Progress in Research on Fire Retardant–Treated Wood and Wood-Based Composites: A Chinese Perspective

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Progress in Research on Fire Retardant–Treated Wood and Wood-Based Composites: A Chinese Perspective

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Abstract

Research on fire retardant–treated wood and wood-based composites has been conducted in China for over two decades. Although many kinds of fire retardants for wood and wood-based composites have been studied, the focus is still mainly on compounds or mixtures containing phosphorus, nitrogen, and boron, which can be used in a water solution for solid wood impregnation. Fire-retardant treatment methods for wood-based panels are either pretreatment of veneers, fibers, particles, or strands before hot pressing or impregnation of waterproof panels with fire-retardant solutions. Though attempts have been made in laboratories and factories to mix the fire retardants with glues, it has proven very difficult to spray the glue smoothly and to deliver effective amounts of fire retardants during the manufacture of panels. The mechanisms of phosphorus–nitrogen–boron fire retardants have been investigated systematically. The results indicate that the phosphorus–nitrogen compounds and the boron compounds are highly synergistic in effective fire-retardant formulations. The catalytic charring effect of a fire retardant on wood is a key factor in its efficacy. A chemical fire-retardant mechanism for boric acid is also proposed.

Research on fire retardants for wood–plastic composites has been attracting more attention in recent years; however, most results are preliminary because of the difficulty in identifying or formulating a fire-retardant system that is effective for both wood and plastics.

Only preliminary research has been conducted on smoke suppression for wood; innovative efforts will be needed to conduct further research.

The history of the use of fire retardants in wood can be traced back to early civilizations such as ancient Rome, when wood was impregnated with vinegar and lime to build fire-resistant warships and housing (Shfizadeh 1968). Research on fire retardants for wood continued in the following centuries. The earliest references found relating to fire retardants were the British patent no. 551 issued to Obadiah Wyld in 1735 and the scientific article published by Gay-Lussac in 1821 (Lawson 2009). Since then, research on fire retardant–treated wood and wood products and their applications have steadily increased throughout the world.

In the 1980s, guanidine phosphates were synthesized and used as fire retardants for wood at Northeast Forestry University (Luo and Li 1989; Zhao et al. 1994, 1995). Since the 1990s, more research efforts have been focused on wood fire retardants in China (Liu 1997, Hu 2006). Fire retardants containing phosphorus, nitrogen, and boron compounds or mixtures of these are among the most important and can be classified into different categories such as inorganic, organic, resin based, reactive, or other types, according to their chemical nature and application characteristics. However, only a few fire retardants display the performance required for use in wood treatment applications in China (Wang 1999).

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The requirements for fire retardants for wood have expanded from an initial focus on fire retardancy to encompass other factors such as smoke inhibition, environmental impact, additional performance (such as preservative, antitermite, etc.), and economic aspects. The stipulations in relevant regulations and standards for wood fire retardants have become stricter, making the design and development of new wood fire retardants more difficult (Wang 1999). For some time now, several research institutions in China have been extensively involved in developing fire retardants for wood and wood products; these include Northeast Forestry University, the Chinese Academy of Forestry, Beijing Forestry University, the Central South University of Forestry & Technology, Nanjing Forestry University, Fujian Agriculture and Forestry University, and Southwest Forestry University, as well as some fire departments and corporations. Some new types of high-performance and multifunctional wood fire retardants have made their appearance in China over the last 20 years (Wang 2000a; Jiang and Liu 2006; Long et al. 2006; Wang et al. 2008a, 2008b).

In the beginning of the 2000s, extensive work was conducted to develop new types of wood-based composites and wood–plastic composites (WPCs), and some of these have shown great potential for commercial applications in indoor decoration and furniture manufacturing. As WPCs are usually more flammable and release much more heat than wood, fire retardancy research for WPCs has attracted more attention in recent years (Li et al. 2004, Li 2006b, Fang et al. 2008, Shao et al. 2008, Song et al. 2011).

Fire-Retardant Technology for Wood and Wood-Based Composites

Wood treated with fire retardants

Laminating and coating treatments.—In many cases, the combustible wood is laminated or coated with fire-resistant or noncombustible materials in order to achieve fire retardancy. For example, laminating a layer of metal material or gypsum board can effectively separate the wooden panel from the external environment; thus, if a fire ignites outside, the wood does not easily or immediately ignite, providing enough time for building evacuation and fire suppression. However, if the covered wood is exposed to the fire for a long period of time, the fire-retardant layer is eventually destroyed along with its protective function.

Among the different techniques available for surface treatment and protection, the fire retardant–coating method has been commonly used to enhance the fire retardancy of wood (Gu 1996, Chen-Yang et al. 1998). Work conducted recently suggests that the use of intumescent fire-retardant coatings may be one of the easiest, most economical, and efficient ways to protect wood against fire (Zheng 2004; Huang 2005; Zhou 2006; Chou et al. 2009, 2010; Wang et al. 2010). The intumescent coating, with its high fire-retardant effect and safety factor, is a novel type of treatment. When exposed to fire, the intumescent coating changes into a foam charring layer. The charring layer can isolate the wood substrate from heat and oxygen, and delay the onset of wood pyrolysis, effectively protecting the wood structure for a period of time. The main shortcoming of this approach, however, is that if the coating layer is damaged or the charring layer falls off during the fire, the fire-retardant performance is lost.

Impregnation treatment.—The impregnation process is a fire-retardant treatment technique that involves injecting a fire-retardant solution into the wood under different conditions of pressure (atmospheric pressure, vacuum, or high pressure). The type of equipment required and the effect of the treatment vary considerably depending on the type of pressure condition used. The most common methods of treatment currently used in China are pressure impregnation and soaking. The pressure impregnation method is commonly used to treat large-sized wood pieces, while the soaking method is used for thin veneers, wood particles, wood fibers, and other wood raw materials; this latter method yields a better treatment effect and cost advantage compared with other methods.

