

Synthesis and Evaluation of Borates derived from Boric Acid for Fire and Decay Protections

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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) can only protect wood from decay. Dual protections of wood against decay and fire or decay and UV if achievable are more desirable. Many phosphorus and boron compounds possess fire retardant and decay resistant properties. In our previous investigation, we found that wood reacted with phosphoramides produced *in situ* by reacting phosphorus pentoxide with amines was able to protect wood from fungal decay and fire, and the phosphoramides that bonded to wood were resistant to water leaching. The purposes of this research were to synthesize leach resistant borates and to evaluate their fungal decay resistance and thermal properties.

EXPERIMENTAL

Synthesis and Characterization

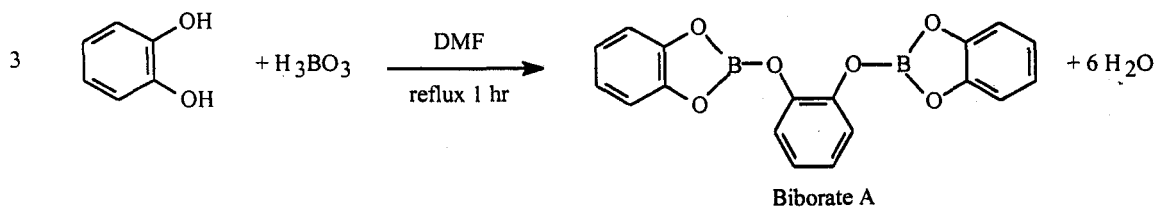


Figure 1. Synthesis of biborate A

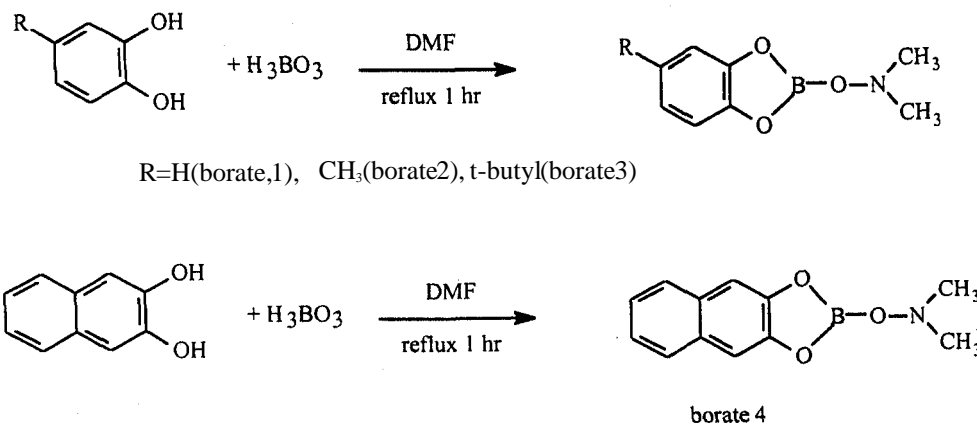


Figure 2. Synthesis of borates

We were trying to synthesize a diborate A (Figure 1) by refluxing stoichiometric amount of boric acid with catechol in N,N-dimethyl formamide(DMF). However, the product after one hour reflux was not a diborate but a borate 1(Figure 2). The borate was formed as a result of condensation of catechol borate with solvent DMF.

Other aromatic diols including 4-methyl catechol, 4-t-butyl catechol and 2,3-dihydroxy naphthalene were also formed the borates(borate 2,3 and 4, respectively) (Figure 2). Electron donating groups including methyl, t-butyl groups on the aromatic ring of diols are able to form the borates but electron withdrawing groups including aldehydic, nitro and carboxyl groups on the aromatic ring of diols are unable to form the borates.

The borates have a very low solubility in water and are insoluble in most organic solvents except in DMF and dimethyl sulfoxide(DMSO). The borates can be crystallized from DMF.

Synthesis and characterization of borates are described below.

Borate 1(N,N-dimethyl amino catechol borate)

Catechol(11g,0.1 moles) and boric acid(6.2 g, 0.1 moles) dissolved in DMF(25 ml) were refluxed under dry atmosphere for 1 hour. After 30 minutes reflux, insoluble solid appeared in the solution. The solution was evaporated to dryness to give a solid. The solid was triturated with acetone(50 ml) , and the insoluble solid was recovered by filtration to give a white solid(12.98 g, 62.2%). The solid can be recrystallized from hot methanol or DMF. The solid did not melt when heated to 210 C.

