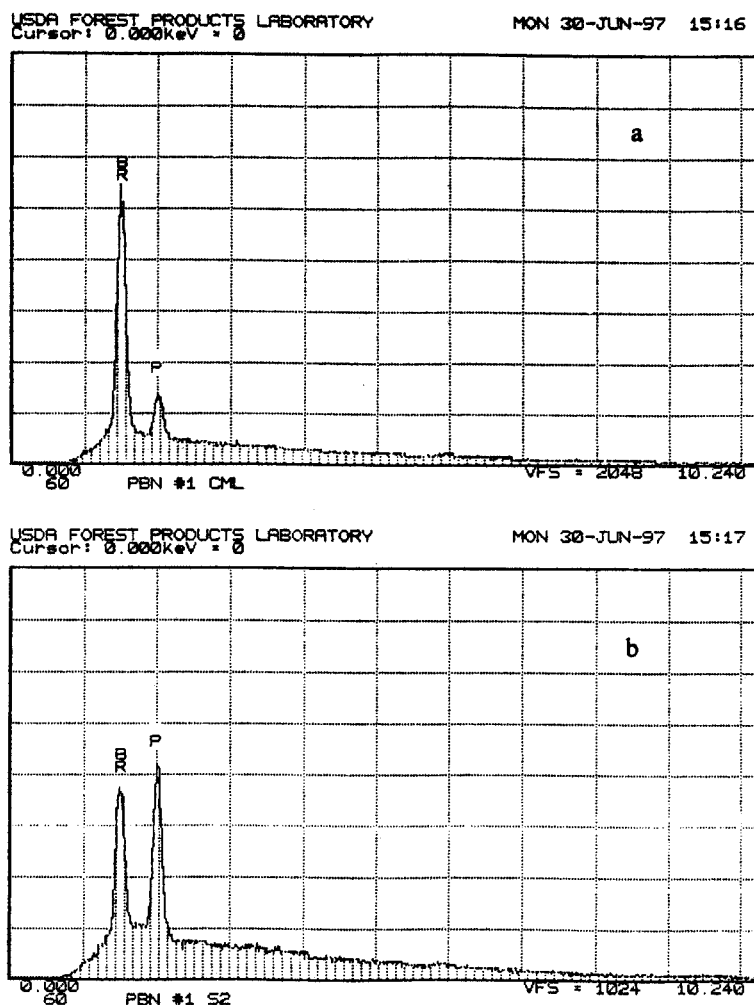
All TGA experiments were conducted on an Omnitherm TGA-1000 instrument. Derivative thermogravimetric analysis (DTG) provides a derivative form (rate of mass loss) of the thermogravimetric signal and was calculated by computer. The char residue, maximum temperature of pyrolysis, and rate of weight loss can be obtained from TGA and DTG. The particle size of specimens was reduced to pass a 100-mesh screen and 5 mg of the reacted wood with retention at 50 mmol/100 g wood of each tested in TGA under a nitrogen or air flow rate of 20 mL/min. The pyrolysis temperature was programmed from 40 to 600°C, and the percentage of char residue was calculated at 600°C.

## RESULTS AND DISCUSSION

#### Characterization of reacted wood

FTIR spectra of reacted wood with phosphorus pentoxide/butylamine at 52% chemical weight gain are shown in Figure 1. Bond formation between wood fiber and phosphoramidate was evidenced by the characteristic infrared absorptions of phosphoryl (P—O), P—OH, and P—N groups at 2480, 1240, and 926  $\text{cm}^{-1}$ , respectively.<sup>10</sup>

EDXA of monobromophenyl phosphoramidate-reacted wood with 12.8% chemical weight gain (50 mmol/100 g wood) showed that the bromine and phosphorus were present in the cell walls of reacted wood (Figs. 2 and 3). The results indicated that chemical bonds were formed as a result of the reaction of wood and phosphoramidate. The distribution of bromine in the middle lamella was higher than that of phosphorus, which suggested that these reactive chemicals were able to react preferably with lignin in wood. The distribution of bromine and phosphorus were the same in the  $S_2$  layer of cell walls. Evidence of bond formation between wood and butylphosphor-



**Figure 3** EDXA spectrum of pine wood reacted with PBAN at 50 mmoles/100 g wood retention, leached ( $\times 1000$ ): (a) middle lamella; (b) cell wall (S2).

amide at 52% chemical weight gain was also observed with 10% phosphorus and 3.5% nitrogen from elemental analysis (Table II).

#### DSC analysis

DSC thermograms for the pyrolysis of wood components and unreacted wood in nitrogen are shown in Figure 4. The results revealed that active pyrolysis occurred after the temperature approached 150°C.

Among all wood components, xylan showed the lowest thermal stability, starting to decompose at about 150°C. Lack of crystallinity may be one reason causing the lowest endothermic peak as observed at 197°C.<sup>11,12</sup> The DSC thermogram of cellulose showed that pyrolysis started at about 300°C with a large endothermic reaction (peak at 344°C), which was attributed to depolymerization, decomposition, and volatilization, followed by two large exothermic reactions (peaks at 380 and 425°C) attributed to flaming combustion and

**TABLE II**  
Phosphorus and Nitrogen Contents of Wood Fiber, Cellulose, and Lignin Reacted with PBAM

Specimen	Weight gain (%)	Phosphorus (%)	Nitrogen (%)	P/N (mole ratio)
Wood fiber	52.0	10.0	3.4	3:2
Cellulose	32.5	7.2	3.3	1:1
Lignin	10.5	2.9	2.6	1:2

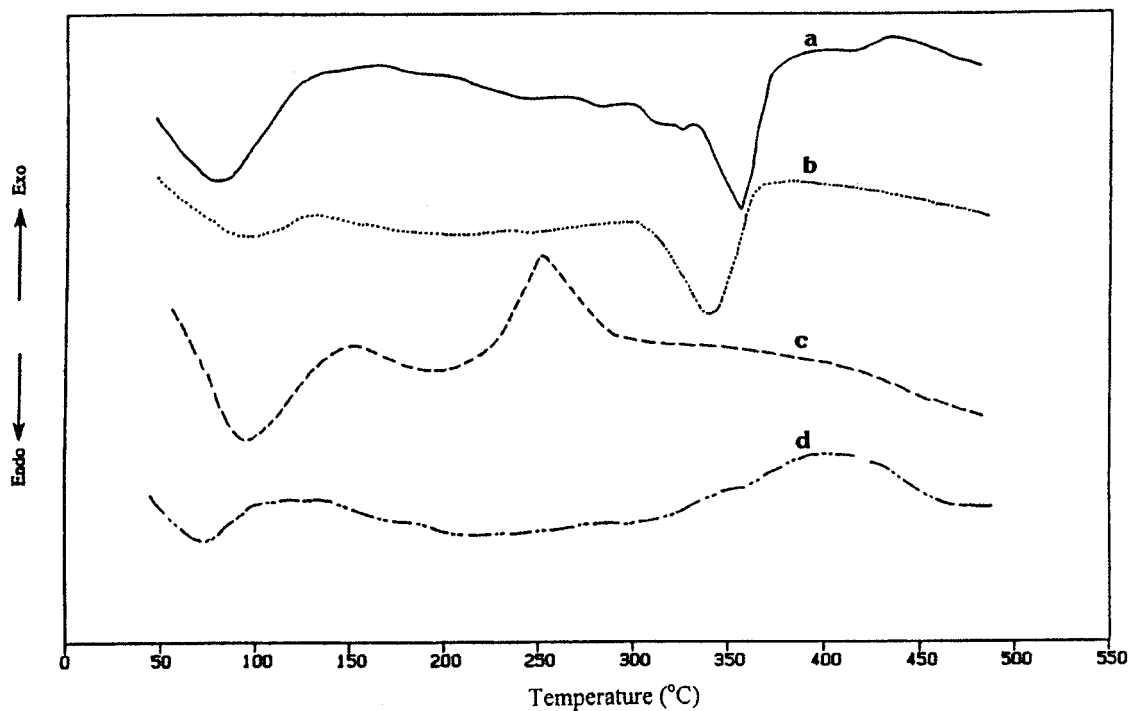


Figure 4 DSC curves in nitrogen of wood components: (a) wood; (b) cellulose; (c) xylan; (d) lignin.

char oxidation.<sup>13-15</sup> Pyrolysis of lignin was slow at temperature 200–350°C and its active pyrolysis was attributed to char oxidation from 350°C with exothermic reaction.<sup>13</sup>

Thermal degradation of wood is highly dependent on its components. Pyrolysis of wood began with an early decomposition of hemicelluloses, followed by an early stage of pyrolysis of lignin and then depolymer-