In the 1990s, a new fire retardant for wood was synthesized. This fire retardant is mainly composed of pure guanylurea phosphate (GUP), boric acid, and minor amounts of additives (GUP-B; Wang 2000a); it has excellent fire retardancy, smoke inhibition, and preservative and antitermite performance (Wang et al. 1999a, 1999b; Li et al. 1999a, 1999b; Zhang et al. 2007). Besides its suitability for treating solid wood, GUP-B has been used in the fire-retardant treatment of wood-based composites, such as plywood (Liu et al. 2004), medium-density fiberboard (MDF; Liu et al. 2003b), and oriented strand board (OSB; Winandy et al. 2008).

As some fire retardants for wood are also catalysts that can cause wood degradation, especially at elevated temperature and humidity conditions, it is important to determine the mechanical properties of fire retardant–treated wood after a long exposure to such conditions. Research on the mechanical performance of fire retardant–treated wood exposed to elevated temperatures was performed at Northeast Forestry University and the US Department of Agriculture (USDA) Forest Products Laboratory. Clear specimens of Korean pine (*Pinus koraiensis*) treated with GUP-B were either air dried after treatment or kiln dried at 70°C, and were then subjected to a steady-state exposure at 66°C and 75 percent relative humidity for various amounts of time (Wang et al. 2005b). No significant differences in thermal degradation between the controls and the GUP-B–treated Korean pine specimens were found, regardless of whether the specimen had been air dried or kiln dried after treatment. However, for other tested fire retardants with much lower pH values, the kiln-redried materials displayed significantly more degradation compared with the air-redried materials. On exposure to elevated temperatures, the strength and stiffness of GUP-B–treated Korean pine deteriorated, but the extent was less than that previously reported for the standardized GUP-B formulations produced using different manufacturing processes (Winandy 1995; Table 1). Because of the lower acidity resulting from the modified manufacturing process, the stability with respect to thermal degradation was improved for this enhanced GUP-B.

Some progress was made by Li et al. (2006) using microwave and ultrasonic techniques during the impregnation process of the wood with fire retardants. A mixture containing a resinous type of fire retardant and low-molecular-weight phenol-formaldehyde resin was used to treat Ussuri poplar in order to achieve the desired fire retardancy (Li et al. 2009).

Chemical modification.—A permanent fire-retardant effect can be achieved by treating wood with a reactive fire retardant. The fire-retardant elements and/or chemical groups

Table 1.—*Changes in modulus of elasticity (MOE) and modulus of rupture (MOR) of treated wood specimens during exposure to 66°C.*[a]

Exposure time (days)	GUP-B kiln dried		Standardized GUP-B formulation	
	MOE (GPa)	MOR (MPa)	MOE (GPa)	MOR (MPa)
0	8.56	79.8		
7			14.1	105.9
21	8.02	69.7	13.3	104.9
60			13.3	98.8
70	7.88	64.6		
125	7.72	62.8		
160			12.2	78.3
200	7.53	58.1		
290			13.3	69.8
Slope (dx/dt)	−0.004	−0.092	−0.002	−0.136
r^2	0.791	0.809	0.186	0.953

[a] Data compiled from Wang et al. (2005a). GUP = guanylurea phosphate; B = boric acid.

containing these elements can be bonded to wood molecules by stable chemical bonds. Because the fire-retardant elements become distributed in the wood as single molecules, the durability, leaching resistance, and fire retardancy associated with reactive fire retardants are usually superior to those achieved using additive-type fire retardants (Wang 2000b). Hydroxyl groups and benzene rings are useful functional groups located on the walls of wood cells, through which fire-retardant elements can be attached by reactions such as esterification, transesterification, etherification, and halogenation. The reaction taking place between the reactive fire retardant (such as phosphoryl chemicals) and wood can occur at the liquid–solid interface. It may also occur at the gas–solid interface, for instance by using a low-molecular-weight boric acid ester in a gas treatment. This method has not yet reached the practical stage, but has opened a new path for the manufacture of special purpose fire retardant–treated wood products (Wang 2000b).

Fire retardant–treated wood-based composites

At present, development in the wood-based composites industry is rapid and its application field is wide. According to an online source (CIConsulting 2010), wood-based composite product capacity in China has grown by more than 20 percent annually in the past 10 years. Application sectors include furniture, building finishing and decoration, vehicles, and vessels, to name just a few. These products, however, have very poor fire performance because of their flammability. Fire-retardant performance requirements of wood-based composites are gradually receiving more attention from users, regulators, standards developers, and wood scientists. Fire-retardancy standards designed for particleboard (GA 87-94, public security standard), plywood (GB 18101-2000, national standard), and MDF (GB/T 18958-2003, national standard recommended) have been developed and successively implemented in China. Standards GB 8624-2006 (Classification for Burning Behavior of Building Materials and Products) and GB 20286-2006 (Requirements and Mark on Burning Behavior of Fire-Retarding Products and Sub-Assemblies in Public Places) were issued on June 19, 2006, and implemented on March 1, 2007. The implementation of mandatory national standards (GB 8624-2006 and GB 20286-2006) shows that the fire-retardant material industry, including fire retardant–treated wood and wood-based composites, is stepping into a new development era. In 2009, 400 industry leaders, experts, and scholars, and corporation delegates attended the First National Seminar on Fire-Retardant and Environmental Wood-Based Composites in Yanggu, Shandong Province, which provided a forum for in-depth discussion and exchange on the production technology and product applications of fire retardant–treated and environmental wood-based composites. The direction of developments in these composites was an important issue for all of the attendees. This seminar played a positive role in publicizing the national fire codes, exchanging technology and experiences, and promoting development in the fire-retardant wood-based composite industry.

Fire retardant–treated MDF.—MDF is used in China in interior decoration, furniture manufacturing, and architectural structural components. However, because of its flammability and associated fire hazard, its applications have been limited in some areas.