Proton NMR of borate 1(Figure 3) in DMSO-d₆ showed a singlet dimethyl amino protons at 2.5 ppm and a singlet aromatic protons at 5.4 ppm. Carbon 13 NMR of borate 1 in DMSO-d₆ showed a singlet carbon of methyl group at 36 ppm and three singlet carbons of aromatic ring at 109 ppm(C₄,C₅), 118.5 ppm(C₃,C₆) and 152 ppm(C₁, C₂).

IR:

Elemental analysis:

Borate 2(N,N-diethyl amino -4-methyl catechol borate)

4-methyl catechol(24.8 g, 0.2 moles) and boric acid(12.4 g, 0.2 moles) dissolved in DMF(40 ml) were refluxed under dry atmosphere for 1 hour. After reflux, the solvent was removed by a rotary evaporator. The solid was triturated with acetone(100 ml). The acetone insoluble solid was recovered by filtration to give a white solid(25.89 g, 58.1%). The product can be recrystallized from methanol or DMF. The solid did not melt when heated to 210 C.

Proton NMR of borate 2 in DMSO-d₆ showed a singlet 4- methyl protons of aromatic ring at 2.25 ppm, a singlet dimethyl protons of amino group at 2.45 ppm and a multiplet protons between 6.2-6.4 ppm due to three non equivalent protons on the aromatic ring (C₃, C₅ and C₆). Carbon 13 NMR of borate 2 in DMSO-d₆ showed a singlet carbon of aromatic 4-methyl group at 22 ppm, a singlet dimethyl carbon of amino group at 36 ppm, and six non equivalent aromatic carbons at 108 ppm(C₄), 109 ppm(C₅), 118 ppm(C₆), 127 ppm(C₃), 149 ppm(C₂) and 152 ppm(C₁).

Borate 3(N,N-dimethyl amino-4-t-butyl catechol borate)

4-t-butyl catechol(66.44 g, 0.4 moles) and boric acid(24.8 g,0.4 moles) in DMF(200 ml) were stirred for 1 hour to dissolve boric acid and catechol. The solution was refluxed under dry atmosphere for 1 hour. After reflux and cooling the solution, crystals appeared in the solution. The solution was refigerated overnight. The white crystalls(52.67 g, 50.3%) were recovered by filtration. The mother liquid was evaporated to

dryness to give a solid, and the solid was triturated with water. The water insoluble solid was recovered by filtration to give an additional products(2 1.5 1 g). The crystals did not melt when heated to 210 C.

Proton NMR of borate 3 in DMSO-d6 showed a singlet trimethyl protons of t-butyl group at 11.5 ppm, a singlet methyl proton of dimethyl amino group, and a multiplet of three non equivalent protons on the aromatic ring(C3,C5,C6). Carbon 13 NMR of borate 3 in DMSO-d6 showed a singlet carbons of t-butyl group on the aromatic ring at 32 ppm, a singlet dimethyl carbons of amino group at 35 ppm and six non equivalent carbons of aromatic ring at 105 ppm(C4), 107 ppm(C5), 113 ppm(C6), 140 ppm(C3), 148 ppm(C2) and 115.1 ppm(C1).

Borate 4(N,N-dimethyl amino 2,3-naphthyl borate)

2,3-Dihydroxy naphthalene(32.0 g, 0.2 moles) and boric acid(12.4 g, 0.2 moles) dissolved in DMF(150 ml) were refluxed under dry atmosphere for 1 hour. After warming the solution, boric acid and naphthalene were dissolved. The solution after reflux was refrigerated overnight and the insoluble crystals were recovered by filtration to give a white solid(40.32 g, 77.9%). The mother liquid was evaporated to dryness, and the solid was triturated with water(150 ml) to give an additional product(32.19 G). The solid can be recrystallized from DMF. The crystals did not melt when heated to 210 C.

Proton NMR of borate 4 in DMSO-d6 showed a singlet methyl protons of dimethyl amino group at 24.5 ppm and three sets of equivalent protons of aromatic ring at 67 ppm(C7,C8), 70 ppm(C6,C9) and 74.3 ppm(C1,C4). Carbon 13 NMR of borate 4 in DMSO-d6 showed a singlet dimethyl carbons of amino group at 35.5 ppm and 5 sets of equivalent carbons of aromatic ring at 103 ppm(C7,C8), 122 ppm(C6,C9), 126 ppm(C5,C10), 129.5 ppm(C4,C1) and 152 ppm(C2,C3).

