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Research Article

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Fire resistance of boron-containing fire-retardant by TG analysis

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ABSTRACT

Disodium octoborate tetrahydrate (DOT), boric acid (BA), magnesium sulfate ($MgSO_4$) and fire retardant DBM were selected as the main ingredients to develop a fire retardant for Southern Pine. A Thermo Gravimetric Analyzer was used to evaluate the temperature effects of Southern Pine samples treated with the DBM. The results showed that Boron-Containing fire-retardant improved Southern Pine fire retardant performance, the mass loss rate decreased, the char yield and the peak temperature of maximum mass loss increased. Thermokinetic method was used to analyze the TG curves of the treated wood, so as to illustrate the DBM treating agent' mechanism of flame retardant effect on wood, In order to illustrate the activation energy in different combustion stages with quantity, the TG curves were further analyzed by thermokinetic method to obtain thermokinetic parameters of different phases during wood pyrolysis.

Key words: Boron-Containing fire-retardant; fire resistance; TG analysis; thermokinetics

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INTRODUCTION

As important building decorating material, the annual consumption of wood increases greatly, and blindly excessive consumption of wood resource has caused a serious shortage of resources, to which the wood industry is facing now. Through the fire-retardant and preservative treatment of wood, we can expand the applied range and extend its service life, alleviate the problem of wood material resources shortage. Boron-Containing fire-retard a Ant DBM that the author has developed by research have excellent properties such as preservative effectiveness ,the inhibition of flame and smoke[1].

Thermal analysis techniques is widely used as an effective method for evaluating the flame retardant performance of wood and man-made boards and the study of its flame retarding mechanism[2-3]. Thermal analysis includes the thermogravimetric(TG), differential thermal analysis (DTA),differential scanning calorimetry (DSC) etc[4]. The author has adopted the method CONE for primary discussion about the flame retarding mechanism of DBM, to prove that the treating agents have obvious synergistic effect[5]. In this paper, on the basis of above researches[1,3], adopting the test methods of TG and DTG, we had further discussion about the Boron-Containing fire-retardant' effect on Southern Pine fire retardant performance. Meanwhile, the thermal dynamics equation of solid was used to analyze the TG curves, to analyze the thermokinetic parameters and activation energy of different phases during wood pyrolysis, so as to provide evidence about the wood flame retarding mechanism.

EXPERIMENTAL SECTION

1.1 Experiment material

(1) Testing piece

Southern Pine(*Pinus* spp),bought from Yuzhu timber market, the air-dry wood which has uniform annual ring, with no knots, wood decay and stain was elected. Totally 15 specimens(600 mm×140 mm×50 mm),the air-dry density was 0.50g/cm³.

(2) Reagent
Industrial-grade disodium octoborate tetrahydrate (DOT), from Guangzhou Junwei International Trading Co.LTD, analytical pure boric acid (BA),from Tianjing Chengfu Chemical Reagent Factory, analytical pure magnesium sulfate ($MgSO_4$), from Tianjing Chengfu Chemical Reagent Factory.

1.2 Test equipment
DTG-60 Thermo Gravimetric Analyzer, vacuum pressure device

1.3 Method
1.3.1 Design of experiment All living
On the basis of in previous studies[1],it was found that when DOT, BA, and $MgSO_4$ is in the mass ratio 3:1, 5:1.5the integrated performance of flaming combustion inhibition and preservative property, etc. So it was elected as the foundation of the study in this South China Agricultural University, Guangzhou, Guangdong paper.

1.3.2 Experimental test
1)The preparation of flame retardant
According to 1.3.1，take the corresponding mass fraction of powder reagent, put in the beaker, then add it in distilled water, then the corresponding mass fraction of flame retardants were made, stir with magnetic stirrers until the reagent completely dissolved.

Tab.1 The parameter of TG curve of untreated and treated Southern Pine wood during pyrolysis process

Wood sample	Reaction interval(℃)	Reaction interval mass loss rate(%)	The maximum mass loss peak emperature(℃)	Char yield(%)
Untreated wood	247～382	70.46	367	14.01
DOT treated wood	248～363	57.22	349	30.06
BA treated wood	258～370	60.88	351	28.02
MgSO4 treated wood	243～354	65.46	323	22.15
DBM treated wood	265～380	46.05	345	37.72

2) Treatment process
About the specific process of Southern Pine please refer to early research literature[1].Put the treated samples into constant temperature humidity chamber with the relative humidity (RH) (50±2)%,the temperature (23±1)℃, adjust until the weight is constant. Select the powder of 40 ~ 60 mesh for TG, DTG test. The drug-loading rate of the treating wood are listed as followed, the wood treated with DOT 2.82%, the wood treated with BA 2.80%,the wood treated with $MgSO_4$ 2.84%, the wood treated with DBM 2.86%.

