Synthesis and characterization of nitrogen-phosphorus-based fire retardants modified by boride/propanetriol glycidyl ether complex

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Abstract. A Boride/propanetriol glycidyl ether (B/PTGE) complex was employed to intensify the fire resistance capabilities of nitrogen-phosphorus (NP) fire retardants by reacting with phosphoric acid and urea to yield nitrogen-phosphorus-boron-PTGE fire retardants. The effects of NPB-PTGE fire retardants on wooden properties were characterized by limit oxygen index (LOI), cone calorimetry, X-ray Diffraction (XRD) and scanning electron microscopy (SEM). The results depict that the fire resistance of the B/PTGE complex modified by NP-based fire retardants was improved significantly. The PTGE was at 10% boride at 2%, and the treated wood has the LOI of 52%, which is 11.46% higher compared with woods treated with NP fire retardant.

1. Introduction

Wood products have been regularly used for centuries in many industries, particularly the building and construction sector. The advantages wood's worldwide availability, exemplary mechanical properties, and economical effectiveness make the flammability of wooden materials an increasingly worrisome topic [1]. The fire resistance of wood is limited. As no wooden material is completely fireproof, fire retardant treatment becomes a key precautionary tactic to prevent the combustion of structures [2]. To avoid fires, wood and wood-based materials can be treated using many methods, the most promising of which is fire retardant treatment. Nitrogen-phosphorus (NP) fire retardant has received considerable attention because it protects structures from fire with a minimum amount of associated health hazards, and is also convenient when enhancing the fire performance of wood-based materials. Under the heat

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of a young fire, the retardancy is achieved by forming a charred layer (serving as a physical barrier) that deters the heat and mass transfer of flame between gas and the condensed phases [3, 4]. A study focused on the fire propagation of particle boards treated with three commercial fire retardants showed that diammonium phosphate was preferred for reducing heat release, followed by monoammonium phosphate and BP (mixture of 27-33% boric acid, 67-73% guanylurea phosphate and 0.0-4.2% phosphoric acid) [5]. Due to various fire retardant mechanisms, utilization of a single fire retardant is unable to achieve ideal results, and thus the growing industry trend is to modify the basic concept of a fire retardant. In a comprehensive thermal study on the main components in fire-retardant formulas (such as pentacrythritol, melamine, and ammonium phosphate), the transformation mechanism of these substances during thermal degradation was described [6]. Moreover, melamine, melamin-formaldehyde resin, urea–formaldehyde resin (UF), and melamine-modified UF (MUF) mixed with NP fire retardant or the modified fire retardants significantly improved the fire retardancy, such as increasing oxygen index, prolonging ignition time, reducing heat release rate (HRR) and total heat release (THR), and decreasing mass loss rate [7-10].

Boron has the potential to decompose B₂O₃ and fashion a glassy protective layer, which promotes carbon formation and holds back volatile combustibles [11]. A modern form of phosphorus-nitrogen-boron (PNB) wood fire retardant consisting of the optimum formula of phosphoric acid, boric acid, and dicyandiamide was applied when treating wood [12]. High-boron, high-solubility wood preservatives such as SBB and (NH₄)₂HPO₄ were used to examine the overall fire retardant performance and test the swelling property, strength, and fire resistance of the treated wood [13,14]. The study's results showed that the synergetic effect of (NH₄)₂HPO₄ and SBB improved the fire retardant's performance [13, 14]. Wood fire retardant FRW, primarily including high purity amidinourea phosphate (GUP), boric acid, and a small amount of additives was developed, and the fire retardant mechanism of FRW was proposed [15, 16]. The results show that boric acid and GUP were both effective at varying temperatures by different fire retardant mechanisms. The two complement each other as synergistic additives [15, 16].