Fungal Decay Evaluation

Fourteen loblolly pine or sweetgum blocks(1.9 cubic cm in radial, tangential and longitudinal directions) in a 16 oz bottle were vacuumed at 2.1-3.3 kPa for 30 minutes in a desiccator and then impregnated with DMF solutions of borates as well as aqueous solutions of boric acid at four concentration levels: 44.8, 22.4, 11.3, and 1.6 mmoles/100 g solution. Blocks treated with borates were compared with those treated with boric acid to show their effectiveness against fungal degradation.

For each test, wood blocks were placed in a vacuum desiccator for 30 minutes at 2.1-3.3 Kpa. They were then impregnated with one of four DMF solutions and soaked for 1 day. After soaking, seven blocks per treatment were dried in a chemical fume hood for 3 days and then heated in an oven at 105 C for 1 day. The blocks were conditioned at 27 C and 30% relative humidity for 3 weeks. Another seven blocks per treatment were leached in 350 ml of distilled water each day for 2 weeks. After leaching, the blocks were also conditioned at 27 C and 30% relative humidity for 3 weeks.

Soil-blocks fungal decay tests were run according to the ASTM standards(ASTM 1990). *Gloeophyllum trabeum* (pers.: fr) Murr., a brown rot fungi was used with pine blocks and *Coriolus versicolor* (L.:fi.) Quel., a white rot fungus was used with sweetgum blocks. Five replicate blocks from each treatment, five control, and five blocks treat with solvent alone were test for decay resistance over a period of 12 weeks. The extent of fungal attack was determined by weight loss. Solution concentration that resulted in equal or less than 2% weight loss by decay was generally considered the threshold retention.

Thermal Properties Evaluation

Loblolly pine wood treated with borates or boric acid as well as diammonium phosphate at 0.1 moles per 100 g wood was analyzed by TGA and DSC. Five mg of sample was used. For TGA, samples were analyzed by a Perkin Elmer TGA 7. Derivative thermal gravimetric analysis provided a derivative form (rate of mass loss) as a function of temperature and time. Char residue, maximum temperature of pyrolysis, and rate of weight loss were obtained from TGA and DTG.

Samples were also analyzed by a Perkin Elmer DSC 7. Five mg of sample were heated under nitrogen from 50 to 600 C with nitrogen flow rate of 20 ml/minute and heating rate of 10 c /min.

RESULTS and DISCUSSION

Characterization

Borates were characterized by proton NMR and carbon 13 NMR. Borate 1 was further characterized by FTIR and elemental analysis.

Proton and carbon 13 NMR showed that all four borates have dimethyl amino group in the molecular. This indicated that solvent DMF was participating in the reaction. FTIR of borate 1 showed that b-o absorption become weak. Elemental analysis of borate 1 showed that structure assigned in figure 12 was the right structure.

Fungal Decay Evaluation

Brown rot fungus: Weight losses of borate treated pine wood decayed by *G. trabeum* were shown in Table 1. For wood impregnated with borate 1, threshold retention with *G. trabeum* was 7.8 mmoles/100 g wood for both non leached and leached blocks. Leaching did not affect the decay resistance. For borate 2, threshold retention with *G. trabeum* was 8.6 mmoles/100 g wood for non leached blocks and 17.5 mmoles/100 g wood for leached blocks. Leaching reduced the effectiveness of decay protection. For borate 3, threshold retention with *G. trabeum* was 8.0 mmoles/100 g wood for non leached and leached blocks were ineffective. For borate 4, threshold retention with *G. trabeum* was 1.3 moles/100 g wood for non leached blocks and 18.3 mmoles/100 g wood for leached blocks. Leaching reduced the effectiveness of decay resistance.

The above decay tests showed that borates in wood were more effective against *G. trabeum* than that of boric acid. For unleached blocks, threshold retentions ranged from 1.3 to 8.6 mmoles/100 g wood whereas boric acid was 14 mmoles/100 g wood. After leaching, borate 1 did not decrease the decay resistance (threshold retention was 7.8 mmoles) but borate 2 reduced decay resistance (threshold was 17.5 mmoles). Borate 3 and 4 became ineffective.