1.4 TG-DTA test and data processing method
DTG-60 Thermo Gravimetric Analyzer was used for test, the test condition is listed as follows, the flow rate of high pure nitrogen is 50mL/min, the heating rate is 20.0℃/min,the temperature range is 26～800℃. Microsoft Excel software was used for data processing after the test to obtain each parameter.

RESULTS AND DISCUSSION

2.1 Analysis of TG curves
According to the TG curves from Fig.1 to Fig.5,the TG and DTG curves of Southern Pine share the same changing rule. That is at the temperature of 104℃, the samples' mass loss rates of are all 5%.It is mainly due to the mass loss of water evaporation. Before 240℃,with the increase of temperature, the samples show no obvious weight loss, the TG curves are almost horizontal lines at the drying stage .With the further increase of the temperature, obvious mass loss of Southern Pine samples take place due to the wood pyrolysis. Then enter the charring stage, when the initial pyrolysis temperature of untreated wood is about 247℃,while DOT treated wood 248℃,BA treated wood 258℃ and DOT treated wood 243℃.The highest initial pyrolysis temperature is about 265℃. At the stage of wood pyrolysis and charring, with the increase of temperature, followed with the mass loss rate of Southern Pine. As shown in Tab. 1,in the pyrolysis reaction range, the samples' mass loss rates rise sharply, so the TG curve shows a very steep steps. Then the samples' mass loss rates slow down, until after 750℃, the TG curves flatten out, this is the stage of calcinations. According to Table 1, the reaction interval of the wood treated with DBM delayed compared with other treated wood ,and showed a minimum mass loss. It implies that the thermal degradation of DBM treated wood is the slowest, so it has the best flame retardant efficiency. The mass loss rate of the Southern

Pine with only DOT or BA or $MgSO_4$ treated is smaller than that of the untreated wood. It illustrates that each treating agent have certain flame retardant effect for wood. From Tab. 1, we can also see, after dealing with the DBM composite treatment, the Southern Pine's peak temperature of maximum mass loss rate happens earlier than the other treated wood, and the char yield increases. It illustrates that DBM treated wood can have thermal decomposition reaction at low temperature. It is beneficial for the increase of charcoal production and the improvement of flame retardant effect.

From Fig.6, Southern Pine forms char between 247 and 382℃,and the char yield of treated wood increases significantly. It shows the 4 kinds of flame retardants have significant effect for promoting the charring of wood. Among them, the char yield of DBM treated wood is highest, then the DOT treated wood. It shows that the DBM composite treating agent is the optimum flame retardant with the best flame retardant efficiency. Meanwhile the increase of wood char conversion rate and carbonization quickly generates in the surface, which can decrease the speed of temperature transfer from external temperature to wood, slow down the thermal decomposition speed of wood, decrease the generation of combustible volatile matter, thus improve the flame retardant efficiency of wood. It can be seen that DBM treating agent can effectively promote the Southern Pine into charcoal at the calcining stage, playing the role of physical covers, thus achieve the effect of flame retardancy.