Fire retardant–treated MDF is produced mainly by posttreatment of MDF or pretreatment of the fiber with fire retardants. Fire-retardant treatment of the board is similar to that of solid wood, but not identical, since the mechanical properties of the board may be seriously affected by high chemical loading or water content during pressure impregnation. Wang (2007) used inorganic and organic fire retardants to impregnate MDF panels and found that the limited oxygen index (LOI) of the treated panel increased, the temperature range of thermal degradation became wider, and the charring time increased. Fire-retardant treatment of the fibers can be conducted in different stages during the board manufacturing process, such as during refining, before sizing, during sizing, and during the mat forming process, as described below.

Fire-retardant treatment in the refining stage.—In this process, a water-soluble fire retardant is mixed with the wood chips at the time of refining, achieving an effect similar to impregnation. The treated material can then be formed into a mat after drying and sizing. This approach is simple and the cost of running the production equipment is low. However, its main limitation is the fire retardant because the insolubility of a solid chemical or lack of resistance to the hot grinding temperature can make this approach difficult to use.

Fire-retardant treatment before the sizing process.—A fire-retardant solution or fine powder is sprayed onto the fibers, followed by even mixing of the fire retardant and fibers and drying of the mixture before sizing. This treatment method results in a better fire-retardant effect because the fire retardant is more evenly distributed compared with the other methods, but equipment and energy costs are high because of the additional drying step, which complicates the overall production process. At present, this is still the main method used in the production of fire retardant–treated MDF in China, and a more advanced technique needs to be developed. Some studies were conducted by Zhang and Li (2006a, 2006b) on the manufacturing of fire retardant–treated MDF using this method. The LOI of the MDF produced was about 50 percent, exceeding the 48 percent value of fire-retardant grade MDF. The results obtained for the moisture content, thickness swelling, internal bond strength, modulus of

rupture (MOR), and modulus of elasticity (MOE) all met the requirements of the national GB standards. In addition, the formaldehyde emissions were found to be less than the E1 level in the MDF GB/T 11718 standard.

Fire-retardant treatment during the sizing process.—A fire retardant is mixed with an adhesive to form a suspension or emulsion, which is then sprayed onto the fiber, simplifying the production process and reducing operating costs. However, application of this treatment technology is restricted by a number of variables such as particle size for insoluble fire retardants; pH value for soluble fire retardants; compatibility between the fire retardant, the adhesive, and the fibers; as well as other issues. Thus, very few fire retardants are suitable for use with this treatment method. Liu et al. (2003a) made MDF via a dry process with GUP-B fire retardant. GUP-B, adhesive, and waterproofing agents were sprayed on the fibers at the same time. The effect of GUP-B on the mechanical properties and fire retardancy of the MDF produced was excellent: the physical and mechanical properties of GUP-B fire retardant–treated MDF reached the primary requirements of the GB standards, and its performance achieved the primary requirements of JISD 1322-77. Liu and Wang (2009) conducted a detailed investigation of the impact of GUP-B addition and hot-pressing temperature on the performance of the fire-retardant MDF produced.

Fire-retardant treatment in the mat forming process.— With this method, fire retardants are sprinkled in a slab, so that a high concentration can be distributed uniformly at a certain thickness and, consequently, achieve good fire-retardant efficiency with minimal chemical loss. In production, however, it is difficult to achieve distribution of fire retardants on both sides of a mat in the forming machines. In addition, uneven distribution of fire retardant may have a negative effect on the mechanical properties of the MDF panel (Zhang 2005). Wu and Yang (2010) mixed fire retardants with presized fiber and studied the burning behavior of MDF treated with ultrafine aluminum hydroxide [$Al(OH)_3$]. The effect of fire-retardant content on the combustion properties of fire retardant–treated MDF was determined using a cone calorimeter; the results are shown in Table 2. Among the burning behaviors, the decrease in the average specific extinction areas (SEA) and total smoke production was the most significant, which indicated that MDF treated with ultrafine $Al(OH)_3$ had good smoke suppression properties. Ultrafine $Al(OH)_3$ had some effect on the heat release of the treated MDF, and the total heat release (THR) was found to decrease by 40 percent at the highest addition level, about 60 percent in this experiment.

Although many studies on fire retardant–treated MDF have been reported and some MDF factories have now been built to produce fire-resistant products, there are still many challenges and difficulties in the process of industrializing fire-retardant technology. One of the major challenges is that the amount of fire retardant in MDF products usually needs to be applied at very high levels in order to achieve a good fire performance, which obviously affects the mechanical properties of the products; thus, applications for fire retardant–treated MDF are limited. In addition, most traditional fire retardants used in fire retardant–treated MDF are acidic organic or inorganic compounds (such as ammonium sulfate, ammonium phosphate, ammonium polyphosphate, organic phosphates), and when these fire retardants are in direct contact with wood fibers, they catalyze and degrade the wood fibers, especially in regions with hot and humid climates; such environmental conditions may significantly impact the strength of fire retardant–treated MDF (LeVan and Winandy 1990, Li 2006a).

Fire retardant–treated particleboard.—Because of its high strength, ease of production, and low cost, particleboard is suitable for applications in the fields of building decoration, furniture, and transportation. However, since the raw materials for particleboard (wood furnish bonded with organic adhesives) are flammable, the wood furnish and resulting particleboard panels need to be treated with fire retardants. The treatment technology for particleboard is similar to that used for fire retardant–treated MDF, and the possible treatment stages include before sizing, during sizing, during the mat-forming process, and posttreatment of the board.