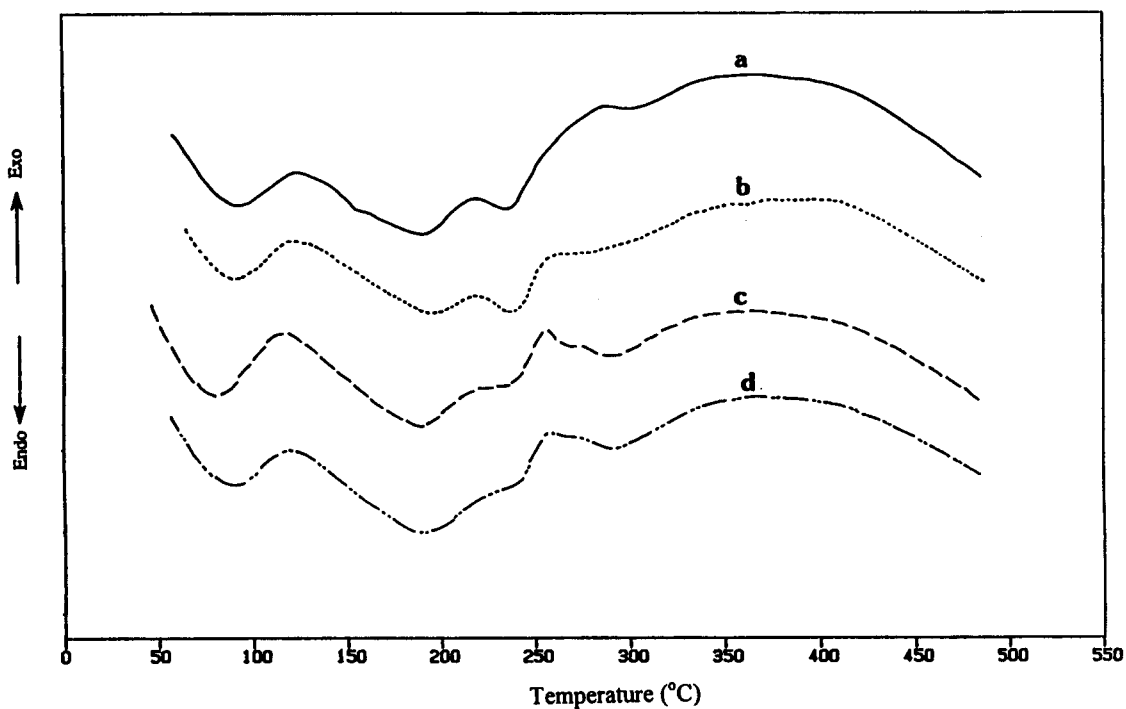


Figure 5 DSC curves in nitrogen of reacted wood with 50 mmol/100 g wood retention of (a) PPAM; (b) PBAM; (c) PHAM; (d) POAM.

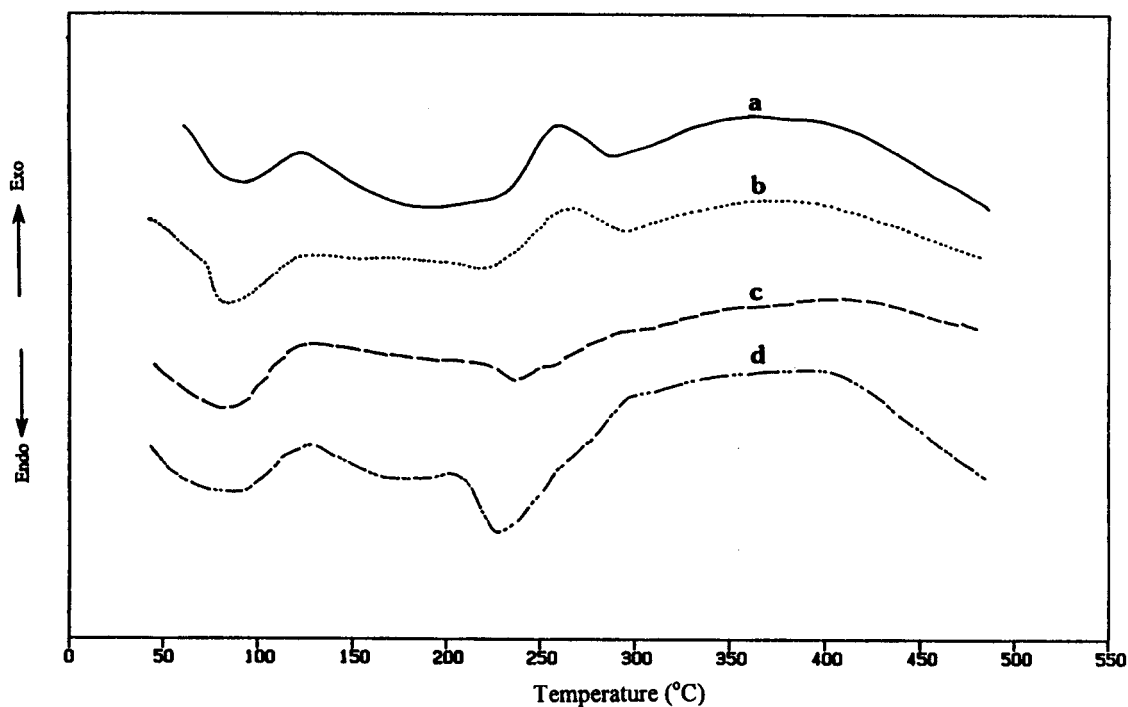


Figure 6 DSC curves in nitrogen of reacted wood with 50 mmol/100 g wood retention of (a) PFAN; (b) PCAN; (c) PBAN; (d) PIAN.

ization of cellulose followed by active flaming combustion and char oxidation.<sup>16,17</sup>

Dehydration and depolymerization were two dominant mechanisms in pyrolysis when wood reacted

with phosphoramides.<sup>18</sup> When wood was treated with fire retardants, the pyrolysis reactions were modified by dehydration during decomposition.<sup>13</sup> DSC curves of wood reacted with diammonium phosphate and

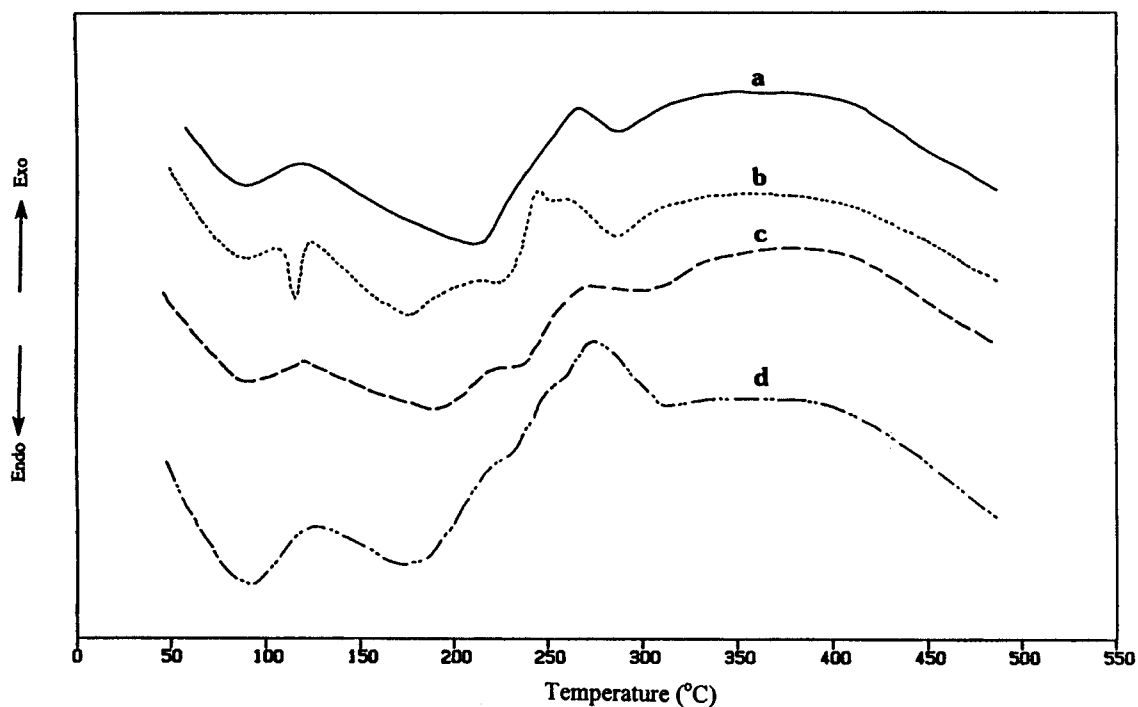


Figure 7 DSC curves in nitrogen of reacted wood with 50 mmol/100 g wood retention of (a) PDBAN; (b) PTBAN; (c) PAN; (d) PNAN.

