Journal of Thermal Analysis and Calorimetry, Vol. 85 (2006) 3, 765–769

THERMAL DEGRADATION OF WOOD TREATED WITH FLAME RETARDANTS

M. Gao[1]*, *C. Y. Sun*[2] *and C. X. Wang*[1]

[1]Department of Safety and Environmental Engineering, North China Institute of Science and Technology, National Safety Training Center of Coal Mines, P. O. Box 206, Yanjiao Beijing 101601, P. R. China
[2]Department of Basic Subject, North China Institute of Science and Technology, National Safety Training Center of Coal Mines P. O. Box 206, Yanjiao Beijing 101601, P. R. China

Wood, one of the most flammable materials, was treated with various compounds containing nitrogen, phosphorus, halogens, and boron. For a study of flame retardance from the standpoint of thermal degradation, the samples were subjected to thermogravimetry (TG), differential thermal analysis (DTA) and differential thermogravimetry (DTG) in nitrogen to determine if there were any characteristic correlations between thermal degradation behaviors and the level of flame retardance. From the resulting data, kinetic parameters for different stages of thermal degradation are obtained using the method of Broido. The energies of activation for the decomposition of samples are found to be from 72 to 109 kJ mol^{-1}. For wood and modified wood, the char yields are found to increase from 10.2 to 30.2%, LOI from 18 to 36.5, which indicates that the flame retardance of wood treated with compounds is improved. The flame retardant mechanism of different compounds has also been proposed.

Keywords: *degradation, DTA, DTG, flame retardant, TG, wood*

Introduction

Wood, which mainly consists of cellulose, lignin and hemicellulose, catches fire easily and burns vigorously with flame. As wood is used for furniture, decorate and building materials, it will be essential to make wood flame retardant. It is well known that materials made of wood can be treated with compounds containing nitrogen, phosphorus, halogens, and boron such as ammonium phosphate, ammonium halide, boric acid and borax to improve fire retardance and accelerate the formation of a carbonized layer on the materials [1, 2]. It is proposed that such additives can lead to a lowering of the decomposition temperature and a higher char yield [3]. However, the systematic studies on the thermal degradation and the kinetic parameters of wood treated with these compounds are relatively rare. In the present study, thermal degradation behaviors of wood treated with different compounds containing nitrogen (N), phosphorus (P), halogens (Cl, Br), and boron (B) was characterized by DTA, TG and DTG techniques. The values of different kinetic parameters of wood and modified wood were obtained using the method of Broido [4]. We compared the thermal degradation behaviors of these samples obtained from DTA, TG and DTG with flame retardance determined by LOI and studied minutely how the different elements effect on degradation behaviors. The further flame retardant mechanism was suggested.

Experimental

Flame-retardants

Condensates of melamine, formaldehyde [DF]: 37% formalin as formaldehyde [F] 4 mol was brought to pH 8–8.5 with NaOH and heated. Then dicyandiamide [D] 1 mol was added to the above solution, stirred until dissolved and heated under reflux for 50 min. Then a methyl etherification dicyandiamide solution was obtained. The reactants were diluted with water up to the prescribed concentration.

Condensates of dicyandiamide, formaldehyde and phosphoric acid [DFP]: 37% formalin as formaldehyde [F] 1 mol was brought to pH 8–8.5 with NaOH and heated. Then dicyandiamide [D] 1 mol was added to the above solution, stirred until dissolved and heated under reflux for 10 min. Heating was stopped and the solution was allowed to cool to 50–60°C. Then 85% phosphoric acid as phosphorus [P] 1 mol was added slowly. Then a solution of hydroxymethyl guanyl urea phosphoric acid was obtained [5].

The following procedures of preparation were similar to that of DFP. DFAP was obtained with dicyandiamide, formaldehyde and ammonium dihydrogen phosphate in the mole ratio 1:1:1. DFDP was obtained dicyandiamide, formaldehyde and diammonium hydrogen phosphate in the mole ratio 1:1:1. DFAC was produced by dicyandiamide, formaldehyde and ammonium chloride in the mole ratio 1:1:1. DFAB was produced by

---

* Author for correspondence: gaoming@ncist.edu.cn

1388–6150/$20.00
© 2006 Akadémiai Kiadó, Budapest

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

dicyandiamide, formaldehyde and ammonium bromide in the mole ratio 1:1:1. DFBB was produced by dicyandiamide, formaldehyde, boric acid and borax in the mole ratio 1:1:0.5:0.5. The reactants were diluted with water up to the prescribed concentration before use.