Wang and Li (2005b) used an environmentally friendly fire retardant to improve the fire-resistant properties of particleboard. The board was treated by impregnation, spraying, and roller coating, respectively. Compared with the untreated board, the fire retardant–treated particleboard had a certain degree of fire retardancy, similar mechanical properties, and decreased formaldehyde emissions. Wang et al. (2006b) used the liquid and powder forms of the BL fire retardant (an inorganic fire retardant formed from phosphoric acid and urea) to treat wood shavings. The results showed that the fire-retardant performance of the powder form was improved. Wang (2006) compared particleboard treated with BL fire retardant with boards treated separately with other inorganic fire retardants mixed with the BL fire retardant (5% aluminum hydroxide + 10% BL, 10% aluminum hydroxide + 5% BL, 5% magnesium hydroxide + 10% BL, and 10% magnesium hydroxide + 5% BL), and found that boards treated with the BL fire retardant alone had the highest LOI among all of the samples tested (Table

Table 2.—Cone calorimetry results of effects of fire-retardant content on combustion properties of fire retardant–treated medium-density fiberboard.[a]

m($Al(OH)_3$): m(wood fiber) (%)	TTI (s)	pk HRR (kW/m²)	Average HRR (kW/m²)	THR (MJ/m²)	Average EHC (MJ/kg)	Average SEA (m²/kg)	Average MLR (g/s/m²)
0	26.5	391.9	100.8	85.4	12.3	43.3	11.1
10	31.8	260.5	83.2	66.3	10.4	31.8	11.3
30	52.5	177.0	90.0	68.2	9.8	73.5	11.2
60	50.7	120.3	60.3	49.2	6.2	5.0	6.8

[a] Data compiled from Wu and Yang (2010). TTI = time to ignition; pk = peak; HRR = heat release rate; THR = total heat release; EHC = effective heat of combustion; SEA = specific extinction area; MLR = mass loss rate.

Table 3.—Physical and mechanical properties and limited oxygen index (LOI) and smoke density rating (SDR) results for particleboard.[a]

Treatment	Density (ρ/g/cm^3)	Moisture content (%)	Internal bond strength (MPa)	Thickness swelling (%)		LOI (%)	SDR
				2 h	24 h		
Control	0.66	7.11	1.12	3.4	8.5	26	51.77
15% BL	0.75	6.21	0.85	5.4	11.6	48.6	53.84
10% BL + 5% Al(OH)$_3$	0.77	6.15	0.72	3.4	13.5	45.8	55.49
5% BL + 10% Al(OH)$_3$	0.74	5.98	0.75	5	15.6	43.1	53.08
10% BL + 5% Mg(OH)$_3$	0.74	7.32	0.76	4.1	13.7	45.8	48.97
5% BL + 10% Mg(OH)$_3$	0.76	6.53	0.70	5.3	14.8	44.4	47.25

[a] Data compiled from Wang (2006). Density, moisture content, internal bond strength, and thickness swelling tested according to GB/T 17657-1999; LOI tested according to GB/T 2406-1993; SDR tested according to GB/T 8627-1999.

3). Jiang et al. (2009) modified the BL fire retardant with melamine, melamine–formaldehyde resin prepolymer, and zinc borate and used this modified BL fire retardant to improve the fire performance of particleboard. It was found that the mechanical properties of the fire retardant–treated particleboard were strengthened, and that the formaldehyde emissions decreased when melamine and melamine–form-aldehyde resin prepolymer were used to modify the BL fire retardant. The results obtained also showed that the LOI of boards containing BL fire retardant modified with zinc borate was 49.6 percent, which was higher than the value of 38.6 percent found for the board containing the unmodified BL fire retardant.

Na and Zhou (2003) grafted halogen-based fire retardants to the main or side chains of phenolic resin to synthesize a fire-retardant phenol-formaldehyde resin. Particleboard pre-pared with the resulting adhesive achieved fire retardancy and mechanical properties that met the requirements for Class A in the GB/T 4897-1992 standard and Class I in the GB 7911.6-1987 standard. Deng and Zhang (2003) selected boron and phosphorus–nitrogen fire retardants and mixed them in different ways at different concentrations. Each mixture was used to manufacture particleboard by adding the mixture to the wood furnish during the blending process. The test results showed that boron and phosphorus–nitrogen fire retardants mixed at a particular ratio improved the fire retardancy of the board, while maintaining the mechanical properties required to meet the GB/T 4897-2003 standard. At Sichuan University, Tang (2007) synthesized two new phosphorus-containing intumescent fire retardants: (1-oxo-l-phosphabic-2,6,7-trioxa-yclo[2.2.2]octane-4-carbonyl) neo-pentyl glycol ester and di(2,2-dimethyl-1,3-propanediol phosphate) urea (DDPPU). It was reported that DDPPU and H_3BO_3 had synergistic effects when they were mixed

together. Under the same condition, the LOI of the mixture was found to be 46.0 percent, which was higher than that obtained for DDPPU by 7.9 percent. Liu et al. (2009) produced excellent particleboard by mixing the fire-retardant GUP-B with glue.

A collaborative project between Northeast Forestry University and the USDA Forest Products Laboratory was conducted regarding the application of GUP-B to wood and wood-based composites. Winandy et al. (2008) treated wood shavings first with GUP-B and dried them to the desired moisture content. Diphenylmethane diisocyanate adhesive was used as the binder in preparing fire retardant–treated OSB. The mechanical properties of this OSB were evaluated according to American Society for Testing and Materials (ASTM) D1037 and ASTM E2102, and the test results indicated that the treatment had little impact on the board mechanical properties (Table 4) but significantly improved the board fire-retardancy performance (Fig. 1). Wang et al. (2008c) manufactured fire retardant–treated low-formalde-hyde-emission particleboard from recycled wood-waste particles using polymeric 4,4′-methylenediphenyl isocya-nate and phenol-formaldehyde resins. This particleboard was found to pass the third grade standard for surface fire resistance performance, as specified by Chinese National Standard 6532.

Fire retardant–treated plywood.—Plywood is used as an engineered material due to its strong antifracture, anti-shrinkage, and antitwist properties, as well as its high strength. However, because of its obvious flammability, in order for plywood to be used in some applications such as airport terminal lobbies, restaurant entertainment areas, office buildings, schools, and storage warehouses, it must be treated to improve its fire performance to meet environ-mental and safety requirements.