Although such systems have been studied extensively, many problems exist. These include the complex synthesis of fire retardants, the high costs, the use of poisonous melamine and dicyandiamide, and the overall effect of some formulas is not ideal. For improving the fire retardant efficiency and reducing the cost in this study, a boride/propanetriol glycidyl ether (B/PTGE) complex was employed to produce NPB- PTGE fire retardants, which can be compared to the boride or PTGE alone modified NP-based fire retardant. The fire resistant performance of the NPB fire retardant was evaluated by an LOI test and cone calorimetry, while the morphology and crystal structure of fire retardant- treated wood samples were investigated using XRD and SEM.

2. Experimental

2.1. Materials

Urea (Henan, ZhongYuan DaHua Company), 85% phosphate (Beijing Chemical Factory), Borax (Beijing Chemical Factory), and Propanetriol Glycidyl Ether (PTGE) (Beijing Chemical Factory) were used during the study. Additionally, wooden poplar specimens (150×6×3 mm³, 100×100×10 mm³) were used for the LOI and CONE experiments.

2.2. Synthesis of modified fire-retardants

Into a four-neck round-bottom flask:
- add pure phosphoric acid heat to 45°C under frequently stirring;
- add urea and heat to 90°C under stirring;
- add a given amount of catalysts and borax or PTGE or B/PTGE complex (see details in table 1);

after, heat to 135°C, hold for about 10 minutes, then pour the mixture out and obtain the fire retardant.
Table 1. Nitrogen and phosphorus fire retardant compound experiment with B/PTGE.

|     | NP/ (%) | Boride/ (%) | PTGE/ (%) |
|-----|---------|-------------|-----------|
| A   | 15      | -           | 10        |
| B   | 15      | 2           | -         |
| C₁  | 15      | 2           | 5         |
| C₂  | 15      | 2           | 10        |
| C₃  | 15      | 2           | 15        |
| C₄  | 15      | 2           | 20        |

2.3. Fire-retarding treatment of wood samples
The fire-retardants were dissolved in water, with the mass concentration of 15% for preparing the fire retardant woods. The wood specimens (150×6×3 mm³ and 100×100×10 mm³) were immersed in the four fire-retardants/aqueous solutions for 8 hours, then oven-dried at 105±2°C. The control group was set simultaneously. The samples were then stored in desiccators for tests.

2.4. LOI test
LOI is the minimum oxygen percentage required for maintaining a subject’s flaming combustion under specific laboratory conditions. LOI was measured by an LFY-606 LOI instrument (Shandong textile academy of sciences), and tests were conducted according to the method described in the National Standard of People’s Republic of China (GB/T2406-93).

2.5. CONE test
The CONE tests (ISO 1993) were conducted using an FTT cone calorimeter (East Grinstead, UK). The specimens were then encased in aluminum foil and horizontally exposed to a 35 kW/m² external heat flux to 750°C. The specimens were then ignited with a spark igniter. The parameters of combustion were later calculated based on basic data derived from the CONE test on Microsoft Excel.

2.6. XRD analysis [7]
XRD examination of untreated vs. treated wood samples was performed on an X-ray 6000 (Shimadzu, Japan) machine. All of the samples were initially grounded to pass an 80-mesh sieve, and air-dried prior to analysis. The X-ray beam was Cu-Ka (k = 0.1540 nm) radiation, operated at 40 kV and 30 mA. The scanning rate was 2.0°/minute, and 20 ranged from 5° to 50° with the rotation speed of 30 r/minute.

2.7. SEM analysis
Observations of the morphologies of untreated and treated wood specimen after the CONE test was performed by a Philips S-3400 SEM analyzer (Hitachi, Japan) using an acceleration voltage of 10 kV.

3. Results and Discussion

3.1. LOI of fire retardant treated wood
The LOI results are depicted in figure 1. Clearly, the LOIs increase significantly after being treated with fire retardants. As shown in our previous study [17], when the levels of Boride came to reach 2%, the fire retardant property is enhanced. The oxygen index of the fire retardant increases first, then decreases as the amount of PTGE increases, which is respectively 49%, 52%, 45% and 38%, and when compared with NP fire retardant processing material, the oxygen indexes are increased by 32.43%, 40.54%, 40.54% and 32.43%. When PTGE is at 10% and Boride lies at 2%, the oxygen index reaches its peak at 52%. This occurs primarily because the interactions between the boride and the fire
retardant. Additionally, the epoxy groups in PTGE can form chemical bonds with hydroxyl groups in the wood, ensuring the fixation.