White rot fungus: Weight losses of borate treated sweetgum wood decayed by *C. versicolor* were shown in Table 2. For wood impregnated with borate 1, threshold retention with *C. versicolor* was 1.1 mmoles/100 g wood for non leached and leached blocks. Leaching did not reduce the effectiveness of decay resistant. For borate 2, threshold retention was 1.2 mmoles for non leached blocks and 36.1 moles for leached blocks. Leaching reduced the effectiveness of decay resistant significantly. For borate 3, threshold retention was 1.1 mmoles for non leached blocks but was ineffective for leached blocks. For borate 4, threshold retention was 1.3 moles for non leached blocks and 37.8 mmoles for leached blocks. Leaching significantly reduced the effectiveness of decay resistant

The above decay tests showed that borates in wood were as effective as that of boric acid in preventing decay by *C. versicolor*. For non leached blocks, threshold retentions ranged from 1.1 to 1.3 mmoles whereas that of boric acid was 2 mmoles. After leaching, borate 1 did not decrease decay resistant with threshold retention of 1.1 mmoles. Borate 2 and 4 significantly reduced the decay resistant, threshold retentions were 36.1 and 37.8 mmoles, respectively. Borate 3 was ineffective.

Table 1. Effect of borates on decay of pine blocks by *Gloeophyllum trabeum* in a 12-week soil-block fungal decay test

Treatment	Solution concentration (mmoles/100 g wood)	Retention (mmoles/100 g wood)	Weight loss by Decay(%)	
			Non leached	Leached
Boric acid	1.6(0.10)	2.0(0.12)	20.2	
	11.3(0.70)	11.4(0.70)	0.1	
	22.4(0.70)	28.5(1.760)	0.4	
	44.8(2.770)	555(3.43)	1.0	
Borate 1	1.0(0.210)	1.1(0.220)	2.1	8.0
	7.4(1.54)	7.8(1.62)	1.6	1.9
	14.7(3.10)	15.9(3.310)	2.5	2.4
	29.5(6.20)	32.9(6.86)	3.2	3.2
Borate 2	1.2(0.30)	1.2(0.30)	18.9	37.1
	8.1(2.1)	8.6(2.2)	0.6	15.1
	16.3(8.4)	17.5(4.5)	1.0	0.0
	32.6(8.4)	36.5(9.4)	1.0	0.0

Borate 3	1.1(0.24)	1.1(0.25)	12.6	34.7
	7.6(1.70)	8.0(1.780)	1.4	36.5
	14.7(3.10)	16.2(3.62)	2.1	39.8
	30.5(6.790)	33.5(7.470)	3.1	42.0
Borate 4	1.2(0.31)	1.3(0.320)	0.7	30.8
	8.6(2.20)	9.0(2.27)	0.6	26.1
	17.2(4.34)	18.3(4.620)	0.9	2.1
	34.4(8.69)	38.0(9.630)	0.7	0.00
Control			34.5	-
Solvent(DMF)			30.3	

a Values in parenthesis are percentage(w/w, g borate/100 g wood)

b Average of five replicates

Table 2. Effect of borates on decay of sweetgum blocks by *Coriolus versicolor* in a 12-week soil-block fungal decay test

Treatment	Solution concentration (mmoles/100 g wood)	Retention (mmoles/100 g wood)	Weight loss by decay(%)	
			Non leached	Leached
Boric acid	1.6(0.10)	2.0(0.12)	0.2	-
	11.3(0.700)	11.4(0.710)	0.2	-
	22.6(1.38)	22.8(1.41)	0.5	-
	44.8(2.77)	56.0(3.41)	1.75	-
Borate 1	1.1(0.220)	1.1(0.22)	0.6	0.8
	11.3(2.36)	11.8(2.46)	0.7	1.1
	14.7(3.07)	15.8(3.30)	1.6	1.7
	29.6(6.16)	32.7(6.83)	1.9	1.5
Borate 2	1.2(0.30)	1.2(0.30)	1.9	36.3
	8.1(2.11)	8.5(2.19)	1.1	32.7
	16.3(4.22)	17.3(4.48)	1.2	6.9
	32.6(8.42)	36.1(9.34)	1.5	0.0
Borate 3	1.1(0.24)	1.1(0.30)	1.5	36.3
	7.6(1.69)	8.0(1.78)	0.9	35.0
	15.2(3.39)	16.2(3.62)	0.9	38.8
	30.5(6.79)	3.5(7.470)	0.7	32.8
Borate 4	1.2(0.31)	1.3(0.32)	0.9	42.6
	8.6(2.17)	9.0(2.27)	0.6	52.0

	17.2(4.34)	18.3(4.63)	1.0	36.9
	34.4(8.70)	37.8(9.55)	1.1	0.3
Control			32.3	
Solvent(DMF)			32.0	

a Values in parentheses are percentage(w/w; g borate/100 g wood)

b Average of five replicates

Thermal Evaluation

TGA analysis: Thermal gravimetric analysis of wood in the presence of fire retardants has been used to evaluate the effectiveness of fire retardant to protect wood from thermal degradation. Char yield at 500 c or 600 C in nitrogen has been shown to correlate well with fire retardant efficacy in wood products treated with fire retardants(Shafizadeh 1975). The char yields of wood treated with borates at 500 C in nitrogen (Table3) were compared with that of wood treated with known fire retardants including diammonium phosphate and boric acid.