Table 4.—Means and standard deviations (in parentheses) of physical and mechanical tests for flexural and internal bonding properties evaluated according to ASTM Standard D 1037.[a]

BOP-FR loading levels[b]	Static bending properties		Specific gravity	Internal bond strength (MPa)	
	MOE (GPa)	MOR (MPa)		Dry	Wet
Control: untreated	5.274 (0.863)	28.508 (7.686)	0.60 (0.05)	0.72 (0.26)	0.64 (0.14)
Control: water-treated	4.725 (0.762)	25.414 (3.934)	0.60 (0.03)	0.73 (0.10)	0.55 (0.16)
5.30%	5.503 (1.298)	28.380 (8.972)	0.65 (0.04)	1.20 (0.12)	0.79 (0.27)
9.80%	5.043 (0.443)	25.775 (5.336)	0.69 (0.03)	1.14 (0.22)	1.11 (0.17)
13.80%	5.804 (0.370)	27.762 (5.563)	0.75 (0.04)	1.20 (0.10)	1.00 (0.27)

[a] Data compiled from Winandy et al. (2008).
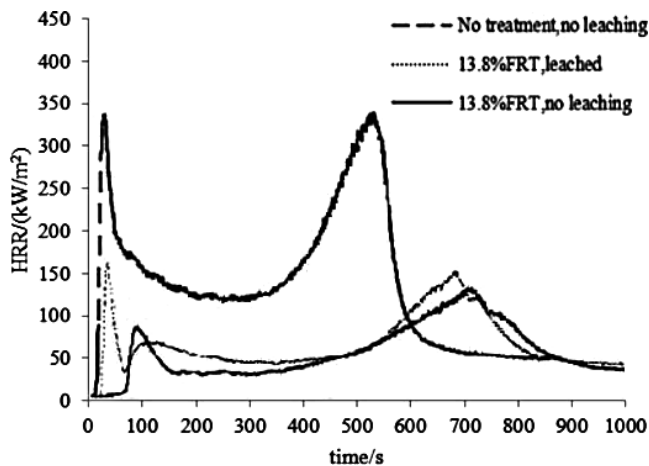[b] BOP-FR = 30 percent boric acid and 70 percent guanylurea phosphate.

Figure 1.—Selected heat release rate (HRR) curves for untreated and boric acid and guanylurea phosphate fire retardant–treated samples.

Plywood fire-retardant treatment methods include veneer impregnation, finished panel impregnation, fire-retardant adhesives, and surface coating or painting. Each of these treatment methods is described in the following sections.

Veneer impregnation.—This method can only be used with fire retardants that have a very specific combination of properties in terms of solubility, pH, and impact of buffer capacity on wood. If the solubility is poor, the low chemical loading will not yield the required fire-retardancy performance. If the pH value is too high, chemical erosion of the panels will occur, resulting in reduced mechanical properties and shortened service life. If the change in the acid-base buffer capacity is too large, the strength of the original panels will be reduced. Hu et al. (2008) used a new guanylurea phosphate-boron–based fire retardant (FRW-1) at a concentration of 10 percent (by weight of wood) to soak 2-mm-thick poplar veneer, and achieved a chemical loading of 8 to 10 percent. The cone calorimeter test results showed that, at an incident heat flux of 50 kW/m^2, the peak of the rate of heat release curve (pk HRR), THR, the peak of the rate of smoke release curve (pk RSR), and the total smoke release (TSR) of the fire retardant–treated plywood had significantly declined. However, the charring formation yield was 10.5 percent higher than that of the untreated plywood, indicating that better fire retardancy and smoke inhibition had been achieved with the incorporation of FRW-1. Liu et al. (2004) used *Betula* veneers to prepare plywood with fire retardants. The results of LOI, wood stack method, and mechanical property tests showed that plywood treated with GUP-B had excellent performance, meeting the requirements of the first class in the Japanese Standard JISD 1322-77 and the GB standards, while the board strength properties were almost unaffected. Currently, impregnating veneers with strong hygroscopic ammonium salts is the most commonly used method in the industry for improving plywood fire performance.

Impregnation of the finished panel.—Impregnation using this method is usually conducted through a vacuum process; the processing time must be short, and the board must have been manufactured using a water-resistant adhesive. However, this approach frequently affects gluing performance and often causes warping, deformation, and cracks during drying, which affect subsequent processing and applications. Gu

(2007) treated a finished plywood panel with BL fire retardant at atmospheric pressure. The test results showed that the fire retardancy of the resulting treated panel was not satisfactory, formaldehyde emissions were high in plywood panels with three or more layers, and fire-retardant crystallization as well as panel deformation occurred after drying.

Use of a fire-retardant adhesive.—This method is suitable for preparing plywood products with low fire-retardancy requirements.

Surface coating or painting.—With this method, the inner and outer surfaces of the plywood are coated with refractory materials such as asbestos and vermiculite expansion materials or directly painted with intumescent fire-retardant coatings. This treatment does not affect the plywood production process, and good fire-retardant efficiency can be achieved at low chemical loadings and equipment costs. However, once the cover or coating is damaged, the fire-retardant performance is immediately lost and the materials will be in jeopardy. Wang et al. (2007) developed an intumescent waterborne modified amino resin fire-retardant coating, which was tested by cone calorimeter and thermogravimetric analysis (TGA). The results showed that the presence of the coating reduced the heat release rate and total heat release significantly, extending the time to ignition. These coated panels displayed the best fire-retardant and smoke suppression performances, when compared with the other commercial fire-retardant coatings included in the evaluation. This intumescent coating also showed excellent charring properties (Fig. 2), which could effectively decrease the risk of fire and be a positive factor in the evacuation of people and fire suppression.

Although there are many treatment methods to choose from to improve the fire performance of different types of wood-based composites, it is not always possible to achieve the performance required using only one treatment method. For example, when the coating treatment is used alone, the fire-retardant effect is lower; however, if the coating treatment is chosen in combination with other compatible fire-retardant treatments, the fire properties of the composites could be greatly improved. Therefore, in the actual production of fire retardant–treated wood-based composites, superior performance can be achieved by using a variety of fire-retardant treatment methods at the same time.
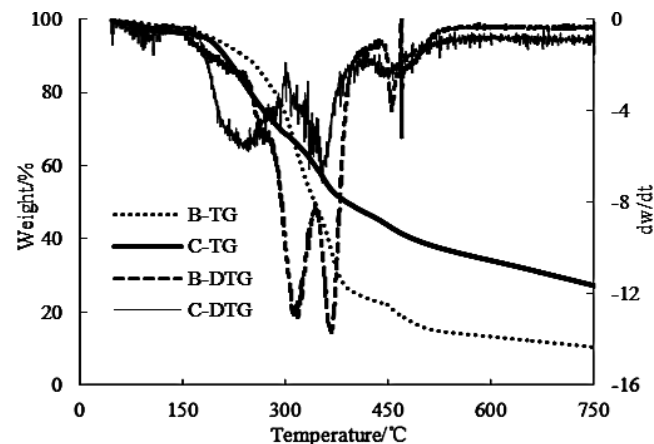

Figure 2.—Thermogravimetric and differential thermogravimetric curves of Sample B (film-builder) and Sample C (intumescent coating).