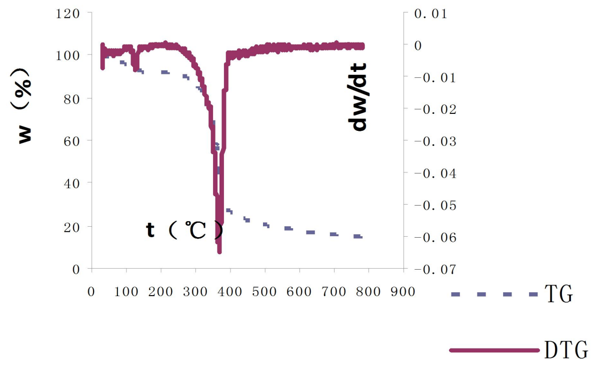

Fig.1 TG & DTG curves of untreated Southern Pine

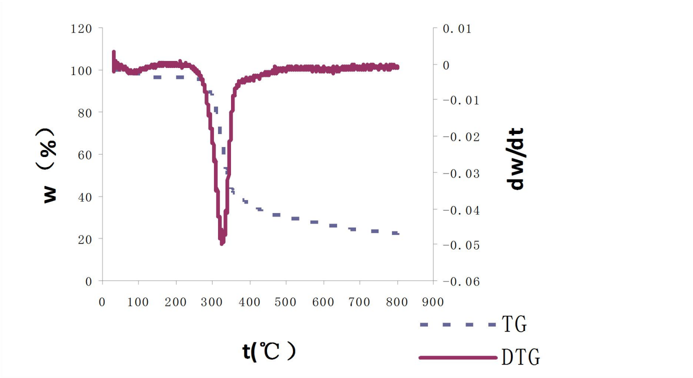

Fig.2 TG & DTG curves of treated Southern Pine by DOT

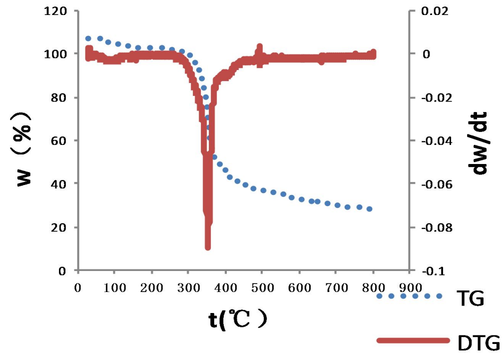

Fig.3 TG & DTG curves of treated Southern Pine by BA

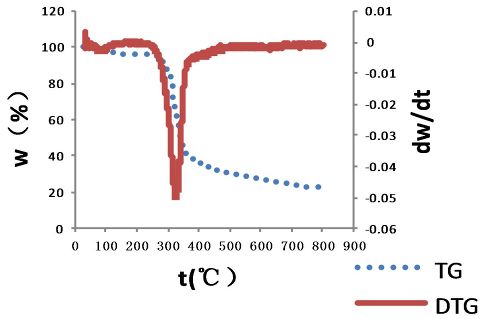

Fig.4 TG & DTG curves of treated Southern Pine by $MgSO_4$

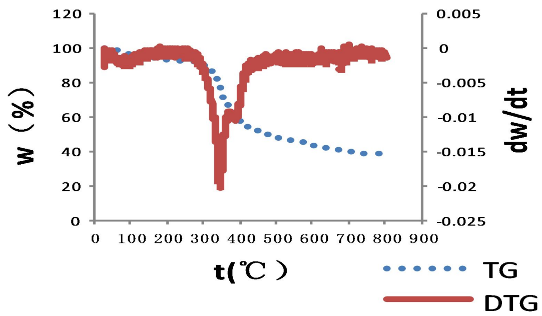

Fig.5 TG & DTG curves of treated Southern Pine by DBM

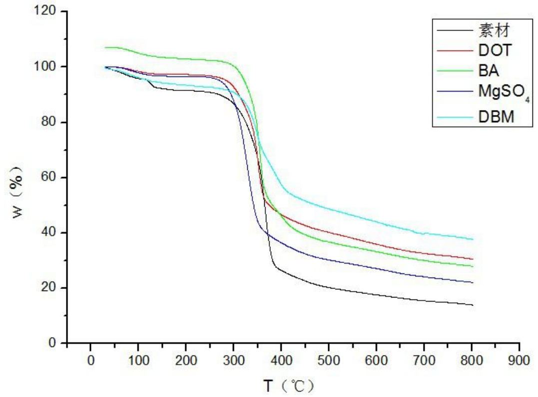

Fig.6 The comparison of TG curves of untreated and treated Southern Pine

2.2 Thermal dynamic equation analysis

From TG curves, it can be seen that wood heating process is divided into three stages, the drying stage, the charring stage and calcining stage. According to the thermal decomposition dynamics equation of solid, the thermal dynamic parameters at each stage of the heating process when treating Southern Pine are worked out to discuss the mechanism of flame retardant.