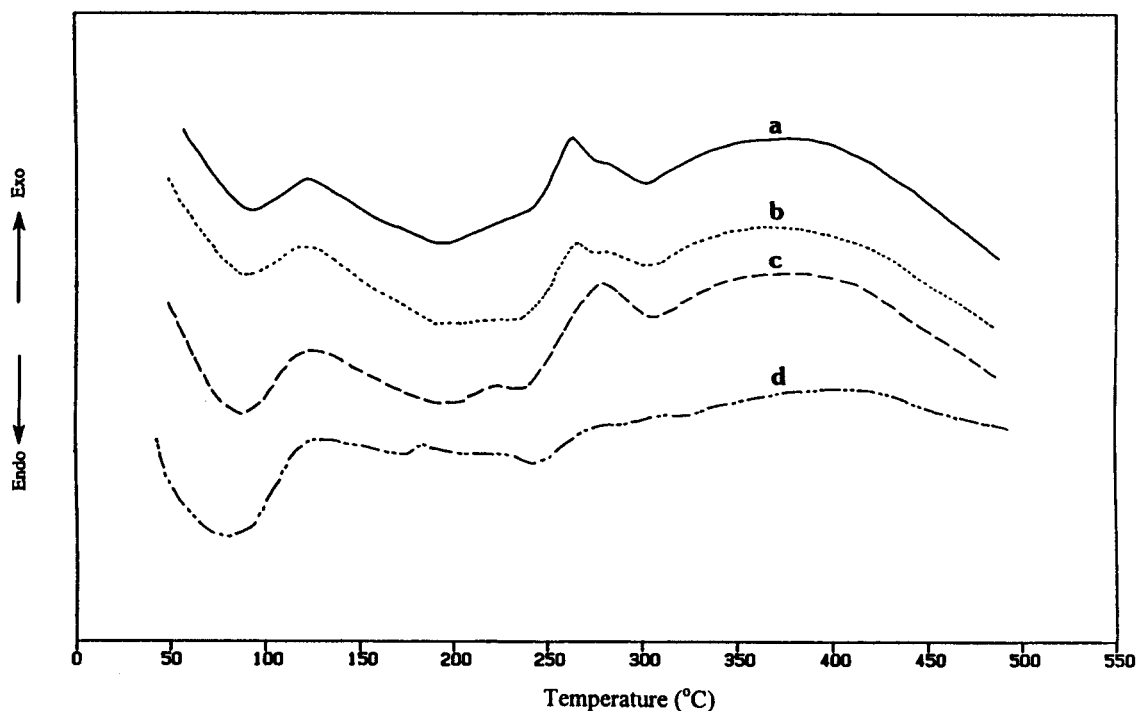


Figure 8 DSC curves in nitrogen of reacted wood with 50 mmol/100 g wood retention of (a) PASD; (b) PTLD; (c) PDMPDA; (d) PPDAM.

with phosphoramides are shown in Figures 5–8 and Table III. All DSC curves of reacted wood showed a similar trend of shifting the endothermic peak to 150–250°C. The reacted wood showed decreased temperatures for volatilization and condensation, as observed previously by Tang.<sup>16,17</sup> The lower volatilization and

condensation temperatures further promoted exothermic reactions to occur beyond approximately 250°C. Among all phosphoramide-reacted woods, pyrolysis of wood reacted with alkyl, fluoro, bromo, and chloro monosubstituted halophenyl phosphoramides were predominant by dehydration. However, the pyrolysis of iodo and nitro derivatives was predominant by depolymerization reaction. The advantages of pyrolysis that proceeded by dehydration were to decrease volatiles and rate of char oxidation and to increase char formation.<sup>13,14,19,20</sup>

TABLE III  
Analysis of DSC Responses of Reacted Wood with 50 mmol/100 g Wood Retention of Fire Retardants Under Flowing Nitrogen

Specimen	Peak of temperature (°C)	
	Endothermic	Exothermic
Control	362	—
DAP	193, 216	272
PPAM	190, 239	376
PBAM	197, 240	433
PHAM	191, 238	263, 370
POAM	195, 238	263, 380
PFAN	190, 233	265, 369
PCAN	156, 219	270, 393
PBAN	200, 241	306, 413
PIAN	173, 230	313, 377
PDBAN	214	271, 368
PTBAN	119, 180, 227	248, 363
PAN	193, 239	280, 407
PASD	200, 240	267, 379
PTLD	192, 238	269, 371
PNAN	177	275
PDMPDA	198, 238	283, 382
PPDAM	177, 245	320, 410

Thermal decomposition in air of phosphoramide-reacted woods showed that active combustion took place at 200°C and ended at 520°C with two major peaks at 339 and 496°C (Table IV and Figs. 9–13). Sekiguchi et al.<sup>15</sup> reported that the first peak was attributed to flaming combustion of the volatiles and the second peak was attributed to char oxidation. Temperature of combustion of unreacted wood was intensively concentrated in a narrow temperature range, and heat flow at the first and second peaks was produced at 5.7 and 5.5 mcal/s, respectively. In contrast, the combustion and heat release of reacted wood occurred earlier, and the rate of char oxidation was slower than that of unreacted wood. This indicates that all reacted wood was effective in glowing retardance, reducing heat flow to 3.2–4.7 mcal/s at the first peak, and to 3.2–4.1 mcal/s at the second peak, respectively. For the alkyl derivative, the increased alkyl

TABLE IV  
DSC Results in Air of Phosphoramidate-Reacted Woods  
with 50 mmol/100 g Wood Retention

Specimen	Peak temperature (°C)		Heat flow at peak (mcal/s)	
	1st	2nd	1st	2nd
Control	339	496	5.7	5.5
DAP	333	500	3.5	3.2
PPAM	333	500	3.6	3.2
PBAM	340	496	4.0	3.2
PHAM	335	505	3.7	3.4
POAM	336	505	3.8	3.3
PFAN	331	505	3.2	3.6
PCAN	334	503	3.3	3.9
PBAN	339	498	3.8	4.1
PIAN	338	493	3.7	3.7
PDBAN	333	500	3.4	3.9
PTBAN	322	507	3.0	3.2
PAN	341	500	3.9	4.0
PASD	345	499	3.6	3.8
PTLD	341	500	3.9	3.9
PNAN	333	497	3.7	4.1
PDMPDA	339	495	4.1	3.8
PPDAM	336	491	4.7	3.7

chain also increased flaming combustion. Among the halophenyl derivatives, bromine derivatives had better results to reduce the flaming combustion, and the tribromo derivative reduced flaming combustion and char oxidation even further.

Heat of combustion values derived from DSC thermograms of phosphoramidate-reacted woods are summarized in Table V. Heat released from the first exothermic peak attributed to flaming combustion was reduced significantly by phosphoramidate-reacted

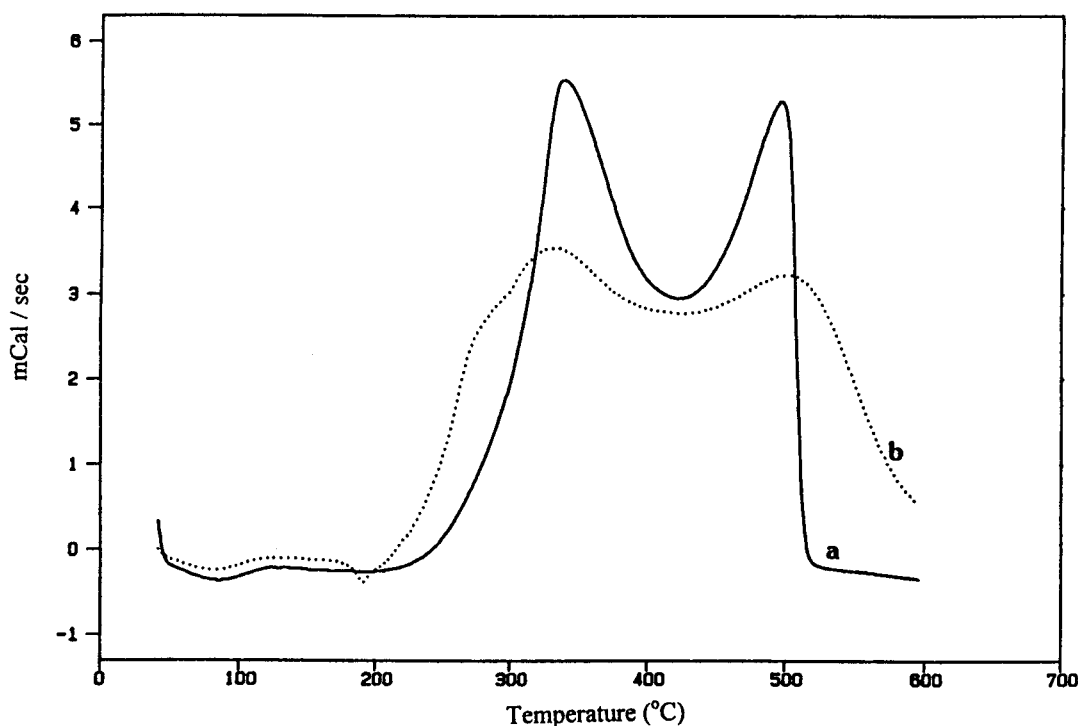


Figure 9 DSC curves in air of (a) unreacted wood and (b) wood reacted with diammonium phosphate at 50 mmol/100 g wood retention.