Fire retardant–treated WPCs

WPCs, which are made mainly from two types of combustible materials (wood fiber and plastic), can be considered a serious fire hazard. With the industrial scope of WPCs expanding rapidly into applications in the building, interior decoration, door, window, flooring, furniture, and automotive interior sectors, the development of suitable methods to produce fire-resistant WPCs is essential.

Shao et al. (2008) applied ammonium polyphosphate (APP) to wood flour–high density polyethylene (WF-HDPE) composites as a fire retardant. The combustion performance of these WF-HDPE composites was studied with a cone calorimeter. Kinetically, the combustion was found to be a first-order reaction described by $\ln(1 - \alpha) = -kt + C$, where α is fraction of reaction, k is the rate constant, t is the time, and C is integration constant. Considerable fire retardancy was obtained with the addition of APP to the WF-HDPE composites. This was accompanied by an increase in the rigidity of the treated composite. The impact resistance of the treated composite was almost unaffected when the addition of APP was kept under 20 percent. The optimal addition level of APP was about 15 percent. Fang et al. (2008) investigated wood flour–polystyrene (WF-PS) composites produced from wood flour treated with APP starch. The results of cone calorimeter tests conducted under a heat flux of 35 kW/m^2 showed that, with the addition of APP, HRR and THR were decreased, while the degree of charring was increased and time to ignition was prolonged. Adding starch as a charring agent improved the fire-retardant efficiency of APP, indicating that APP starch was an effective intumescent fire-retardant system for WF-PS composites. The APP-starch system affected the mechanical properties of WF-PS composites negatively when the addition level was too high, but only minor effects were observed when the dosage of APP was under 10 percent and that of starch was under 2 percent.

Bai et al. (2008) evaluated the effects of transition metal oxides on the combustion properties of wood flour–polyvinylchloride (WF-PVC) composites using cone calorimetry and TGA. It was found that the addition of transition metal oxides such as CuO, La$_2$O$_3$, and TiO$_2$ improved the fire-retardant performance of the composites. A comparison indicated that the CuO-treated composite had better fire-resistant properties than composites treated with the other two metal oxides, such as much lowered HRR and THR. All of these metal oxides promoted the yield of charring. Smoke production rate and TSR of the composites decreased as a result of the addition of the transition metal oxides, especially CuO, which was more effective than the others in the flaming stage.

Dong and Li (2007) prepared a fire retardant–treated polypropylene–wood (PP-wood) composite containing APP, pentaerythritol, and a laboratory-made vesicant carbon foaming agent. The resultant fire-retardant composite was studied to determine the effects of different formulations and contents on the mechanical properties, fire retardancy, rheological properties, and thermal decomposition of the PP-wood composites. The test results indicated that the LOI and charring at 800°C increased with increasing levels of addition of intumescent fire retardant. The tensile and bending strengths of the composites were also improved by the addition of this fire retardant at an appropriate content. A similar intumescent fire-retardant system for WPCs was studied by Li et al.

(2004), in which APP and melamine were used as the acid source and gas source, respectively.

Zhao et al. (2006) used organic montmorillonite to improve the fire retardancy of WF-PVC composites by preparing composites from wood flour modified with a silane coupling agent and PVC. The test results showed that adding a small amount of organic montmorillonite in the composites with the modified wood flour could significantly improve the impact and tensile strengths of the composites, delay the ignition time and significantly increase the ratio of charring.

Besides research on fire retardant–treated WPCs made by an extrusion or injection process, research has also been performed on WPCs prepared by the hot pressing of a mixture of polypropylene and wood fiber (Gao 2007). The fire retardancy performance and mechanism of WF-PVC composites that were treated with APP, pentaerythritol, and melamine are discussed by Deng (2009).

Song et al. (2011) studied the synergistic effects of combining expandable graphite (EG) with APP on the flame retardancy of WPCs. The cone calorimetric analysis showed that fire retardancy and smoke suppression of the WPCs were improved with the addition of EG and APP. Also, incorporation of EG and APP showed good synergistic effects (Fig. 3; Table 5).

In summary, the fire-retardant treatment of WPCs is mainly limited to adding fire retardants to wood and/or plastics. This research field is still in its infancy.

Fire Retardancy and Smoke Suppression Mechanism in Wood

It is believed that the roles played by fire retardants in improving the fire performance of wood can be explained by one or more theories such as the coverage theory, thermal theory, dilution theory, and chemical theory (Liu 1997, Guo 1998).

In the research on the fire retardant mechanisms in wood, cone calorimetry can simultaneously provide four types of
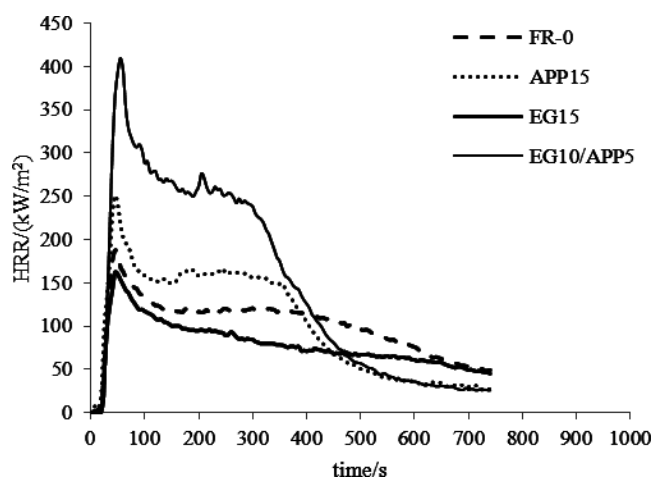
Figure 3.—Heat release rate (HRR) as a function of time for samples FR-0, APP15, EG15, and EG10/APP5, tested by cone calorimeter. FR-0 = no fire retardant contained; AP15 = 15 percent (wt/wt) ammonium polyphosphate; EG15 = 15 percent (wt/wt) expandable graphite; EG10/APP5 = 10 percent (wt/wt) expandable graphite and 5 percent (wt/wt) ammonium polyphosphate.