Sample preparation

Samples of white pine (North of China) were heated for 1 h in boiling water. After this procedure, the wood was dried at 60°C. Then the wood was immersed in treating solution at 60°C for 2 h, and each sample was dried at 60°C. Samples milled passing 50 meshes were used for thermal analysis. Sizes were 100×6×3 mm for LOI test. The samples *i–viii*, pure and treated wood with the aqueous solution of DF, DFP, DFAP, DFDP, DFAC, DFAB and DFBB as flame retardants, respectively, were listed in Tables 1–2.

Limiting-oxygen-index (LOI)

The LOI value is the minimum amount of oxygen in oxygen-nitrogen mixture required to support combustion over 3 min or till specimen is consumed for more than 5 cm from the top. The higher the LOI value is, the more effective the flame-retardant treatment is. LOI values were determined in accordance with ASTM D2863-70 by means of a General Model HC-1 LOI apparatus. The results are given in Table 1.

Thermal analysis

Differential thermal analysis (DTA), thermogravimetry (TG) and differential thermogravimetry (DTG) were carried out on a DT-40 thermal analyzer (Shimadzu, Japan). DTA, TG and DTG were performed under a dynamic nitrogen (dried) atmosphere at a heating rate of 10°C min^{-1}. α-Al_2O_3 was taken as the reference material.

Elemental analysis

The elemental analysis was carried out using a PE-2400 Elemental Analyzer (USA). Phosphorus was estimated by the colorimetric method. Nitrogen was determined by the Kjeldahl method. The results are given in Table 1.

Results and discussion

The simultaneous DTA, TG and DTG curves of samples (*i–viii*) were carried out in a dynamic nitrogen from ambient temperature to 650°C and are shown in Figs 1–8. Temperatures of maxima in DTG curves were measured and given in Table 1.

Table 1 Analytical data for wood and wood treated with flame-retardants

No.	P/	N/	Cl, Br/	LOI	Char yield/ mass%	T_{max}/ DTG
	mass%					
i	–	–	–	18.0	10.2	355
ii	–	3.18	–	25.5	23.8	350
iii	2.01	2.15	–	34.0	20.7	295
iv	2.05	2.33	–	34.5	21.0	295
v	2.46	2.41	–	36.5	26.6	300
vi	–	2.09	1.42	30.0	20.6	240–380
vii		2.26	1.89	32.0	29.8	245–360
viii	–	2.02	–	30.5	30.2	330

Table 2 Results of thermal analysis for different stages of thermal degradation of wood and wood treated with flame-retardants

Sample No.	Flame retardant	Stage	Mass loss/%	Temp. range/°C	E_a/ kJ mol^{-1}
i	–	1st	5.8	225–290	74
		2nd	43.2	290–367	107
		3rd	23.0	367–530	19
ii	DF	1st	8.7	220–290	58
		2nd	31.6	290–348	72
		3rd	38.1	348–590	17
iii	DFP	1st	5.4	185–245	52
		2nd	32.3	245–309	92
		3rd	29.9	309–585	14.5
iv	DFAP	1st	5.9	180–256	36
		2nd	31.8	256–306	109
		3rd	35.4	306–595	13
v	DFDP	1st	5.1	200–262	50
		2nd	31.5	262–310	106
		3rd	31.3	310–595	12
vi	DFAC	1st	3.0	200–247	58
		2nd	44.3	247–360	87
		3rd	19.3	360–520	14
vii	DFAB	1st	3.1	200–245	67
		2nd	29.1	245–350	92
		3rd	30.0	350–620	15
viii	DFBB	1st	6.7	150–290	70
		2nd	29.1	290–360	105
		3rd	24.4	360–560	20