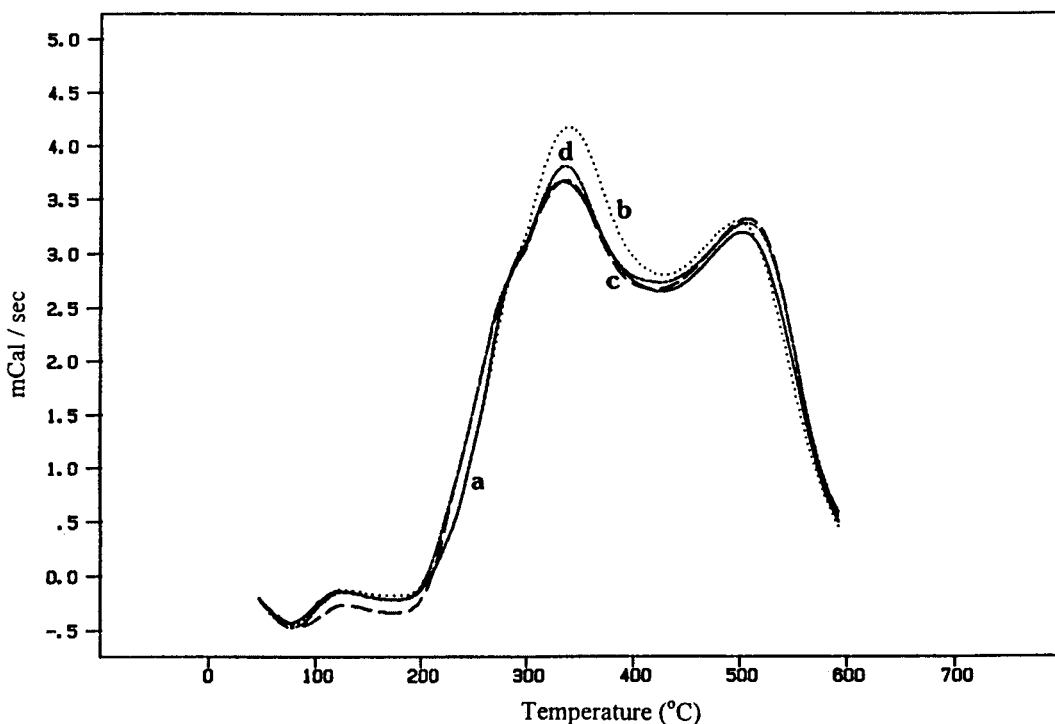


Figure 10 DSC curves in air of wood reacted with (a) PPAM; (b) PBAM; (c) PHAM; and (d) POAM at 50 mmol/100 g wood retention.

woods (490–675 mcal/mg) compared to that of unreacted wood (694 mcal/mg). Among all reacted woods, the results revealed that halophenyl phosphoramides

released less heat (490–580 mcal/mg), which could be attributed to free-radical trapping effects in air by halogen elements. Comparing heat release from the

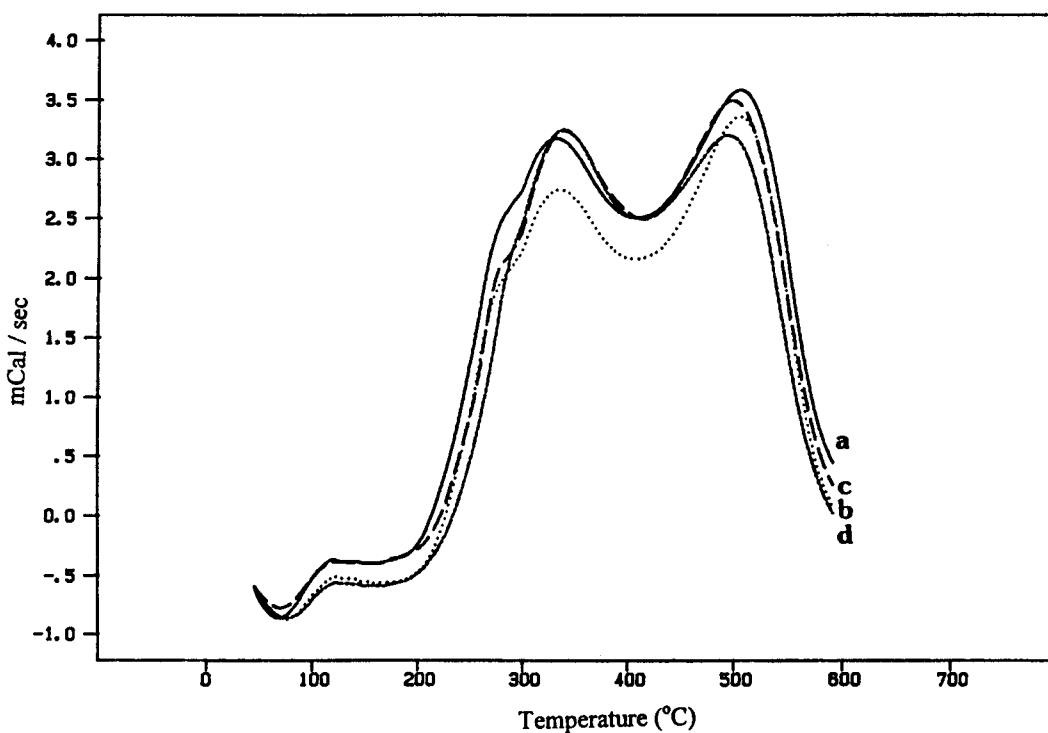
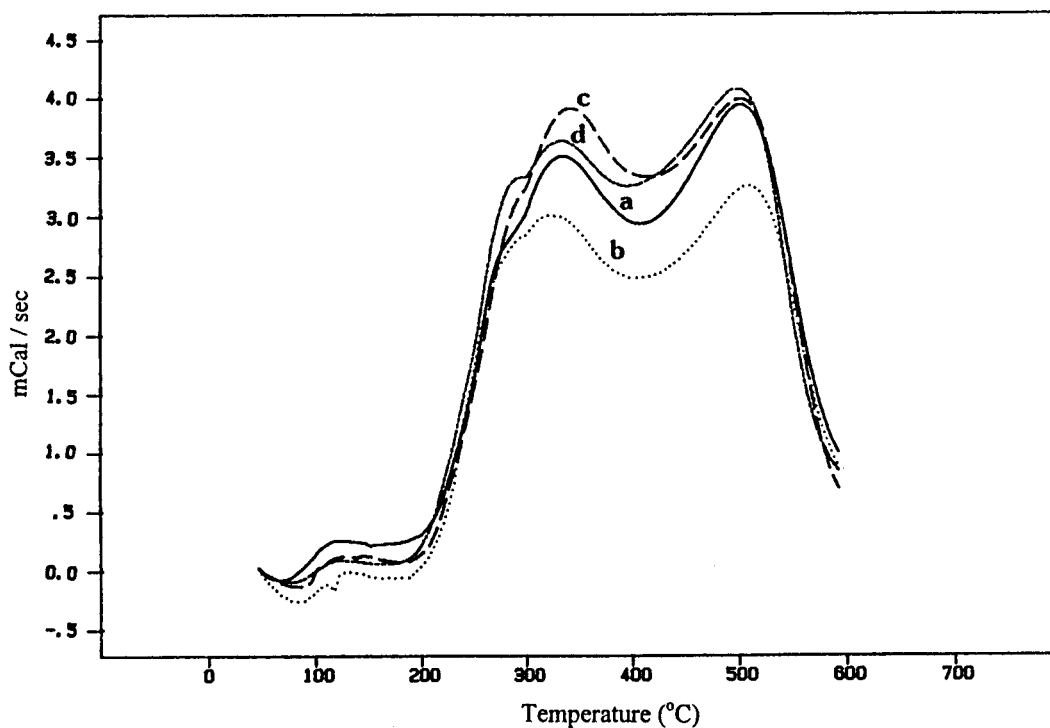