Figure 1. Oxygen index of wood treated with a composite fire retardant.

3.2. CONE test of fire retardant treated wood
Figure 2 presents the curves of the heat release rate (HRR) and the mass loss rate (MLS) of the untreated and treated woods. The typical HRR curve of wood initially increases to a peak, then drops to a steady state. This is followed by a second peak as the final portion of the specimen is consumed [18]. The precise numbers are expressed in table 2. All analyzed samples displayed two separate HRR peaks during combustion, which indicated that gradual burning occurred after the formation of initial charred layers [19].

Table 2. The main fire retardant parameters of different fire retardant for wood.

|   | LOI/% | HRR/KW·m⁻² | THR/MJ·m⁻² | TTI/s | FPI/s·m²·KW⁻¹ |
|---|-------|-------------|-------------|-------|----------------|
|   | pk₁-HRR | pk₂-HRR |             |       | TTI/pk₁-HRR    |
| NP | 37.3 | 57.14(35s) | 119.49(340s) | 26.73(45.42%) | 15 | 0.263 |
| A₂ | 46  | 58.83(25s) | 93.90(340s)  | 22.82(53.40%) | 15 | 0.255 |
| B₂ | 49  | 67.75(75s) | 86.46(310s)  | 23.81(51.39%) | 10 | 0.147 |
| C₂ | 52  | 51.12(30s) | 92.38(335s)  | 21.30(56.5%)  | 12 | 0.235 |
| UW | 25  | 138.67(55s) | 170.75(275s) | 48.97 | 21 | 0.151 |

Figure 2. Heat release rates (left) and mass loss rate of treated and untreated wood (right).
The HRR of fire retardant treated wood (and the heat release rate peak) are lower than that of the untreated wood, indicating that fire retardants effectively inhibit the heat release from wood combustion. When compared to NP fire retardants, the PTGE, Boride and B/PTGE modified fire retardant complex perform more effectively, according to the heat release rate peaks at 21.4%, 27.6% and 22.7%. The first drastic HRR peak seen in the treated samples has been ahead in the A2 and C2 curve, which reveals that modified fire retardants can catalyze wood pyrolysis to a degree. The second sharp HRR peak of B2 curve appears later than others, which is more effective to the fire retardant properties [20].

According to the mass loss rate (MLR) curve of different fire retardant samples, the treated and untreated wood play a big different, the MLR value of the untreated wood is initially higher than the treated samples before 320 s, while, after 320s the MLR value of the treated wood is higher than the untreated one’s both under the continually decrease course. Which is nearly consistent with the HRR curve, therefore, the higher LOI value of the treated wood is due to their lower MLR and HRR value compared to the untreated ones especially at the first 300 seconds during their burning process.

Figure 3. Smoke production rate (left) and total smoke production (right) of treated and untreated wood samples.

Smoke generated rate (SPR) is a dynamic value of the smoke generation, and the area beneath the curve represents the total amount of smoke production (TSP). As depicted in figure 3, the untreated wood appears in two peaks in the SPR curve, and similarly with the HRR. This declares the heat releasing process is accompanied by heavily smoke release. However, the peak of the NP fire retardant treated wood only has one higher smoke peak at 0.0178 m²/s with a time delay compared to the untreated ones. The reason may be due to NP fire retardant’s ability to reduce combustion at the beginning of a burn to control a lower smoke production rate. And then with time extending, the NP fire retardant inhibits the charcoal burning to incompletely combust, emitting a lot of smoke.