It is generally observed that the amount of char formed during thermal degradation of samples is related to the degree of flame retardance exhibited by samples. The function of flame retardant in wood is to increase the char at the cost of flammable volatile products [6]. In order to understand the flame retardant properties of these samples, the char yields (in mass%) determined at 600°C from TG curves are given in Table 1. From Table 1, we can see that samples (*ii–viii*) show high values of LOI and char yield. This suggests that the combustibility of the wood treated with chemicals decreases. Moreover, the samples (*iii–viii*) show higher values of LOI and char yield, which suggests high flame retardance. With the increases of char yields, the LOI values increase, which agrees with mechanism of flame retardant. Introduction of flame-retardants leads to more char formed at the expense of flammable volatile products of thermal degradation, thus suppressing combustion and increasing the LOI value.

For the various stages of thermal degradation of wood, assuming the thermal degradation is first-order reaction, the kinetic parameters for various stages were determined using the following equation, given by Broido [4]:

$$\ln\left(\ln\frac{1}{y}\right)=-\frac{E_a}{R}\frac{1}{T}+\ln\left(\frac{R}{E_a}\frac{Z}{\beta}T_m^2\right)$$

where y is the fraction of initial molecules not yet decomposed. T_m is the temperature of maximum reaction rate, β is the rate of heating, Z is the frequency factor, and E_a is the activation energy. From the slopes of the TG curves in Figs 1–8, plots of $\ln(\ln 1/y)$ *vs.* $1/T$ for various stages of pyrolysis were drawn. The activation energies, E_a, determined from the slopes of these plots are given in Table 2 [7].

For the thermal degradation, of the three components in wood, it is proposed that the thermal degradation of hemicellulose occurs firstly while cellulose, then, thermally decomposes through two competing pathways [8, 9]. At lower temperatures, gradual degradation ultimately forms a carbonaceous residue. At higher temperatures, a rapid volatilization occurs via the formation of laevoglucose which can be further decomposed into volatile and flammable products. On the other hand, lignin decomposes with lower rates by char oxidation [10]. The pyrolytic behavior of wood is the overall behaviors of the three components, which makes it extremely complicated. However, the thermal degradation of wood is affected to a large extend by cellulose [11, 12].

TG curve of wood shows three stages of the thermal degradation (Fig. 1). There is a mass loss of 5.8% in the temperature range 235–290°C with activation energy 74 kJ mol^{-1} in the first stage, which is due to decomposition or dehydration of hemicellulose. For the second stage, 43.2% mass loss occurs in the temperature range 290–367°C with activation energy 107 kJ mol^{-1} which is due to the decomposition of cellulose. This corresponds to the first exotherm peaking at 385°C in DTA curve which is due to the recombination of the degradation products like phenols and phenolic derivatives [8]. The temperature of the maxima in DTG curve is 355°C, which shows a rapid decomposition in this temperature. After the second stage, mass losses of the residual materials of wood are found to be slow in the temperature range 367–530°C. 23.0% mass loss in TG curve is observed in this (third) stage with activation energy 19 kJ mol^{-1}. High temperature exotherm in DTA curve is connected with char formation from cellulose and lignin.