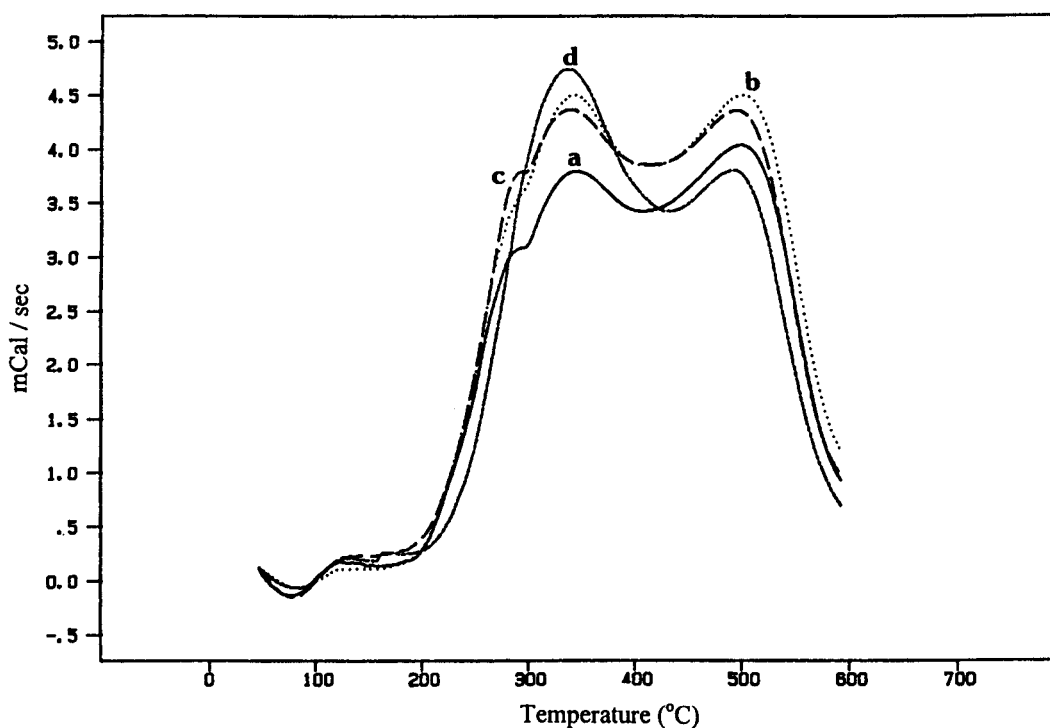
Figure 11 DSC curves in air of wood reacted with (a) PFAN; (b) PCAN; (c) PBAN; and (d) PIAN at 50 mmol/100 g wood retention.



**Figure 12** DSC curves in air of wood reacted with (a) PDBAN; (b) PTBAN; (c) PAN; and (d) PNAN at 50 mmol/100 g wood retention.

second peak area, wood reacted with alkyl phosphoramides released less heat than those with phenyl or with halophenyl phosphoramides. It was suggested

that char formation from alkyl phosphoramides could be more oxygenated than those of halophenyl and phenyl phosphoramides. Thus, alkyl phosphoramide-



**Figure 13** DSC curves in air of wood reacted with (a) PASD; (b) PTLD; (c) PDMPDA; and (d) PPDAM at 50 mmol/100 g wood retention.

**TABLE V**  
**Heat of Combustion in Air from DSC of Phosphoramidate-Reacted Woods**  
**with 50 mmol/100 g Wood Retention**

Specimen	Enthalpy, $-\Delta H$ (mcal/mg)		
	Total	1st area (%)	2nd area (%)
Control	1152	694 (60)	458 (40)
DAP	1059	627 (59)	432 (41)
PPAM	1079	639 (59)	440 (41)
PBAM	1102	667 (61)	435 (39)
PHAM	1090	649 (60)	441 (40)
POAM	1087	652 (60)	435 (40)
PFAN	1092	560 (51)	532 (49)
PCAN	1050	515 (49)	535 (51)
PBAN	1064	551 (52)	513 (48)
PIAN	1092	580 (53)	512 (47)
PDBAN	993	498 (50)	495 (50)
PTBAN	927	490 (53)	437 (47)
PAN	1159	626 (54)	533 (46)
PASD	1129	581 (51)	548 (49)
PTLD	1259	675 (54)	584 (46)
PNAN	1127	557 (49)	570 (51)
PDMPDA	1222	672 (55)	550 (45)
PPDAM	1154	734 (64)	420 (36)

reacted wood was attributed to more heat released in the first peak area and less heat released in the second peak area. Heat release from combustion at the first and second peak areas was significantly influenced by the nature of the treatment chemicals.

**Thermogravimetric analysis**

Data of TGA and DTG curves in nitrogen of unreacted wood and reacted woods are shown in Figure 14.

Among wood components, cellulose had the highest threshold temperature for active pyrolysis at 283°C, the highest weight loss rate at 1.43%, and the lowest char yield of 13.5% at 600°C. Cellulose causes and feeds more flaming combustion than any other wood component, as observed by Shafizadeh.<sup>15</sup> Thus cellulose could be the main component of wood responsible for producing flammable gas.<sup>15-17</sup> The effect of fire retardants on TGA pyrolysis curves of reacted woods is shown in Figures 15-18 and Table VI. TGA curves

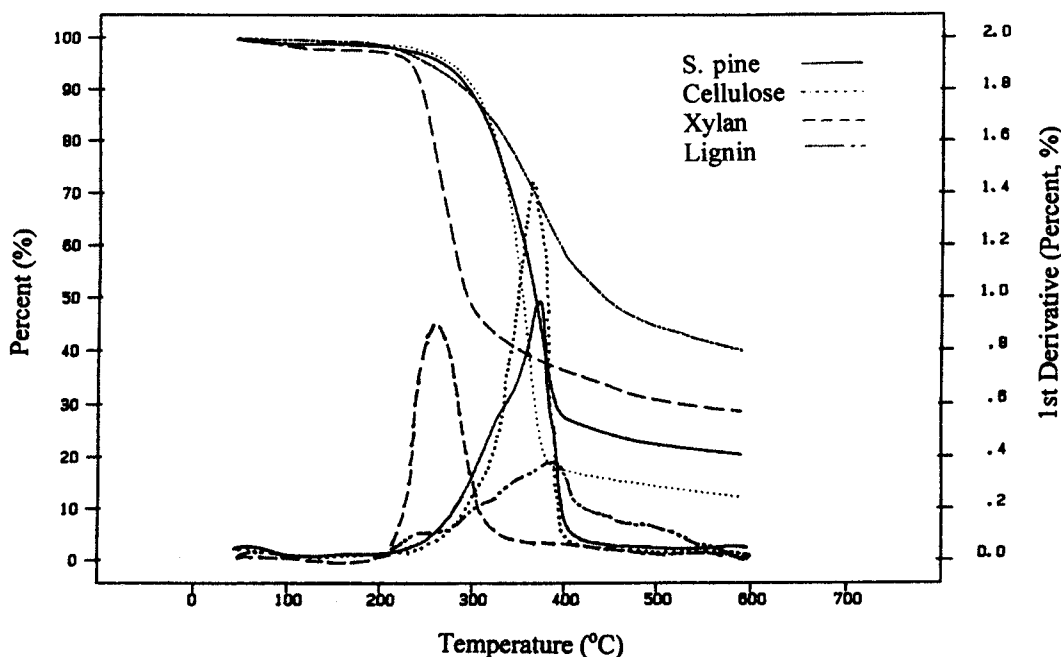


Figure 14 TGA and DTG curves in nitrogen of wood, cellulose, xylan, and lignin.

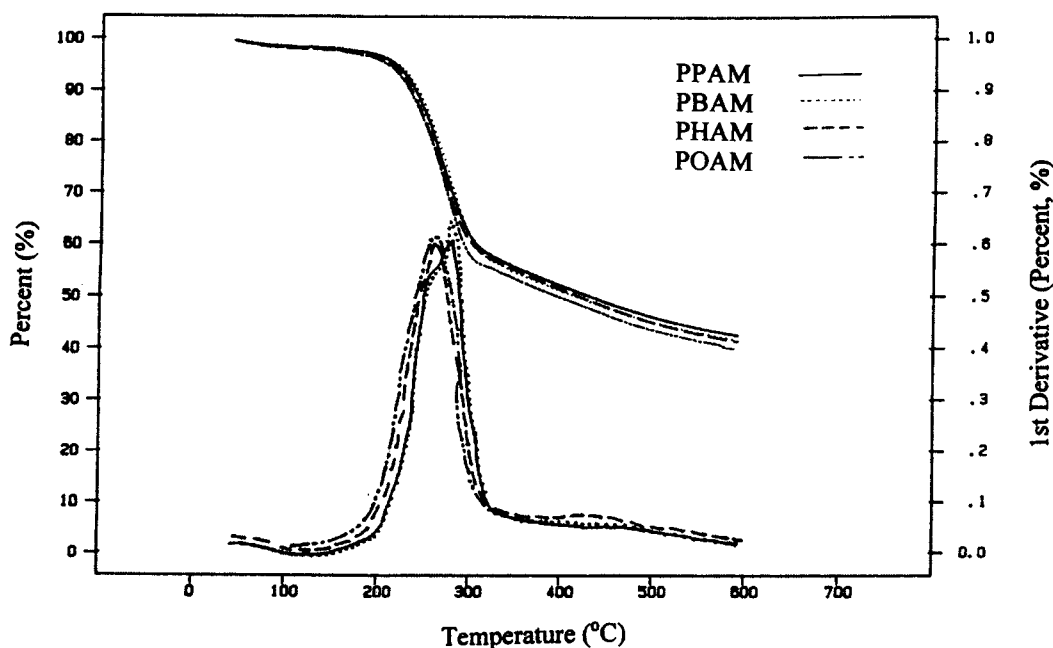


Figure 15 TGA and DTG curves in nitrogen of wood reacted with 50 mmol/100 g wood retention of PPAM, PBAM, PHAM, and POAM.

showed that temperatures corresponding to the initial weight loss of reacted woods were decreased from 266°C for unreacted wood to a range of 201 to 231°C. Most of the phosphoramidate-reacted woods in nitrogen at 600°C gave higher char yields of 40.4–44.7% than those of wood impregnated with diammonium phosphate of 40.4% and unreacted wood of 20.1%.