Table 3. Char yields of wood impregnated with borates or diammonium phosphate or boric acid at 500 C in nitrogen by a TGA

Treatment (0.1 moles/100 g wood)	Char yield (%)
Diammonium phosphate (DAP)	44.0
Borate 1	37.4
Borate 2	33.6
Borate 3	24.6
Borate 4	37.3
Boric acid	32.0
Southern pine (Control)	24.6

The above results of TGA analysis indicated that wood treated with borate 1 and 4 have high char yields than that of boric acid but were less than that of diammonium phosphate. Borate 1 and 4 are better fire retardants in wood than that of boric acid.

DSC analysis:

Pyrolysis of wood components and wood in nitrogen (Figure) showed that active pyrolysis took place after 150 C. Xylan pyrolyzed at lower temperature (160 -170 C) with endothermic reaction which may be attributed to depolymerization of xylan, followed by active pyrolysis with exothermic reaction (215 C to 300 C) which may be attributed to pyrolysis of aliphatic char. Pyrolysis of aromatic char occurred above 300 C and proceeded at slower rate. For cellulose, active pyrolysis started at 300 C with large endothermic reaction (340 C) which was attributed to depolymerization of cellulose and volatilization of volatile compounds. This was followed by two exothermic reactions (peaks at 380 C and 425 C) which were attributed to pyrolysis of aliphatic and aromatic chars (Shafizadeh 1984, Pastorova 1994). Lignin pyrolyzed slowly between 200 to 350 C and active pyrolysis of aromatic char begins at 350 C with exothermic reaction (Peak at 400 C). Pyrolysis of wood reflected the pyrolysis of wood components which started with the early decomposition of hemicelluloses, slow pyrolysis of lignin and then depolymerization of cellulose, followed by active pyrolysis of aliphatic and aromatic chars.

Pyrolysis pathway of wood treated with borates in nitrogen was similar to that of boric acid which proceeded by depolymerization of cellulose, followed by active pyrolysis of aliphatic and aromatic chars. (Figure). The depolymerization of cellulose is the major pyrolysis pathway for wood treated with borates. This pathway is similar to the pathway of high temperature pyrolysis of wood. However, the endothermic peak of wood treated with borates appeared at lower temperatures (around 345 C to 350 C) and rate of pyrolysis was higher than that of high temperature pyrolysis of wood. Moreover, the rate of aliphatic and aromatic char pyrolysis was slower. This indicated that chars formed from borates treated wood was more stable to thermal degradation. The more stable chars may contribute to high char yields as indicated in TGA.

Pyrolysis of wood in the presence of diammonium phosphate proceeds by dehydration pathway which produces less volatiles and more char (Shafizadeh 1983, 1984, Granzow 1978, Byrne 1966). The endothermic peak due to depolymerization of cellulose became very small and appeared at lower temperature (200 C). The exothermic reactions due to pyrolysis of char appeared at two temperature regions. The peak temperature at 265 C was attributed to pyrolysis of aliphatic char and the peak temperature at 370 C was attributed to pyrolysis of aromatic char (Figure) (Kur 1986, Shafizadeh 1984). The rate of char pyrolysis for these two exothermic reactions was slow which indicated that the char formed in the presence of diammonium phosphate is more stable to thermal degradation.

Conclusions

Borate 1, 2 or 4 in wood was resistant to water leaching and able to prevent wood from decayed by a brown- and white rot fungus. Borate 1 in wood after 2 week water leaching was more effective than that of boric acid without leaching in preventing decay by a brown- and white rot fungus. Threshold retentions for borate 1 with C_f and C_v were 7.8 and 1.1 mmol/100 g wood whereas boric acid was 11.4 and 2 mmol/100 g wood respectively.

