

THE ROLE OF BORIC ACID IN THE PYROLYSIS AND FIRE RETARDATION OF WOOD

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Abstract

It is commonly known that the mechanism of fire retardancy of boric acid is by forming a coating or protective layer on wood surface at high temperature. However, this mechanism could not explain the phenomena in our previous work, in which boric acid influenced the pyrolysis of wood at much lower temperature. To understand better the fire retarding mechanism of boric acid on wood, in this paper the effect of boric acid on the pyrolysis and fire retardancy of wood was studied by thermal analysis and cone calorimetry (CONE). Basswood (*Tilia amurensis* Rupr.) was treated with boric acid, guanylurea phosphate (GUP) and GUP boric acid respectively. The treated woods were analyzed by thermogravimetry (TG/DTG), differential thermal analysis (DTA) and by CONE. It was found in TG that the weight loss of boric acid treated basswood was about 3 times of GUP treated wood or untreated wood at 165 °C, the temperature at which GUP is stable. The DTA curve showed that boric acid treated basswood has an exothermal peak at 420 °C, indicating the exothermal polymerization reaction of charring. The CONE result showed that boric acid and GUP had considerable synergistic fire retardant effect on wood. It is concluded that boric acid has fire retardant effect on wood through mechanisms other than coating or protective layer, it has different effects in the different stages of the combustion of wood, it catalyzes the dehydration and decomposition of wood and promotes the charring of wood. The fire retardant synergism of boric acid and GUP is due to their functioning by different mechanisms.

1 Introduction

Boric acid is an important component of many fire retardants for wood (Lyons 1970) and has been used widely for a very long time. It is commonly known that the mechanism of fire retardancy of boric acid is by forming a coating or protective layer on wood surface at high temperature (Kandola and Horrocks 1996). However, it is doubtful that this very thin and/or uneven layer can effect so well when the boric acid loading in wood is very low. Further more, the coating or protective layer formation mechanism could not explain the phenomena in our previous work (Wang 1999, 2000), in which boric acid treated wood and boric acid guanylurea phosphate treated wood pyrolyzed at much lower temperature than untreated wood, the boron phosphorous synergism was observed in wide temperature range.

In order to understand better the fire retarding mechanism of boric acid on wood, in this paper the effect of boric acid on the pyrolysis and fire retardancy of wood was studied by thermal analysis and cone calorimetry (CONE).

2 Material and Method

2.1 Preparation of Samples

Air dry basswood (*T.amurensis* Rupr.) was cut into wood blocks of the size of 100mm (longitude) \times 100mm(radial) \times 10mm (tangential). The wood blocks were treated respectively with the aqueous treating solution of boric acid(B), Guanylurea phosphate(GUP) and GUP-B mixture that has the same molar ratio (FRW). The treating conditions were as follows: prior to the introduction of the treating solution, the wood blocks in the treating cylinder was subjected to a vacuum of -0.05MPa for 10 minutes. After the introduction (in vacuum) of the treating solution, the pressure was increased to 0.50MPa and maintained for 10minutes. The wood blocks were kiln dried at 70°C and conditioned at 23°C and 50% relative humidity to constant weight. The resulted wood blocks were used as wood samples for cone test. In order to make wood samples for thermoanalysis, the wood blocks were ground and filtrated separately to get the wood powder of 40 to 60 meshes. The wood powders were dried at 50°C and then used for thermoanalysis. For comparison, the three chemicals (boric acid, GUP and GUP-B) were also ground to 40~60 meshes. Prior to thermoanalysis wood and chemical powders were dried in a desiccator to constant weight.

2.2 Thermoanalysis

The thermogravimetry and differential thermal analysis were carried out using a Perkin Elmer TGA-7 thermogravimetric analyzer and a Perkin-Elmer 1700 differential thermal analyzer respectively. The TG and DTA curves were run under a dynamic nitrogen atmosphere flowing at 50mL/min and at a scanning rate of 10.0°C/min .