Also, temperatures corresponding to the maximum peak in DTG dramatically decreased to 257–304°C for reacted woods compared to 377°C for unreacted wood. In addition, maximum weight loss rates were 0.37–0.65% for reacted wood and 0.97% for unreacted wood. Wood reacted with PNAN exerted the best fire-retardancy effect on wood with the lowest weight

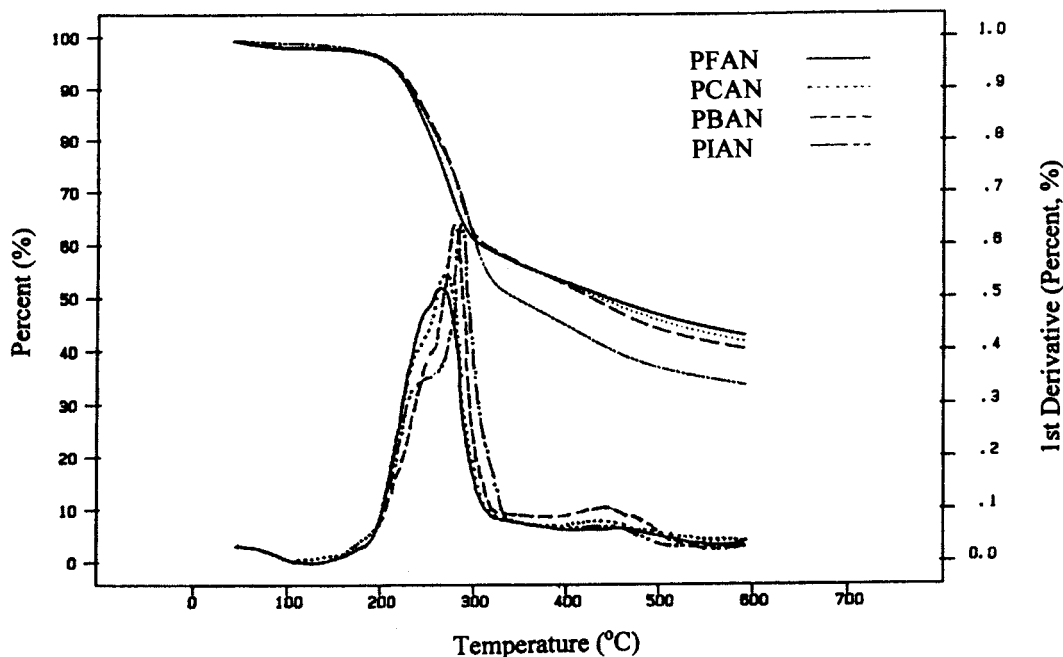


Figure 16 TGA and DTG curves in nitrogen of wood reacted with 50 mmol/100 g wood retention of PFAN, PCAN, PBAN, and PIAN.

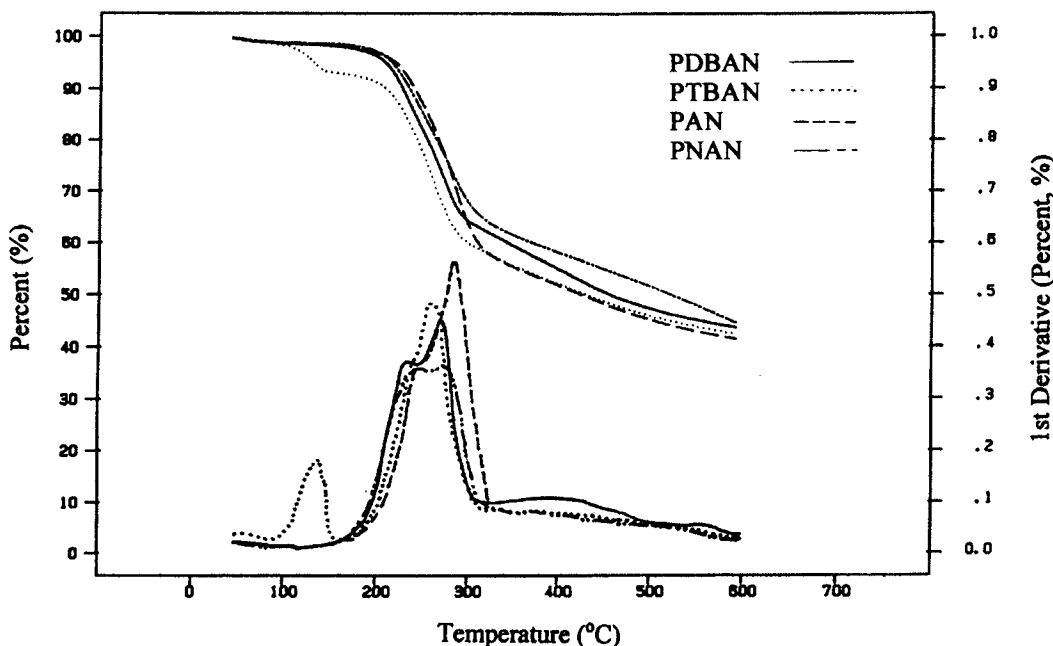


Figure 17 TGA and DTG curves in nitrogen of wood reacted with 50 mmol/100 g wood retention of PDBAN, PTBAN, PAN, and PNAN.

loss rate of 0.37% and the highest char residue of 44.7%. Thus phosphoramidate accelerated the onset of the rapid weight loss stage but lowered its peak rate. All of these data indicate that phosphoramidate can improve the fire retardancy of wood by lowering its weight loss rate and increasing its char yield.

The TGA and DTG tendency of the reacted woods in oxidizing atmosphere was basically similar to those found in nitrogen. However, char produced in an oxidizing atmosphere after the main weight loss has occurred can be further oxidized by oxygen. Data of TGA and DTG curves of wood components and both

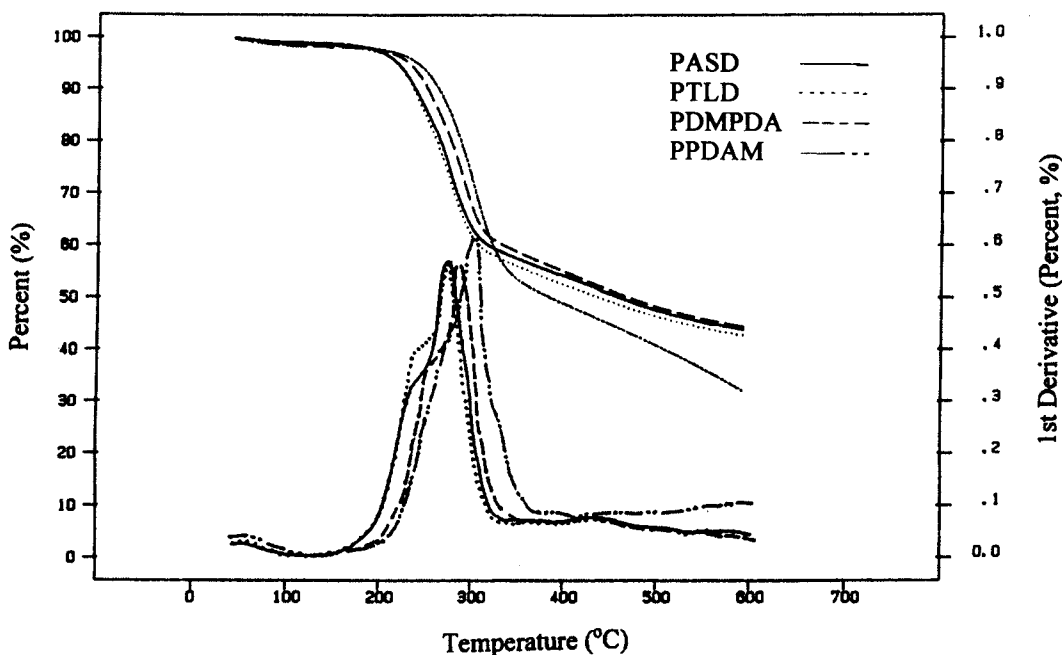


Figure 18 TGA and DTG curves in nitrogen of wood reacted with 50 mmol/100 g wood retention of PASD, PTLD, PDMPDA, and PPDAM.