Char yield by TGA analysis in nitrogen at 500 C showed the following decrease order:

DAP > borate 1 > borate 4 > borate 2 > boric acid > borate 3 > southern pine (control)

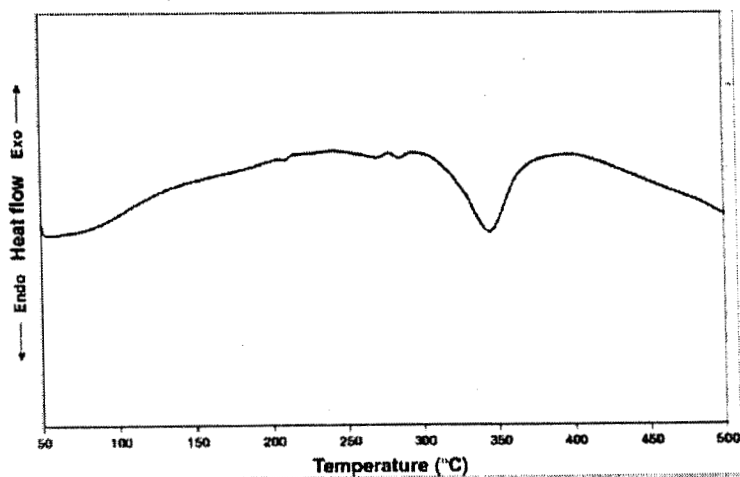
Wood treated with borate 1, 4, or 2 has better fire retardant properties than that of boric acid.

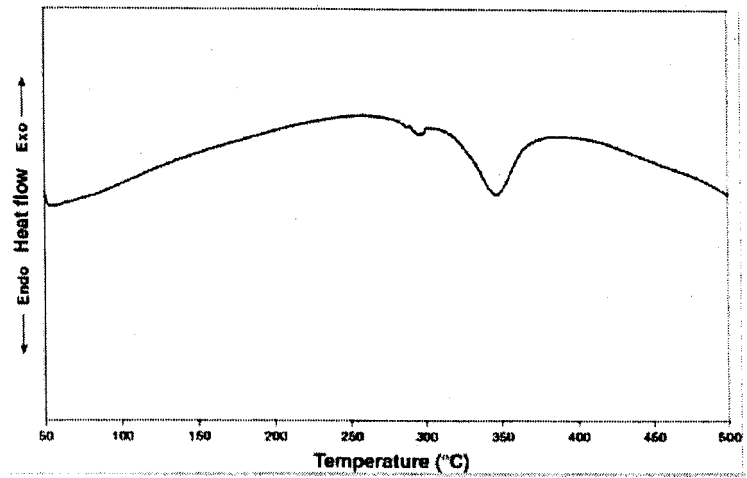
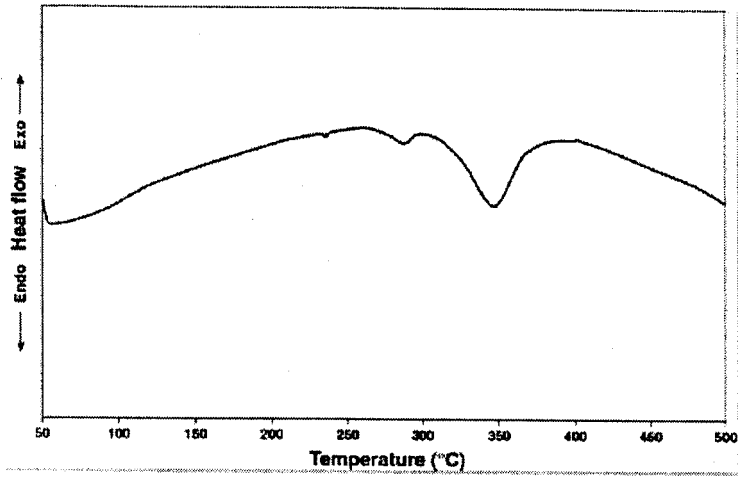
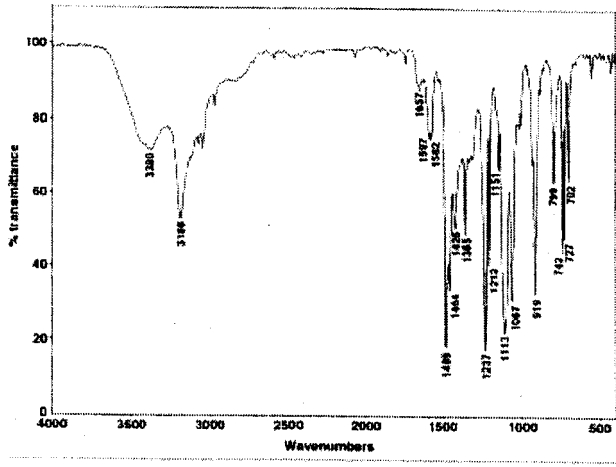
DSC showed that the pyrolysis pathway of wood treated with borates was similar to that of wood treated with boric acid which proceeds by cellulose depolymerization. However, the rate of cellulose