2.3 Cone Calorimetry

The cone calorimetric tests were done using a Standon Redcroft cone calorimeter under a heat reflux of 50kW/m^2 corresponding to a temperature of 780°C . The parameters of combustion were calculated from the basic data of the cone test by Microsoft Excel software.

3 Results and Discussion

3.1 Thermogravimetry(TG and DTG) of Fire Retardant Chemicals

The results of the thermogravimetric analysis were expressed by the thermogravimetric curves(TG) and its derivatives (DTG). The TG and DTG curves of boric acid (B) and guanylurea phosphate (GUP) and GUP-B(FRW) are shown in Fig.1~3. Fig 4 is the comparison of the TG curves of B, GUP and FRW.

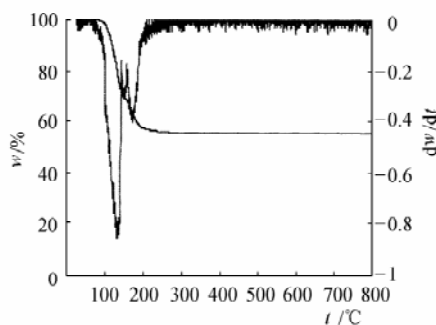


Fig.1 The TG and DTG curves of B

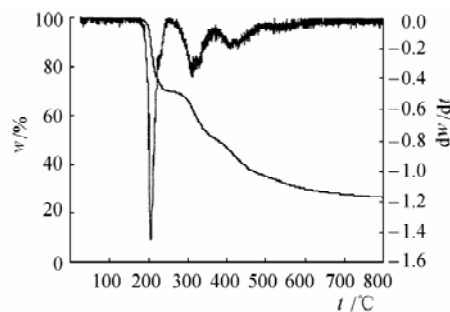


Fig.2 The TG and DTG curves of GUP

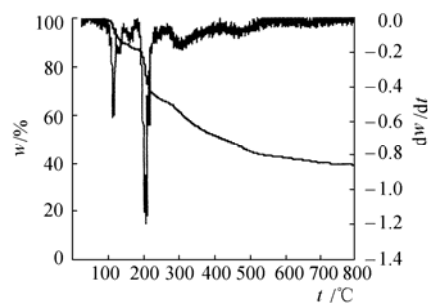


Fig.3 The TG and DTG curves of FRW

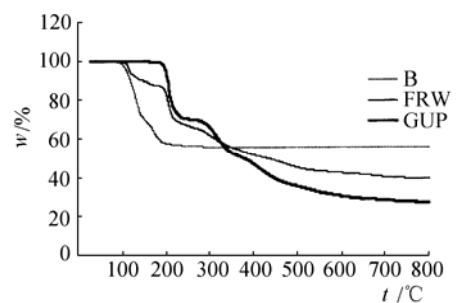


Fig.4 Comparison of the TG curves of B,GUP and FRW

By analyzing and comparing Fig.1~4, we know that the peak number of the TG(or DTG) curves of GUP-B(FRW) is equal to the sum of the corresponding peak number of B and GUP. The position (temperature) of peaks of FRW is the same as the corresponding peak of B or GUP. In other words, the TG or DTG curve of FRW is the linear combination of the corresponding curves of B and GUP. This explains that the decompositions of B and GUP in FRW take place separately. The decomposition temperature and products can be derived from these TG and DTG curves, and the results are shown in Table 1. The decomposition temperatures in Table 1 are the temperatures at which the chemicals begin to decompose obviously.

Table.1 The decomposition temperature and the corresponding products of FRW and its components

Samples	Temperature/°C				
	95	160	180	285	385
H ₃ BO ₃	H ₂ BO ₂	B ₂ O ₃	—	—	—
GUP	—	—	guanidine polyphosphate NH ₃ , CO ₂	ammonium polyphosphate NCNH ₂	polyphosphoric acid NH ₃
GUP-B	H ₂ BO ₂	B ₂ O ₃	guanidine polyphosphate NH ₃ , CO ₂	ammonium polyphosphate NCNH ₂	polyphosphoric acid NH ₃

3.2 Thermogravimetry (TG and DTG) of Wood Samples

Fig.5~8 are the TG and DTG curves of untreated basswood (UZ), boric acid treated basswood (BZ), GUP treated basswood (GZ) and GUP-B treated basswood (FZ) respectively. Fig.9 is the comparison of the TG curves of UZ, BZ, GZ and FZ.