TABLE VI  
Thermal and Flammability Data in Nitrogen of TGA and DTG Curves from  
Phosphoramidate-Reacted Woods with 50 mmol/100 g Wood Retention

Specimen	$T_i$ (°C)	$T_{max}$ (°C)	Max. weight loss rate (%)	Char yield at 600°C
Control	266	377	0.97	20.1
DAP	206	281	0.65	40.4
PPAM	217	266	0.56	42.4
PBAM	218	280	0.58	41.4
PHAM	211	268	0.57	41.2
POAM	214	268	0.58	40.4
PFAN	210	272	0.52	42.7
PCAN	208	275	0.52	41.6
PBAN	211	282	0.63	41.2
PIAN	215	295	0.62	33.9
PDBAN	201	273	0.44	43.5
PTBAN	201	257	0.49	42.3
PAN	211	284	0.56	41.4
PASD	212	277	0.57	43.8
PTLD	210	279	0.58	42.7
PNAN	209	281	0.37	44.7
PDMPDA	222	290	0.57	44.3
PPDAM	231	304	0.64	32.0

unreacted and reacted woods are shown in Figures 19–23 and Table VII. All tested materials, including wood components and wood, whether reacted or not, underwent rapid weight loss by evaporation of their pyrolysis products. The fast weight loss was superimposed upon and followed by a slower weight loss through the oxidation of charred residues. Meanwhile, DTG also showed two peaks like those in DSC. The first peak corresponded to the rate of weight loss resulting from both the evaporation of the volatiles

and the almost simultaneous oxidation of the aliphatic components of the char. The second peak showed the rate of weight loss caused by the oxidation of aromatic components of the char.<sup>15,20</sup>

In air, the initial weight loss of wood components, wood, and reacted wood occurred at temperature lower than in nitrogen. When unreacted wood was burned in air, oxygen accelerated weight loss, shifting the maximum peak to lower temperatures. This resulted in a higher weight loss rate of 1.24%, and max-

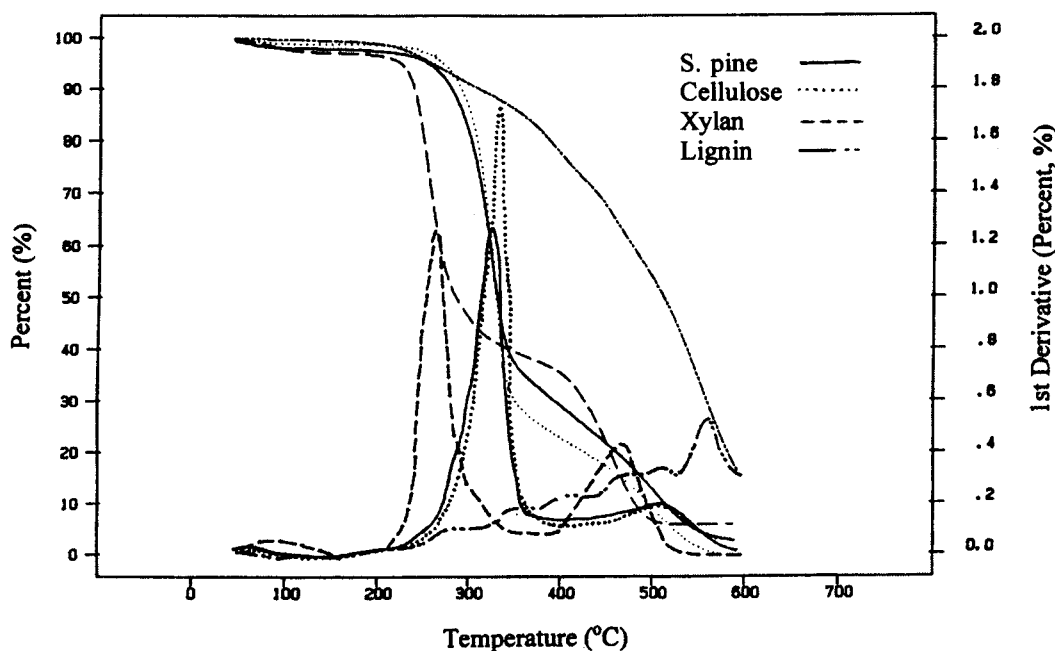


Figure 19 TGA and DTG curves in air of wood, cellulose, xylan, and lignin.

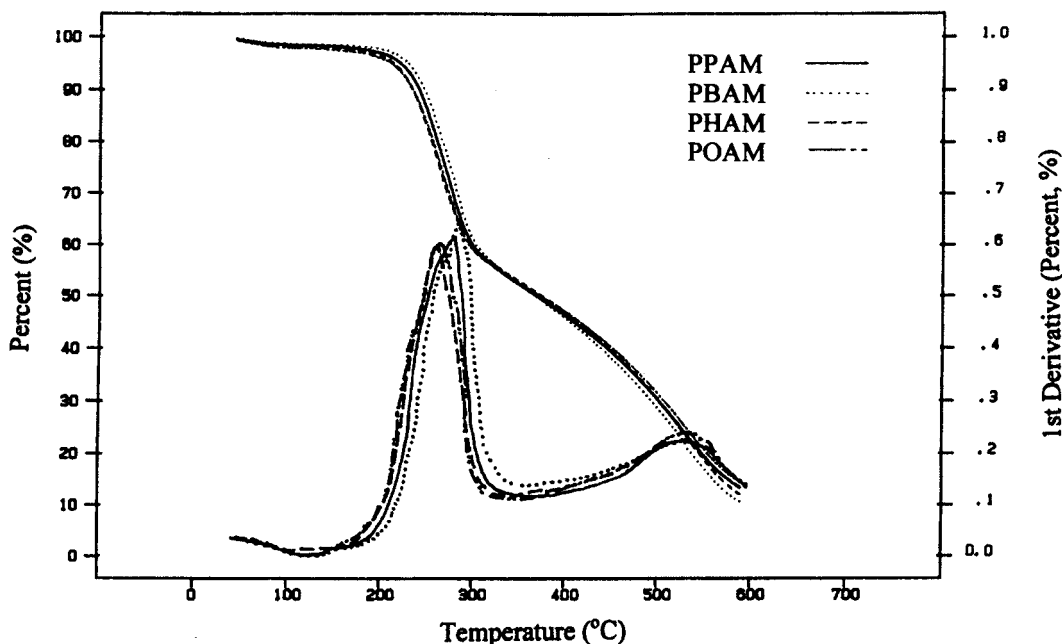


Figure 20 TGA and DTG curves in air of wood reacted with 50 mmol/100 g wood retention of PPAM, PBAM, PHAM, and POAM.

imum peak at 327°C and also produced lower char residue (2.7%) at 600°C compared to that burned in nitrogen. The fire retardancy of reacted wood in air could be improved by reacting with phosphoramidate. The results of phosphoramidate-reated woods from TGA and DTG in air at 600°C revealed that most of the reacted woods preserved higher char yields of 11.1–

17.7% than that of unreacted wood of 2.7%. Also, maximum weight loss rates of first peak in DTG curves were 0.42–0.70% for reacted wood and 1.24% for unreacted wood. By comparing fire retardancy of wood reacted with diammonium phosphate or phosphoramidates when burned in air, all phosphoramidate treatments except that with PIAN or PPDAM, showed