Table 5.—Cone calorimetry results for fire-retardant wood flour/polypropylene composites.[a]

Data[b]	pk HRR (kW/m²)	Average HRR (kW/m²)	Average EHC (MJ/kg)	Average MLR (g/s)	Average SEA (m²/kg)
FR-0	410	153.1	25.8	0.05	418
APP15	251	105.5	23.3	0.04	478
EG15	188	101.2	26.6	0.03	232
EG10/APP5	162	80.6	21.9	0.03	195

[a] Data compiled from Song et al. (2011). pk = peak; HRR = heat release rate; EHC = effective heat of combustion; MLR = mass loss rate; SEA = specific extinction area.

[b] FR-0 = no fire retardant added; APP15 = 15 percent (wt/wt) ammonium polyphosphate; EG15 = 15 percent (wt/wt) expandable graphite; EG10/APP5 = 10 percent (wt/wt) expandable graphite and 5 percent (wt/wt) ammonium polyphosphate.

information on the specimens during combustion: mass (weight) change, heat release, smoke production, and tail gas yield, which are all interrelated. Li et al. (2002) treated wood with the fire retardant GUP-B and evaluated the properties using cone calorimetry. The analysis showed that the heat release of wood was decreased considerably by treatment with GUP-B, the synergistic fire-retardant effect between GUP and boric acid was strong, and the char formation of the wood was markedly accelerated by the presence of GUP-B. These results also indicated that the catalytic charring effect of GUP-B on wood is the primary aspect in its fire-retardation mechanism (Wang and Li 2004a). Wang and Li (2004b) analyzed the thermo-decomposition of the fire retardant GUP-B and its main components (namely boric acid and GUP), as well as the pyrolysis of basswood treated with boric acid, GUP, GUP-B, and untreated basswood, by TGA and differential thermal analysis. It was found that when the fire retardant GUP-B was heated to its decomposition temperature, its components decomposed independently. The pyrolysis process of basswood was found to be changed by treatment with GUP-B or its components. The TGA curve of GUP-B was not related to the sum of the GUP and boric acid curves, but intersected with these two curves, indicating a fire-retardant synergistic effect between GUP and boric acid.

It is commonly accepted that the fire-retardant mechanism of boric acid is physical and achieved by the formation of a coating or protective layer on the wood surface at high temperatures (Kandola et al. 1996). Although a char-forming catalytic mechanism has been proposed by some researchers, little direct experimental support has been provided for such a chemical mechanism. Wang et al. (2004) presented their experimental results using differential thermal analysis, cone calorimetry, and gas chromatography–Fourier transform infrared spectroscopy (GC-FTIR) analysis, and discussed the fire-retardant mechanism of boric acid on wood. Basswood was treated with boric acid, GUP, and GUP-B. Thermogravimetric analysis showed that the weight loss of basswood treated with boric acid was about three times that of the untreated or GUP-treated wood at 165°C, a temperature at which GUP is stable. The differential thermal analysis curves showed that boric acid–treated basswood had an exothermal peak at 420°C, associated with the exothermal charring polymerization reaction. The GC-FTIR spectra indicated that compounds generated by boric acid–treated wood were different than those generated by untreated wood. It was concluded that boric acid catalyzed the dehydration and other oxygen-eliminating reactions of wood at relatively low temperatures (approximately 100°C to 300°C) and may catalyze the isomerization of the newly formed polymeric materials by forming aromatic structures.

This was partially attributed to the effects of boric acid on promoting the charring and fire retardancy of wood. The cone calorimetric test results showed that boric acid and GUP had a considerable synergistic fire-retardant effect on wood. The structures of the solid state products formed by the limited combustion of Korean pine wood treated with GUP-B were analyzed by microscopic FTIR by Wang et al. (2005a). The results showed that upon heating and by the catalysis effected by GUP-B, the decomposition reactions of the wood took place successively, namely dehydration of polysaccharides, elimination of acetic acid from hemicellulose, degradation of polysaccharides, degradation of lignin, polymerization of the pyrolytic products of wood, reactions of oxygen-element, elimination of aliphatic polymers, and structural changes to form aromatic structures and charring. The pyrolysis process of wood was altered and the yield of volatile pyrolytic products was reduced by GUP-B treatment. The mechanism of the strong fire-retardant synergism between boric acid and GUP is due to the different fire retardant mechanisms of boric acid and GUP and the different activation temperatures of these two chemicals (Wang and Li 2005a).

Smoke, which contains tiny solid particles, tiny fluid drops, and gaseous compounds generated by the burning of a material, is a complex mixture and is usually more harmful than heat for people in a fire disaster. Because of the complex nature of its composition and formation process, research on smoke suppression mechanisms is challenging. Wang et al. (2002) systematically studied the smoke inhibition of GUP-B and a commercial fire retardant (Dricon) using a cone calorimeter. They found that the values of the smoke ratio, SEA, the concentration of carbon dioxide (CO_2), and the yield of carbon dioxide (Y_{CO_2}) decreased significantly compared with untreated wood for GUP-B–treated wood and Dricon-treated wood. The GUP-B treatment of the wood had only a minor influence on the generation of carbon monoxide (CO). Both GUP-B and Dricon had a strong smoke inhibiting effect on wood and their efficiencies were similar.