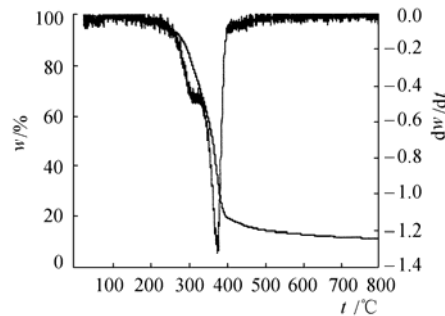


Fig.5 The TG and DTG curves of UZ

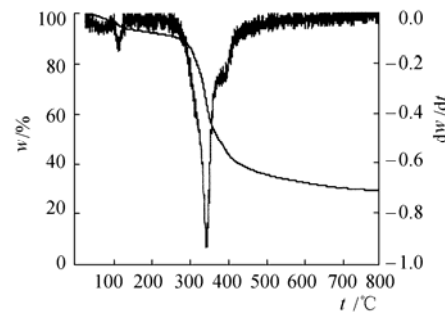


Fig.6 The TG and DTG curves of BZ

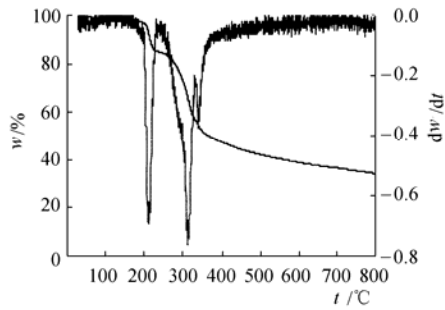


Fig.7 The TG and DTG curves of GZ

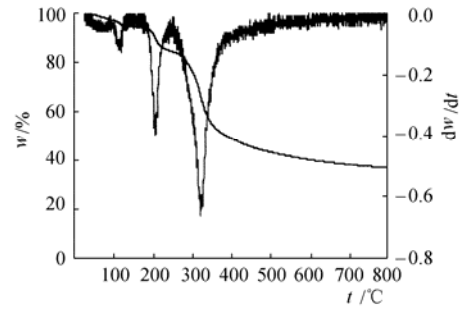


Fig.8 The TG and DTG curves of FZ

GUP or GUP-B treatment of wood increases its weight loss at lower temperature and decreases its weight loss at higher temperature. The fire retardant treatments of wood promote its charring. To perform a detailed analysis of the influences of the chemicals on the weight loss of the wood, the weight loss ratio of the wood samples were calculated and listed in Table 2. Concerning the lower thermal conductivity of wood, the higher decomposition temperatures (plus 5°C) than the corresponding values in Table 1 were selected.

Table 2 The weight losses of wood Samples at different temperature

Sample	Ratio of weight loss/%					
	100°C	165°C	185°C	290°C	390°C	800°C
UZ	1.6	2.0	2.4	11.6	77.9	88.9
BZ	3.3	6.8	7.3	11.6	53.6	71.1
GZ	1.6	2.0	2.6	23.5	51.9	65.1
FZ	3.1	5.7	6.2	20.4	50.3	63.3

Table 2 indicates that the final weight losses of the wood samples are of the following order: UZ > BZ > GZ > FZ, or the charring order is: FZ > GZ > BZ > UZ. The later is just the fire retardancy order of the corresponding chemicals. However, in the temperature range of 100~180°C, deducting the weight loss of boric acid itself, the weight loss of boric acid treated wood (BZ) are substantially higher than the values of untreated wood (UZ) and GUP treated wood (GZ), indicating that boric acid promoted the weight loss at lower temperature. Because boric acid treated wood considerably lose weight at a temperature lower than 165°C, the temperature at which untreated wood and GUP treated wood can only lose their absorbent water, we can deduce that boric acid catalyzed the dehydration of the wood.