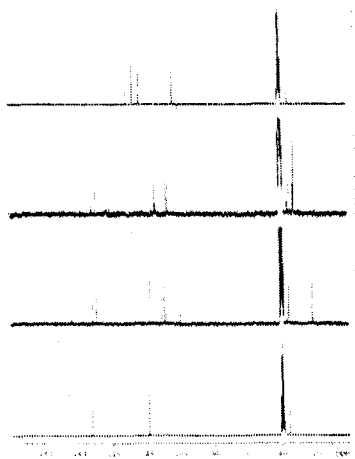
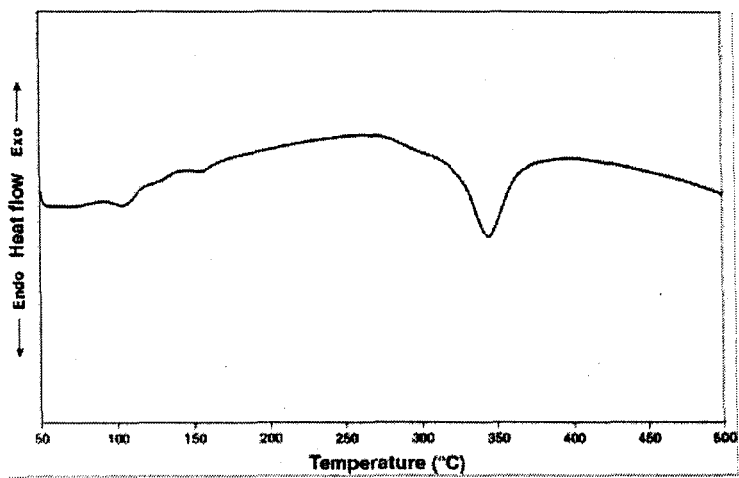
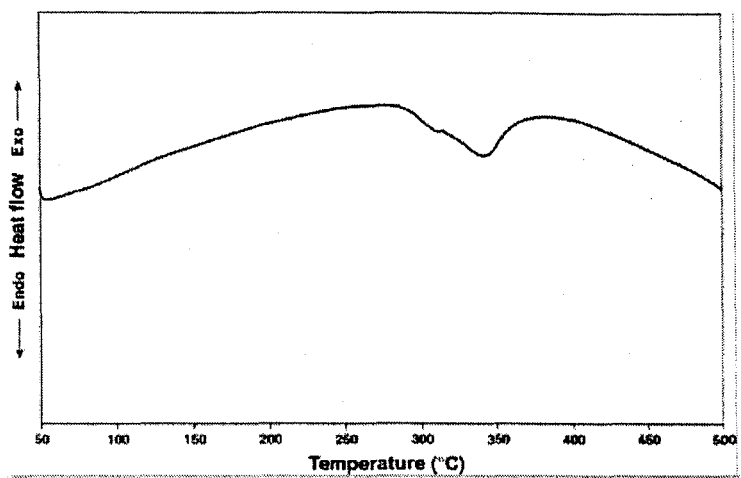
depolymerization was higher but the temperature of cellulose depolymerization and the rate of char pyrolysis were lower.