Generally the linear thermal dynamics equation of wood can be described as follows[6]

$$n=1,\quad ln[-ln(1-\alpha)] = ln\frac{AE}{\beta R} - 2.315 - 0.457\frac{E}{RT} \tag{2}$$

$$n\neq1,\quad ln\left[\frac{(1-\alpha)^{n-1}}{n-1}\right] = ln\frac{AE}{\beta R} - 2.315 - 0.457\frac{E}{RT} \tag{3}$$

The thermal dynamics equation[6] **of solid samples can be described as follows:**

$$V=\frac{da}{dt}=k(1-a)^n \tag{1}$$

Tab.2 Thermodynamic parameters of treated and untreated Southern Pine

Wood samples	Decomposition process	E(kJ·mol^{-1})	A(min^{-1})
Untreated wood	Drying stage	53.032	6.85×10^3
	Charring stage	97.262	8.36×10^3
	Calcining stage	29.669	620
DOT treated wood	Drying stage	24.167	2.88×10^3
	Charring stage	49.321	5.72×10^3
	Calcining stage	29.727	474
BA treated wood	Drying stage	34.430	1.53×10^3
	Charring stage	107.936	3.08×10^3
	Calcining stage	32.432	593
$MgSO_4$treated wood	Drying stage	22.451	3.17×10^3
	Charring stage	219.194	9.61×10^3
	Calcining stage	112.416	558
DBM treated wood	Drying stage	22.353	1.58×10^3
	Charring stage	143.798	5.27×10^3
	Calcining stage	16.160	581.5

In the expressions,
V——reaction rate (min^{-1});
t——reaction time (min);

a——reaction degree, as for TG method, $\alpha = \frac{W_0 - W_t}{W_0 - W_\infty}$, in it, W_0——the mass of wood before losing weight(mg),

W_t——the mass of wood when it's time t(mg), W_∞——the mass of wood when it stops losing weight;
n——reaction series;
k——reaction rate constant, according to Arrhenius Equation[7],the reaction rate constant has exponent relation to the temperature index, that is $k = Ae^{-\frac{E}{RT}}$.In it , A——apparent frequency factor(min^{-1}), E——apparent activation energy(kJ·mol^{-1}, R——universal gas constant 8.31kJ·kmol^{-1}, T——the reaction temperature when it's time t;

Linear thermal dynamic equation of wood can be deduced from Formula 1.

$$n=1,\quad ln[-ln(1-\alpha)] = ln\frac{AE}{\beta R} - 2.315 - 0.457\frac{E}{RT} \tag{2}$$

$$n\neq1,\quad ln\left[\frac{(1-\alpha)^{n-1}}{n-1}\right] = ln\frac{AE}{\beta R} - 2.315 - 0.457\frac{E}{RT} \tag{3}$$

in it, $\beta = \frac{\Delta T}{\Delta t}$

For better comparative analysis, it was assumed that the thermal decomposition of wood is the first order reaction[7], thus n = 1 linear thermal dynamic equation was chosen to analyze each stage of the reaction conditions of South Pine. From TG curves, the remaining amount of wood(W_1, W_2, W_3……)at certain temperature (T_1, T_2, T_3……)was read, to obtain the corresponding reaction degree, thus to work out the corresponding thermal dynamic parameters, activation energy(E) and frequency factor(A).The results are listed in Tab.2

From the thermal dynamic parameters listed in Tab.2,it can be seen that the activation energy for drying is 20～60 kJ·mol^{-1} ,which is equivalent to the energy dissipations of water evaporation in the drying process[8,9],In addition, after comparing the activation energy of different samples at the drying stage, we found that the activation energy decreases after flame resistant processing, it shows that flame resistant treatment makes the drying process more easier, which is in agreement with the previous report[6,10]. The activation energy of charring stage after flame resistant treatment increases, it indicates that the wood flaming combustion is inhibited by treating agent. Among the four treating agents, $MgSO_4$ has the most significant effect to inhibit the wood flaming combustion, the second is the DBM composite treatment agent.

CONCLUSION

1)After treating with Boron-Containing fire-retardant DBM, the Southern Pine mass loss rate decreases and the char yield increases. The rise of peak temperature of maximum mass loss rate indicates that the treating agent can have thermal decomposition at low temperature, which is beneficial for the generation of wood charcoal, playing a role as physical covers for Southern Pine, then improve the fire retardant performance of Southern Pine

2)Thermokinetic method is used to analyze the TG curves of the treated wood, and the DBM treating agent' mechanism of flame retardant effect to wood is illustrated by analyze thermokinetic parameters and combustion activation energy at each stage.

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