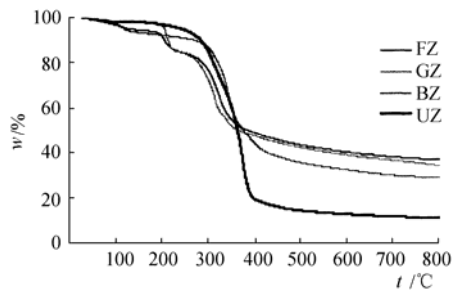


Fig.9 Comparison of the TG curves of UZ, BZ, GZ and FZ

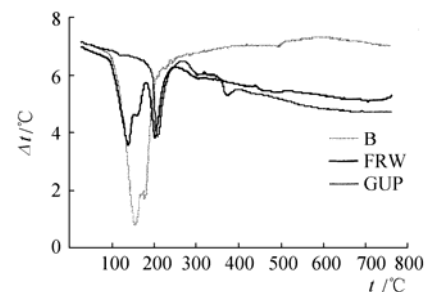


Fig.10 The DTA curves of B, GUP and FRW

In Fig.9, the trends of FZ,GZ andBZ curves are different and intercross. The FZ curve is between BZ and GZ at lower temperature, while in higher temperature period the FZ curve is the highest. We hence deduce that a synergistic effect is present between boric acid and GUP. Because no reaction takes place between boric acid and GUP and therefore no new chemicals formed, the synergistic fire retardant effect arises from the different fire retardant mechanisms and different activation temperatures of boric acid and GUP.

3.3 Differential Thermoanalysis (DTA) of Chemicals and Wood Samples

The DTA curves of B and GUP and CUP-B(FRW) are in Fig.10. Fig.11~13 are the comparisons of the chemicals, their treated wood and untreated wood respectively.

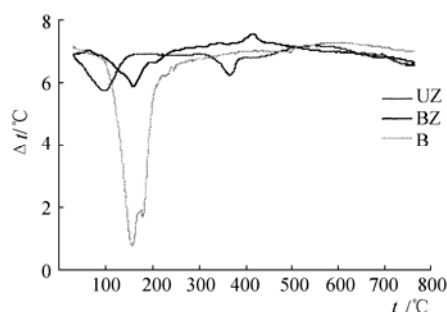


Fig.11 The DTA curves of B, BZ and UZ

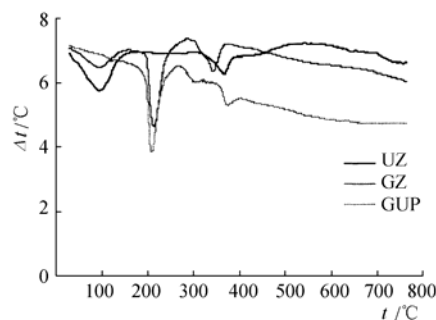


Fig.12 The DTA curves of GUP, GZ and UZ

Fig.10 indicates that the GUP-B (FRW) curve is the linear sum of boric acid and GUP, and this is consistent with the results of TG analysis. The endothermal peaks of boric acid and GUP in DTA curves are relevant to the weight loss peaks in the corresponding TG curves. This indicates that some of the decomposition products of B and GUP are volatile, like in Table 1.

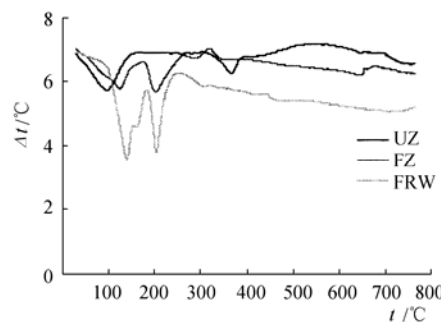


Fig.13 The DTA curves of FRW, FZ and UZ

The DTA curve of boric acid treated wood (BZ) has an exothermal peak at 425°C. This peak may be contributed to the catalytic effect of boron oxide on the charring of the polymeric products that are formed by the condensation and polymerization of wood decomposition products, resulting in aromatic structure. Reactions resulting in the structural change from aliphatic structure to aromatic structure are exothermal and can be catalyzed by Lewis acid at high temperature. There is a similar exothermal peak in the GUP-B treated wood (FRW) DTA curve, but at lower temperature. The reason of this phenomenon may be the co-catalysis of polyphosphoric acid (proton acid) and boron oxide(Lewis acid).