The smoke production rate curve of the modified fire retardants vary from the former ones. The Boride and PTGE modified fire retardants respectively at 10 seconds and 14 seconds get the SPR peak, which suggests the wood released heavily smoke at the time of initial lighting. The first broad peak appears at approximately 30 seconds, while the second peak of the modified NP-based fire retardant (Boride, PTGE, and B/PTGE complex modified NP-based fire retardant numbered A2, B2, and C2) show different tendency: the A2 curve at the 370 second mark come out the second mild peak about 0.005 m²/s; the second peak in B2 curve is reduced to disappear; the SPR of C2 keeps in a low state around 0.0015 m²/s.

We can also see that the TSP curves differ from the treated and untreated wood samples. While the untreated wood sample has the largest amount of 2.5 m² with a rapid increasing rate, the NP fire retardant, A2, B2, and C2 are shockingly lower than the untreated one, being 1.72 m², 0.87 m², 0.49 m² and 0.27 m². Additionally the TSP of NP fire retardant is higher than A2, B2, and C2, meaning that the
NP fire retardant can only manage the smoke release, not change its burning mechanism. And the results of C₂ are fulfilled, showing the synergy effect of boride and PTGE in the smoke release control.

3.3. XRD analysis of fire retardant treated woods
LOI is the lowest oxygen percentage appropriate for maintaining a specimen’s flaming combustion under specified laboratory conditions. In the study, LOI was measured by an LFY-606 LOI instrument (Shandong Textile Academy of Sciences) according to the technique communicated in the National Standard of People’s Republic of China (GB/T2406-93). Figure 4 shows the XRD patterns of the untreated and treated wood. The characteristic peaks for the untreated woods appear at 2θ=16°, 22° and 35°, which corresponds to the crystal plane diffraction peaks of (101), (002) and (040), respectively. On the diffractograms of the treated woods, peak (101) were enhanced and three additional peaks around 2θ=23.5°, 33.6° and 45° were registered in the XRD curves, and are related to the crystalline structure of fire retardants.

The crystallization of the wood was enhanced to 38.55% (NP), 40.18% (A₂), 39.96% (B₂) and 41.14% (C₂). PTGE can improve the wood’s cellulose crystallinity, because it can react with the hydroxyl groups on cellulose in the amorphous region while rearranging the microfibril, and drag them to the crystalline region to increase the cellulose crystallinity. Therefore, the B/PTGE complex modified NP-based fire retardant is the optimal for wood modification [21].

![Figure 4. XRD of untreated wood and treated wood.](image)

3.4. The morphologies of the fire retardant treated woods residuals after combustion
The morphology of the char residue that was formed after the CONE test was observed through SEM. As shown in figure 5, the char residue generated from the untreated wood reveals a gray sprawled structure (seen in figures 5a), while those generated from the treated wood show a dense form (figures 5b-5e). Additionally, the fiber structures of the Boride, PTGE or B/PTGE complex modified by the NP fire retardant treated wood samples retain relatively complete, and a dense carbon layer is formed at the surface. The justification may be that the NP fire retardant has the capability to thermally decompose acid material, which can promote the PTGE decomposing into a viscous polymer containing massive N/P elements. Therefore, the carbon layer structure and its properties may be regulated to a denser one, which can create a non-flammable coating, beneficial to the improvement of fire retardant capabilities on the surface of the burnt wood.

4. Conclusions
The fire retardant properties of wood were significantly enhanced after being treated with the B/PTGE complex modified NP-based fire retardant. When the PTGE levels were at 10% and Boride at 2%, the treated wood maintained the LOI of 52%, which is 11.46% higher compared with woods treated with NP fire retardant. The HRR and MLR curves show the wood treated with fire retardants had undergone obvious improvements.
XRD analysis indicated that the main crystalline structure of wood was not affected by the fire retardant treatment. The wood treated with the B/PTGE complex modified NP-based fire retardant has higher crystallization, which is optimal for wood modification.

According to SEM analysis, a dense structure was observed in treated woods, which is beneficial to improving fire retardant properties of wood.

An optimization of the NP-based fire retardant modified by the B/PTGE complex is achieved in this study, as to the formation of a protective cover on the wood surface, which validly inhibits the wood burning process.

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