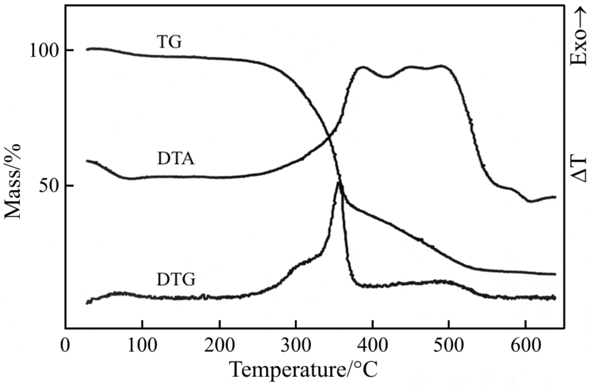

Fig. 1 TG, DTA and DTG curves of wood in nitrogen

TG curves of treated wood with basic nitrogen compound (DF) still show three stages of thermal degradation (Fig. 2). For the first stage, 8.7% mass loss is observed in the temperature range 220–290°C with activation energy 58 kJ mol^{-1}, which is due to decomposition or dehydration of hemicellulose. For the second stage, 31.6% mass loss in the temperature range 290–348°C is due to the decomposition of cellulose. The exotherms of DTA peaking at 350–380°C are due to the recombination of the degradation products. Activation energy in this stage is in a range 72 kJ mol^{-1}. Temperature of the maxima in DTG curve is 350°C. For the third stage, TG curves show a mass loss of 38.1% in the temperature range 348–590°C with activation energy 17 kJ mol^{-1}. There are not any clear exotherms in the last stage, which shows a lowering in heat release for wood treated with basic nitrogen compound.

For the wood treated with basic nitrogen compound, it is evident that the heat release in the third stage is considerably decreased as compared to wood. However, the temperatures of the second stage are not

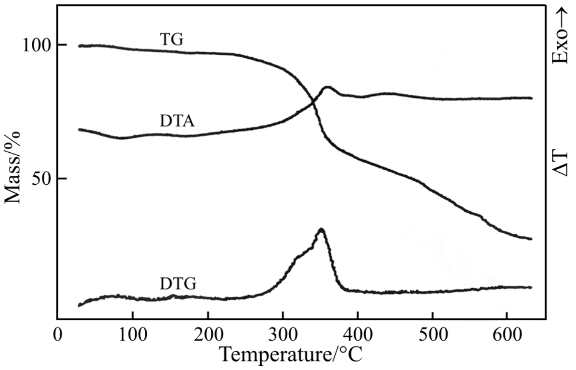

Fig. 2 TG, DTA and DTG curves of sample (*ii*) in nitrogen

changed and the main decomposition of samples still mainly occurs at higher temperatures where large amount of flammable volatile products are formed, which leads to poor flame retardance.

For the wood treated with treated with phosphorus and basic nitrogen compounds (DFP, DFAP, DFDP), there is a mass loss of 5.1–5.9% in the temperature range 180–262°C in the first stage (Figs 3–5). It is suggested that the initial reactions are dephosphorylation of samples and that the released acids then catalyze the decomposition or dehydration of hemicelluloses [9]. Activation energy in this stage is in a range 36–52 kJ mol^{-1}. For the second stage, 31.5–32.3% mass loss in the temperature range 245–310°C with activation energy 92–109 kJ mol^{-1} is due to acid-catalyzed decomposition of cellulose. Temperature of the maxima in DTG curve is in a range 295–300°C. For the third stage, TG curves show a mass loss of 29.9–35.4% in the temperature range 306–595°C with activation energy 12–14.5 kJ mol^{-1}.

For the thermal degradation of wood treated with phosphorus and basic nitrogen compounds, compared with that of wood, it is evident that there are some differences attributed to flame retardance in the terms of following:

- Lowering in decomposition temperatures and activation energies. For samples (*iii*–*v*), the rapid main decomposition (second) stage shifts to lower temperatures, which results in a lower percent of flammable volatile products and correspondingly higher amount of char. The activation energies in the first stage are much decreased. It is suggested that the flame-retardants containing phosphorus are effective in catalyzing the thermal decomposition [13].
- Lowering in heat release and rate of heat release. The exotherms in DTA curves for samples (*iii*–*v*) are much decreased.

For the samples (*vi*–*vii*), which contain nitrogen and halogen. The major mass loss becomes slow – the slope becomes small in TG curves as compared with those of the other samples (Figs 6 and 7). Moreover, there are several maxima in DTG curves, which may be attributed to the different mechanism of thermal degradation of samples. It is suggested [14] that the halogen free radicals (Cl•, Br•) formed in the thermal decomposition as radical scavengers block the formation of volatile combustible products which leads to a low mass loss. The maximum in each DTG is in a broad range 240–380°C, which shows a constant action of halogen free radicals. The heat release is distributed between two broad peaks covering a wider area, resulting in a major reduction in rate of release of heat and the combustible gases which fuel the flaming combustion reaction.

