INVESTIGATION THE FIRE HAZARD OF PLYWOODS USING A CONE CALORIMETER

ZHIGANG WU, XUE DENG, LIFEN LI, LIPING YU, JIE CHEN GUIZHOU UNIVERSITY P.R. CHINA

BENGANG ZHANG, XUEDONG XI UNIVERSITY OF LORRAINE FRANCE

QIAOYAN ZHANG ZHAZUO STATE-OWNED FOREST FARM OF GUIZHOU PROVINCE P.R. CHINA

(RECEIVED JANUARY 2021)

ABSTRACT

A high-efficiency fire retardant composition was prepared with dicyandiamide, phosphoric acid, boric acid, borax, urea and magnesium sulfate and it was used to process veneers which were then to prepare the plywood. Meanwhile, heat release and smoke release from combustion of plywood were tested by a cone calorimeter, including heat release rate, mass loss rate, CO yield, CO₂ yield and oxygen consumption. Results showed that the plywood with this fire retardant treatment had the better flame-retardant performance and smoke suppression effect as well as the stronger char-forming capability compared to plywood without fire retardant treatment. The average heat release rate, total heat release, average effective heat of combustion, total smoke release, CO yield and oxygen consumption of the plywood with fire retardant treatment were decreased by 63.72%, 91.94%, 53.70%, 76.81%, 84.99% and 91.86%, respectively. Moreover, the fire growth index of plywood treated by fire retardant was relatively low $(3.454 \text{ kW} \cdot \text{m}^{-2} \cdot \text{s}^{-1})$ and it took longer time to reach the peak heat release rate, accompanied with slow fire spreading. The fire performance index was relatively high (0.136 $s \cdot m^2 \cdot kW^{-1}$) and it took longer time to be ignited, thus leaving a long time for escaping at fire accidents. The fire hazard of plywood with fire retardant treatment was low, and its safety level was high.

KEYWORDS: Fire retardant, plywood, combustion performance, fire hazard.

INTRODUCTION

With the intensifying shortage of wood resources around the whole world, developing wood-based panels has become an important way to solve this problem. Plywood is one of the most important products in wood-based panels. The output and demands for plywood which is a major material for indoor decoration are increasing significantly. However, plywood is a type of flammable material (Chung 2010, Nicholas and Siau 1973, Qu 2011). Once plywood is ignited, the fire will spread quickly and release a lot of heats to accelerate formation of indoor flashover. Under this circumstance, it is very difficult for the trapped to escape from the fire accident and for the firefighter to extinguish the fire, thus making it extremely easy to cause considerable economic losses and serious casualties. Therefore, fire retardant treatment of plywood has the important practical significance (Cao 2019, Yu et al. 2020, Cao et al. 2020).

Fire hazards are mainly determined by heat and smoke of combustion. Heat hazard refers to heat damages of life, properties and buildings by spreading heats from combustion to surrounding environment through radiation, convection and conduction. Smoke hazard refers to the damages caused by smoke and toxic gases to life and environment (Altun et al. 2010, Dong and Xu 2019). Fire hazard is essentially a comprehensive manifestation of potential heat risks and smoke risks of materials (Zhang et al. 2014, Xue et al. 2006, Son et al. 2012). Therefore, research and development on fire retardant treatment of plywood are focused on decreasing heat release and smoke release. Studies proved that nitrogen-series fire retardants and phosphorus-series fire retardants are characteristic of low price, small volatility and low toxicity. These two series of fire retardants have good flame retardation, but independent use of these fire retardants fails to achieve satisfying effect. Boron-series compounds are equipped with inflaming retardation, smoke suppression, anti-corrosion and mildew prevention and insect prevention (Chu et al. 2017, Zhang et al. 2016, Zhou et al. 2020, Kartal et al. 2007). Magnesium salt has good flame retardation and strong smoke suppression effect (Pan et al. 2014, Cao 2019). To endow good flame retardation for plywood, a composite fire retardant was prepared with dicyandiamide, phosphoric acid, boric acid, borax, urea and magnesium sulfate. Later, high-quality fire retardant was synthesized by supplementation and synergistic interaction of different components.

The cone calorimeter is recognized worldwide as one of the most acceptable fire testing apparatuses. Its testing results are not influenced by the types and complete combustion state of materials (Kim et al. 2012, Fateh et al. 2014). Moreover, cone calorimeter is highly related with large combustion experiment and it can test multi-aspect indexes related with combustion performances of materials comprehensively, including heat release rate, mass loss rate, oxygen content and CO_2 content. It is a very comprehensive combustion performance testing technique. In this study, cone calorimeter was applied to evaluate combustion performance of plywood processed by the prepared fire retardant and it will lay foundations for the improvement and application of the prepared fire retardant.