3.4 Cone Calorimetry

The RHR (Rate of Heat Release) curves of untreated wood (UZ), boric acid treated wood (BZ), GUP treated wood (GZ) and GUP-B treated wood (FZ) are in Fig.14. The peak RHR values (earlier $pkRHR_1$, later $pkRHR_2$) of the wood samples and the differences of the corresponding peak RHR values (earlier Δ_1 , later Δ_2) between treated wood and untreated wood (untreated minus treated) are listed in Table 3.

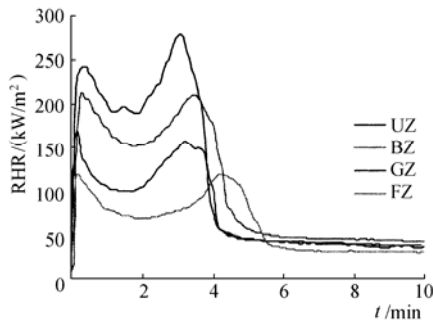


Fig.14 RHR curves of UZ, BZ, GZ and FZ

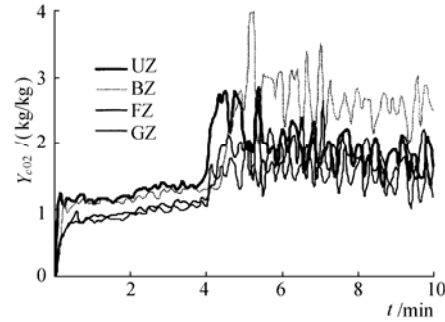


Fig.15 Carbon dioxide yields(Y_{CO_2}) of the woods

Table 3 The $pkRHR$ and Δ values of wood samples treated with different chemicals

Item	UZ	BZ	GZ	FZ
$pkRHR_1/(kW/m^2)$	242	206	169	116
$\Delta_1/\%$	0	15	30	52
$pkRHR_2/(kW/m^2)$	279	209	153	117
$\Delta_2/\%$	0	25	45	58

According to Fig. 14 and table 3, the fire retardant efficiency of GUP-B(FRW) is much better than boric acid and GUP. Suppose boric acid and GUP have additive fire retardant effect, namely, boric acid or GUP has the same fire retardant effects when they are used separately or as mixture, the Δ value can be calculated from the $pkRHR$ and Δ values and the chemical retention of the wood samples. The results are $\Delta_1(FZ)=29.9\%$ and $\Delta_2(FZ)=46.6\%$. The calculated Δ values of GUP-B are considerably higher than the determined value (52% and 58% respectively). It is obvious that boric acid and GUP are synergistic on wood.

The carbon dioxide yield (Y_{CO_2}) curves are listed in Fig.15. Y_{CO_2} is the combustion parameter indicating the carbon dioxide yield per weight loss of wood sample. All treated woods, including boric acid treated wood(BZ), have lower carbon dioxide yields in the flaming period of combustion. This explains that not only GUP but also boric acid catalyzed the dehydration and other oxygen eliminating reactions of wood, because these kind of reactions release products that contain more oxygen and therefore result in lower heat of combustion.

4 Conclusion

Boric acid catalyzes the dehydration and other oxygen eliminating reactions of wood at relatively lower temperature ($100 \sim 300^\circ\text{C}$), and may catalyze the isomerization of the newly formed polymeric materials to form aromatic structure. This contributes partly to the effects of boric acid on promoting the charring and fire retardation of wood.

There is considerable boric acid GUP synergism on wood. The mechanism of the strong fire retardant synergism is due to the different fire retardant mechanism of boric acid and GUP and the different activation temperatures of the two chemicals.

Acknowledgements

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