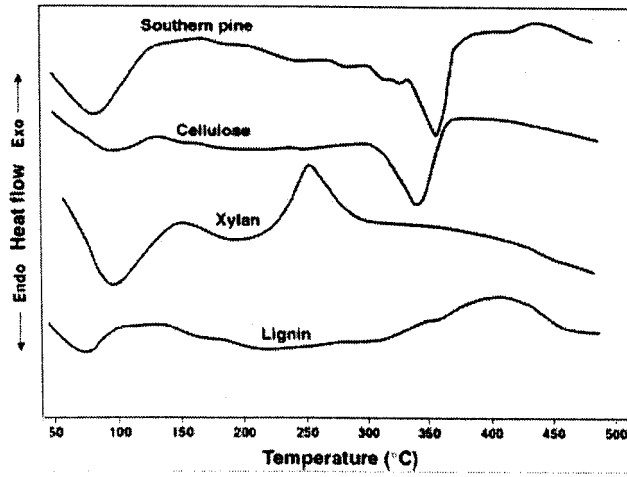
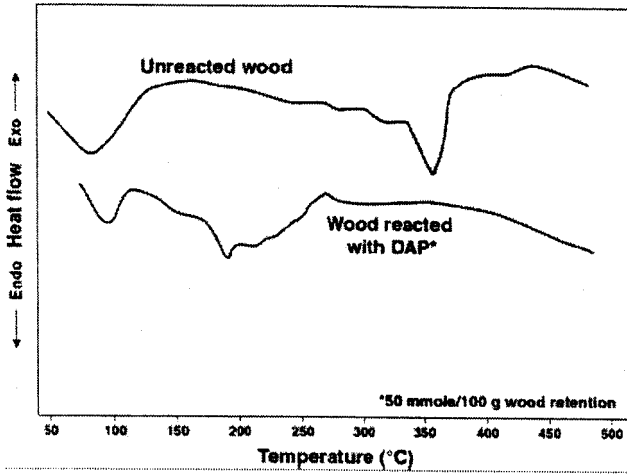
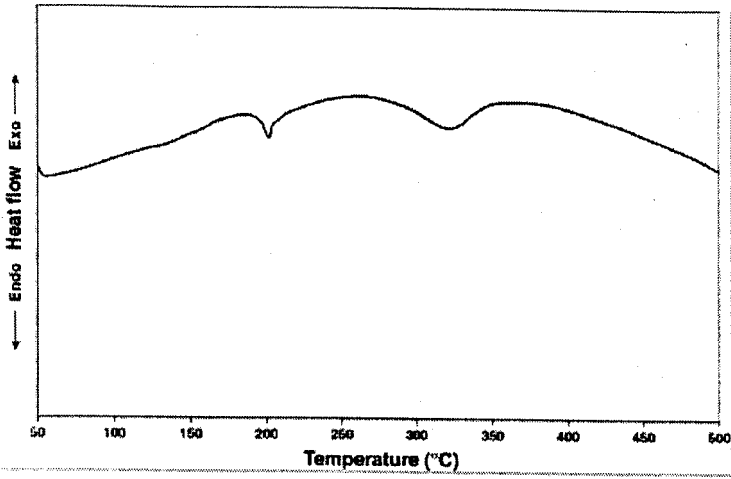
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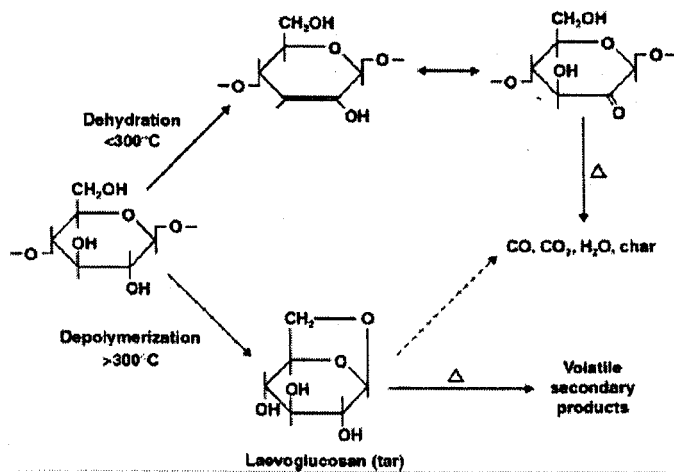
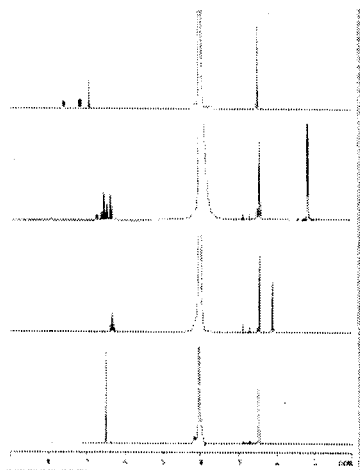
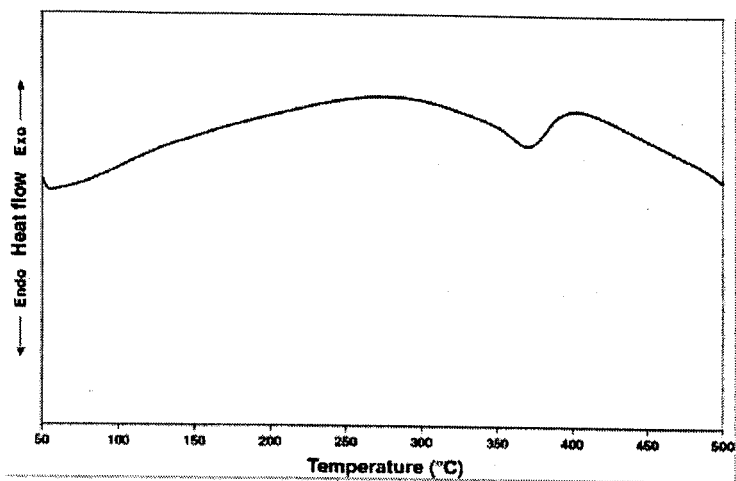
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