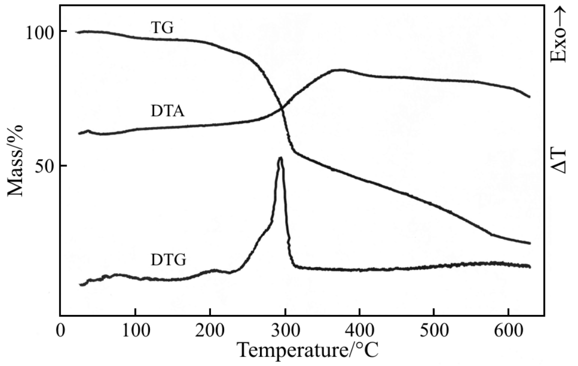

Fig. 3 TG, DTA and DTG curves of sample (*iii*) in nitrogen

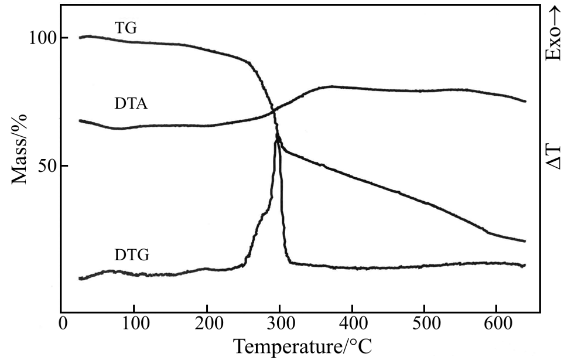

Fig. 4 TG, DTA and DTG curves of sample (*iv*) in nitrogen

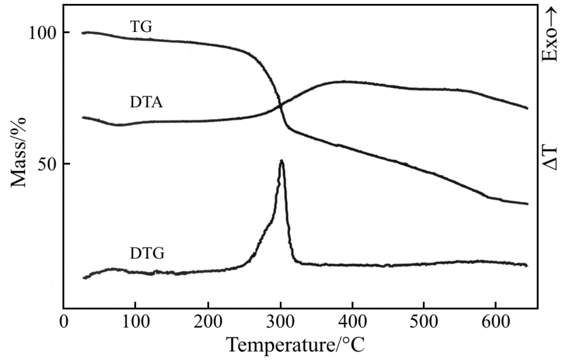

Fig. 5 TG, DTA and DTG curves of sample (*v*) in nitrogen

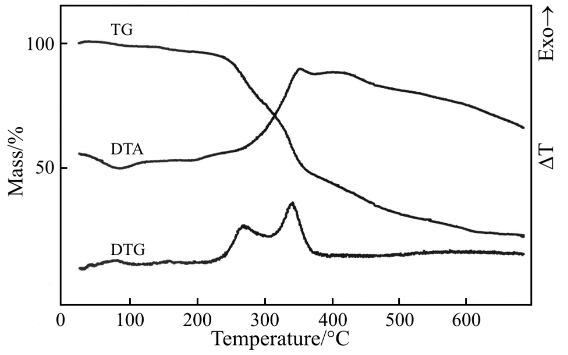

Fig. 6 TG, DTA and DTG curves of sample (*vi*) in nitrogen

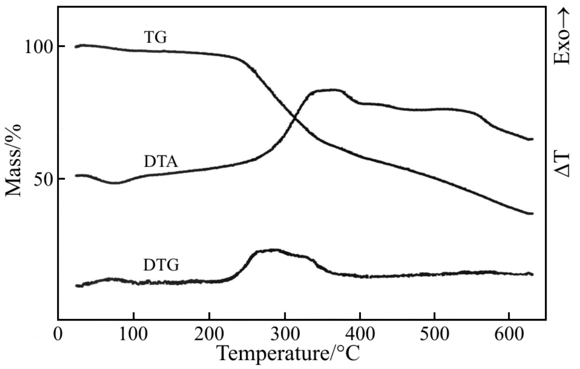

Fig. 7 TG, DTA and DTG curves of sample (*vii*) in nitrogen

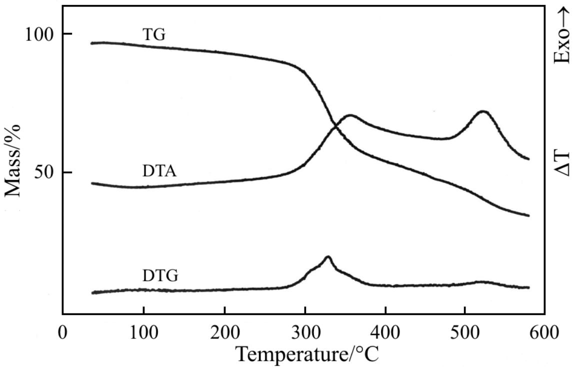

Fig. 8 TG, DTA and DTG curves of sample (*viii*) in nitrogen

For the sample (*viii*), which only contains single element (*B*) contribute to flame retardance, the decrease in decomposition temperature and activation energies is very small as shown in Fig. 8 and Table 2 though the LOI of sample (*viii*) is much higher than that of wood. This shows that the effect of boron on thermal degradation of the sample is very minute (Fig. 8). It is suggested that boron protects physically substance. Borate melts to form an enamel-like film to cover the surface of the substrate, which protects it from the flame and shuts off the supply of oxygen required for burning. Moreover, since borax acts endothermically when exposed to heat because of its water of crystallization, the temperature around the borax film is lowered, which contributes to quenching, in such a case, there is no need for early thermal decomposition as with other flame retardants, which depend on pyrolytic gas formation.

Conclusions

The thermal degradation of various samples is different. For the samples containing phosphorus and nitrogen, the initial reactions are dephosphorylation that the released acids then enhance the dehydration and decomposition, which makes second stage occur at lower temperatures (245–310°C) and produce char at the expense of flammable volatile