In order to evaluate the influence of oxygen concentration on the formation of smoke during the burning of fire retardant–treated wood, Wang et al. (2006a) used a controlled atmosphere cone calorimeter to investigate the smoking properties of *Tilia amurensis* wood treated with the fire retardant monoammonium phosphate (MAP) and of untreated wood as a control. The samples were tested at an incident heat flux of 50 kW/m² and a controlled atmosphere having an oxygen concentration of 15 to 21 percent. The release of dense smoke and poisonous gases (mainly CO) from samples burnt under different oxygen concentrations was evaluated by comprehensive analysis of smoke-related

parameters such as RSR, TSR, SEA, CO production rate (P$_{CO}$), and yield of CO (Y$_{CO}$). The results indicated that the smoke release (RSR, TSR, and SEA) was much higher in the flaming stage than in the after-glow stage. When the oxygen concentration was about 16 percent, the smoke release of the MAP-treated wood was similar to that of the untreated wood. When the oxygen concentration was higher than 16 percent, the MAP-treated wood displayed lower dense smoke release than the untreated wood. On the contrary, when the oxygen concentration was lower than 16 percent, the smoke release of the MAP-treated wood was higher than that of the untreated wood. In the experimental oxygen concentration range, the CO release (P$_{CO}$ and Y$_{CO}$) of MAP-treated wood was higher than that of the untreated wood. The smoke release and CO release of MAP-treated wood was found to decrease with increasing oxygen concentration. On the other hand, the smoke release and P$_{CO}$ of the untreated wood increased with increasing oxygen concentration; this could be due to the oxygen shortage of the system caused by the violent combustion. The decrease in Y$_{CO}$ of the untreated wood may be attributed to the comparatively more complete combustion at a certain weight loss of the wood. It was concluded that the smoke release, including CO formation of burning MAP-treated wood, tends to increase with a decrease in the oxygen concentration in the air.

Chen et al. (2007) analyzed the pyrolysis products of *T. amurensis* lignin treated with boron compounds and/or phosphates by pyrolysis–gas chromatography–mass spectroscopy. During the pyrolysis process, a great deal of CO_2, CO, and H_2O were produced, which was mainly attributed to the elimination of carbonyl, carboxyl, hydroxyl, and methyl groups and further reaction to form polycyclic aromatic hydrocarbons. Most of the fire retardants used in this study promoted the release of CO_2, CO, and H_2O. The pyrolysis of untreated lignin produced more volatile pyrolytic products than that of lignin treated with boric and organic phosphates. Inorganic phosphates and sodium borate reduced the production of aromatic and heterocyclic compounds in the pyrolysis process. GUP and boric acid in GUP-B synergistically influenced the pyrolysis process. Ninety-four compounds in the pyrolysis products of *T. amurensis* lignin were identified. This could provide the basis for revealing the formation mechanisms of lignin pyrolysis products, and even the mechanisms of wood fire retardancy and smoke suppression. A further study by Chen (2007) showed that boron–nitrogen–phosphorus fire retardants have a synergistic effect in the thermal degradation of cellulose, lignin and hemicellulose.

Zinc borate and APP (ZB-APP) is a type of composite fire retardant for wood, which was used by Hu (2006) to treat wood for fire retardancy and smoke inhibition. APP diffused into the wood tissues, and upon being heated, catalyzed wood decomposition and dehydration into charcoal. Meanwhile, the ammonia gas and water vapor decomposition products generated from APP by the heat could dilute the flammable gases emitted from the wood and the oxygen from air, and form a highly concentrated, protective fire-retardant layer by reducing the amount of flammable gases on the surface of the wood. The phosphorus and oxygen free radicals generated from the decomposition of APP could block the combustion chain reaction; this could explain why APP can effectively reduce the heat release and intensity of burning. ZB powder attached to the wood surface to form a loose coating hampers the combustion reaction of the wood through a heat insulation effect and the adsorption of the combustible gases produced by the decomposition of wood in the surrounding oxygen. Consequently, it could catalyze the decomposition products of wood, oxidizing them to CO_2, and effectively reduce smoke and the toxic gas concentrations of the exhaust. Each component of ZB-APP exerts different mechanisms of wood fire retardancy and smoke suppression, with mutual synergies.

Nitrogen–phosphorus–boron composite fire retardants for wood, e.g., GUP-B fire retardants, are not only powerful fire retardants, but are also effective in smoke suppression. The mechanism of fire retardancy and smoke suppression by which this kind of fire retardant acts can be summarized as follows.

When the composite fire retardants are heated in the wood, thermal decomposition reactions occur independently in the boron compounds and phosphate components, through heat absorption, and noncombustible gases and nonvolatile acidic molten materials are produced. This can suppress the rise in the wood temperature, depress the oxygen concentration (dilution effect) in the surrounding air, and shield thermal radiation, which is conducive to a reduction in the thermal decomposition rate of the wood.

The acid decomposition products of the phosphates and the boric acid–polysaccharide complexes catalyze wood dehydration and decomposition to generate unsaturated products; this solid carbonaceous residue then experiences further condensation, polymerization, and aromatization catalyzed by acid. The pyrolytic changes in the wood help generate more solid charcoal, inhibiting the generation of smoke. The significant role of catalyzing wood charring is the main aspect of the fire retardant and smoke suppression mechanisms of nitrogen–phosphorus–boron composite fire retardants for wood.

Boric acid has different fire-retardant mechanisms and different activation temperatures than GUP, guanidine phosphate, or ammonium phosphate salts, which complements these fire retardants, and thus introduces significant synergies.

Conclusions

In China, most of the wood fire retardants used are water-soluble materials applied by coating and impregnation treatments. The study of fire retardants for WPCs is in its infancy. The research and development work for the production of fire-retardant, smoke-suppressing, and environmentally friendly wood-based composites needs to continue exploring ways of meeting safety requirements.

The mechanisms proposed for the nitrogen–phosphorus–boron composite fire retardants in wood are just a simple picture of the basic knowledge obtained from the results of current theoretical research; many details of the fire retardancy and smoke suppression mechanisms of fire retardants in wood-based composites are left for researchers to explore systematically.

Acknowledgments

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