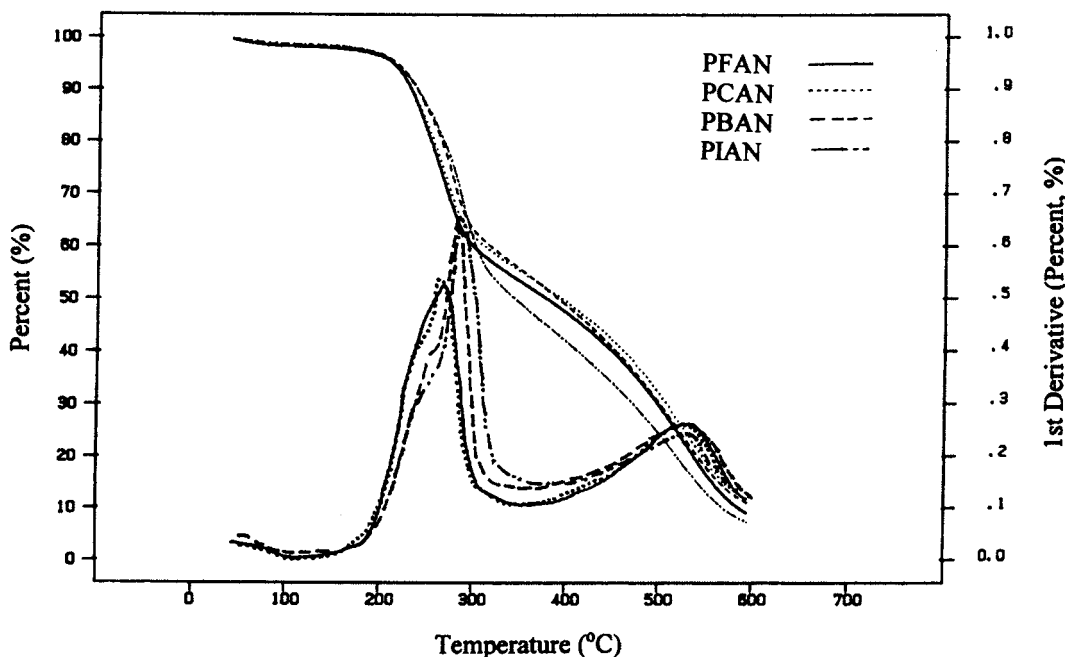


Figure 21 TGA and DTG curves in air of wood reacted with 50 mmol/100 g wood retention of PFAN, PCAN, PBAN, and PIAN.

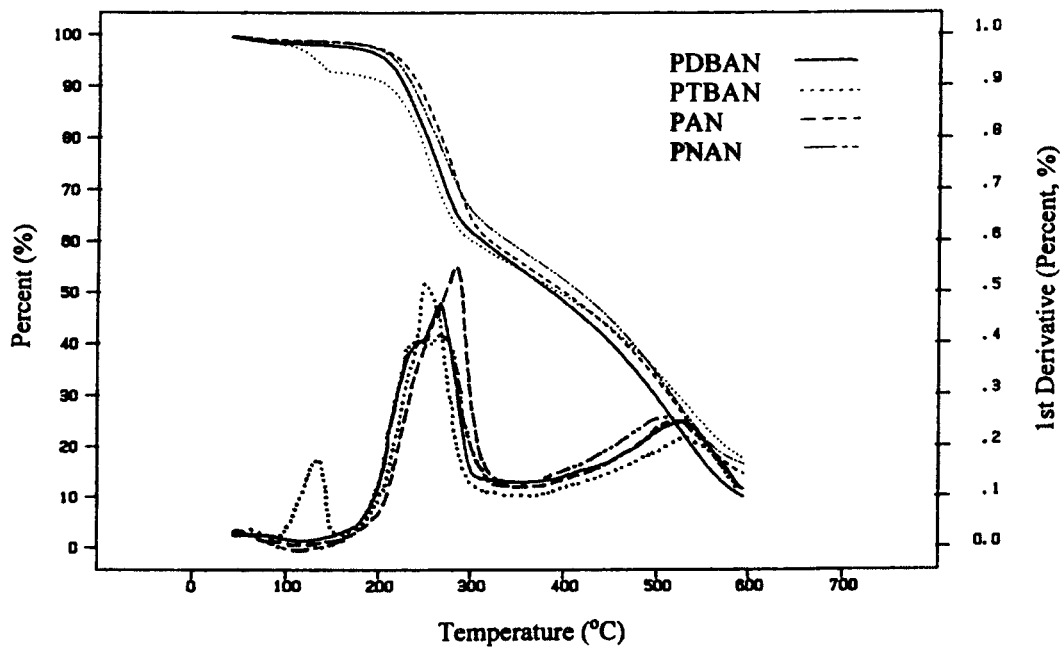


Figure 22 TGA and DTG curves in air of wood reacted with 50 mmol/100 g wood retention of PDBAN, PTBAN, PAN, and PNAN.

greater char residue than that with diammonium phosphate. Among all phosphoramidate treatments, wood reacted with either PTBAN, PDBAN, or PNAN resulted in higher char residue, indicating that better fire retardancy can be achieved by adding any one of these three chemicals. Phosphoramidate accelerated the onset of the rapid weight loss stage, lowered its peak rate, and improved

the fire retardancy of wood by lowering its weight loss rate and increasing its char yield.

## CONCLUSIONS

Phosphoramidates prepared *in situ* by reacting phosphorus pentoxide with amines were able to react with

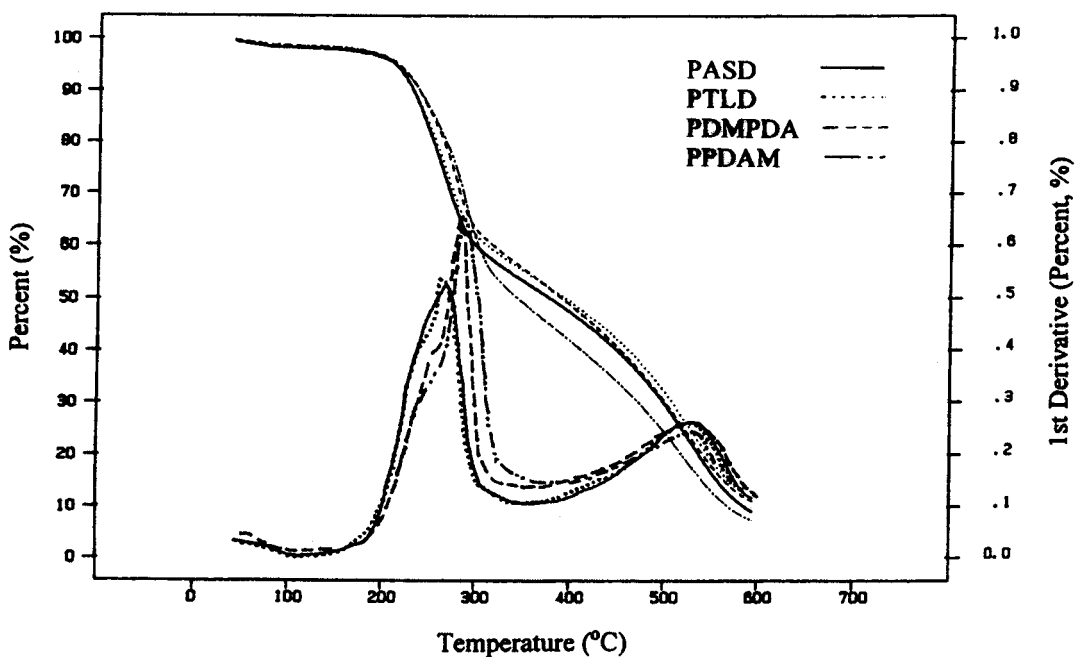


Figure 23 TGA and DTG curves in air of wood reacted with 50 mmol/100 g wood retention of PASD, PTLD, PDMPDA, and PPDAM.



**TABLE VII**  
**Thermal and Flammability Data in Air of TGA and DTG Curves from Phosphoramidate-Reacted Woods with 50 mmol/100 g Wood Retention**

Specimen	$T_i$ (°C)	$T_{max}$ (°C)		Max. weight loss rate (%)		Char yield at 600°C
		1st	2nd	1st	2nd	
Control	255	326	507	1.24	0.21	2.7
DAP	200	272	527	0.62	0.22	11.1
PPAM	213	279	531	0.60	0.22	12.2
PBAM	214	281	524	0.65	0.23	11.2
PHAM	210	261	530	0.57	0.23	12.9
POAM	205	266	530	0.58	0.23	12.4
PFAN	205	267	529	0.52	0.26	12.9
PCAN	204	268	530	0.54	0.26	12.2
PBAN	205	277	521	0.62	0.25	12.3
PIAN	210	287	519	0.66	0.24	7.7
PDBAN	197	266	523	0.49	0.25	14.8
PTBAN	199	253	530	0.51	0.21	17.7
PAN	204	281	525	0.55	0.25	12.0
PASD	204	267	525	0.55	0.24	13.9
PTLD	206	272	526	0.56	0.25	11.5
PNAN	200	273	516	0.42	0.25	16.6
PDMPDA	220	282	521	0.59	0.26	13.8
PPDAM	228	293	520	0.70	0.24	8.5

wood. Chemical bonds were formed between phosphoramidate and wood components as observed by FTIR, EDXA, and elemental analysis, and bonding was affected by the chemical nature of phosphoramidate. Phosphoramidate altered the pyrolysis or charring degradation of carbohydrates in reacted wood by lowering the onset temperature for decomposition and by decreasing the formation of volatile combustibles through promotion of higher char yields as shown by thermal analysis of DSC, TGA, and DTG thermograms. Increased char yields and lowered weight loss rates of phosphoramidate-reacted wood were achieved.

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