products, resulting in a high flame retardant efficiency. The thermal degradation behaviors for samples containing nitrogen and halogens becomes complex which may be because halogen free radicals (Cl•, Br•) formed in the thermal decomposition as radical scavengers block the formation of volatile combustible products which leads to slow down major mass loss. The sample containing single nitrogen show poor flame retardance though the release heat is much decreased, which is due to the degradation in higher temperature. However, the sample only containing boron shows good flame retardance though there are no much changes in the thermal degradation behaviors, which shows the physical action of boron on the flame retardance.

References

1 J. K. Woo and A. P. Schniewind, Holzforsch., 41 (1987) 305.
2 H. Berndt, A. P. Schniewind and J. K. Woo, Holzforsch., 44 (1990) 439.
3 T. P. Brady and H. G. Langer, in W. Hemminger (Ed.) Thermal Analysis, Birkhauser Verlag, Basel, 2 (1980) 443.
4 A. Broido, J. Polym. Sci. Part A-2, 7 (1969) 1761.
5 S. C. Juneja, 1975, U. S. 3,887,511.
6 S. L. Bagga, R. K. Jain, I. S. Gur and H. L. Bhatnagar, British Polymer Journal, 22 (1990) 107.
7 Y. Chen, J. Q. Xie, B. Zhang and X. C. Zeng, J. Therm. Anal. Cal., 75 (2004) 847.
8 H. G. Wiedemann and I. Lamprecht, Chapter 14, Wood, Handbook of Thermal Analysis and Calorimetry, 4 (1999) 765.
9 R. K. Jain, K. Lal and H. L. Bhatnagar, J. Appl. Polym. Sci., 30 (1985) 897.
10 M. Bartkowiak and R. Zakrzewski, J. Therm. Anal. Cal., 77 (2004) 295.
11 T. Hirata and S. Kawamoto, Fire Mater., 15 (1991) 27.
12 M. Gao, K. Zhu and C. Y. Sun, J. Therm. Anal. Cal., 75 (2004) 221.
13 M. Gao, D. X. Pan and C. Y. Sun, J. Fire Sci., 21 (2003) 189.
14 S. Nakanishi and T. Hashimoto, Textile Res J., 68 (1998) 807.

Received: June 10, 2005
In revised form: July 27, 2005
OnlineFirst: January 11 2006

DOI: 10.1007/s10973-005-7225-3