MATERIALS AND METHODS

Materials

Masson pine (*Pinus massoniana* Lamb.) with a size of 2200 mm (length) \times 130 mm (width) \times 2.5 mm (thickness), density 0.48 g cm⁻³ and moisture content 10-14% was purchased from Rongjiang Guizhou, China. Dicyandiamide (with a purity of 98%), boric acid (with a purity of 99.5%), phosphoric acid (with a purity of 85%), borax (with a purity of 99.5%), urea (with a purity of 99%) and magnesium sulfate (with a purity of 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (PR China). All other chemicals mentioned in this work were reagent grade. Powdery urea formaldehyde resin (C360), which was used by mixing with water (mass ratio of resin power to water was 100 : 80) and then adding 0.5% ammonium chloride for the preparation of plywoods, was purchased from Malaysia.

Preparation of fire retardant

Based on a large number of pre-experiments, the compositions of the flame retardant were 4% dicyandiamide, 6% phosphoric acid, 2.25% boric acid, 2.25% borax, 1% urea and 0.5% magnesium sulfate.

Treatments of Pinus massoniana veneers with fire retardant

Pinus massoniana veneers were dried in an oven (101-1AB electric blast drying oven) at $60^{\circ}C \pm 5^{\circ}C$ until reaching constant weights and then moved out and stored in glass drier to cool down to the room temperature, weighted and then put in vacuum chamber. The fire retardant was poured into the chamber until 5 cm higher than the surface of the piles of wood samples under vacuum conditions (-0.09 MPa, 60 min). Next, the samples were taken out and the surface liquids of each wood sample was removed gently by a piece of filter paper. The wood samples were put in indoor environment for about one week and then dried in an oven at $90^{\circ}C \pm 5^{\circ}C$ until the moisture content at 5% - 9%.

Preparation of five-layer plywood

The flame retardant veneers with a double-sided adhesive loading of 220 g m⁻² were rested at room temperature for 15-20 min. The assembled veneers were then exposed to single-layer hot press unit (XLB type) at Shanghai Rubber Machinery Plant and pressed with a pressure of 1.5 MPa at 100°C for 15 min to obtain a plywood panel. The moisture content of control plywood was 16.6%, and that of flame retardant treated plywood was 13.5%.

Evaluation of combustion performance and smoke suppression performance

Cone calorimeter tests were performed according to the procedures indicated in the ISO 5660-1-2015 standard using a Fire Testing Technology cone calorimeter FTT2000 (Fire Testing Technology Ltd., UK). The plywood panel was conditioned in the laboratory at $20 \pm 2^{\circ}$ C and relative humidity of 65% \pm 5% for 1 day and then cutting into specimens with dimensions of 100 mm (length) × 100 mm (width) × 10 mm (thickness) prior to testing. The fire

scenario was comprised of four steps: ignition, growth, fully developed, and decay. The tests were conducted with 50 kW \cdot m⁻² of heat flux which corresponded to the fully developed step.

RESULTS AND DISCUSION

Heat release rate (HRR) analysis

Heat release rate (HRR) refers to the heat release from per unit area of material combustion and it reflects the rate of heat release of materials during combustion, HRR, peak HRR (pk-HRR) and average HRR (av-HRR) are often used to evaluate combustion performances of materials and they all can reflect degree of material combustion and output of volatile combustibles. These three indexes can be used to evaluate spreading trend of flames and rate of fire hazard. The smaller HRR, pk-HRR and av-HRR indicates the lower heat release from material combustion and the lower fire hazards (Li et al. 2019).

The HRR curve during combustion of plywood is shown in Fig. 1. Seen from Fig. 1 that the HRR curve of plywood with fire retardant treatment was relatively stable after 120 s, indicating fire retardant decreased the production rate of combustible volatiles, weakened transmission of heats of plywood from surrounding environment and relieved the risk of plywood pyrolysis in fire accidents. pk-HRR of plywood without fire retardant treatment was 187.13 kW^{m⁻²}, which was 40.93% higher than that of plywood with fire retardant treatment (110.53 kW·m⁻²). The av-HRR of plywood with fire retardant treatment was decreased by 63.73% to 39.48 kW^{m⁻²} compared to that of plywood without fire retardant treatment (108.85 kW^{m⁻²}). HRR, pk-HRR and av-HRR of plywood with fire retardant treatment were decreased significantly than those of plywood without fire retardant treatment, indicating that the fire hazard caused by plywood after fire retardant treatment was small.



Fig. 1: The HRR curves of plywoods.

Total heat release (THR) analysis

Total heat release (THR) refers to the total heats released by unit area of materials from ignition to extinguishment. The fire hazard is more serious when THR is higher. Combustibility and flame retardation of materials could be evaluated better by combining HRR and THR (Mo et al. 2007). The THR curve during combustion of plywood is shown in Fig. 2. As shown in Fig. 2, heat release begun to be generated by plywoods with and without fire retardant treatment at about 30 s. THR curve of plywood without fire retardant treatment increased quickly as time went on, while THR curve of plywood with fire retardant treatment increased at a stable rate. These also proved the conclusions of HRR. In other words, the introduction of fire retardant decreased the production rate of possible volatiles and releasing of possible volatiles or combustion heats was relatively uniform. THR of plywood without fire retardant treatment was 69.21 MJ^{·m⁻²} and the THR of plywood with fire retardant treatment was 5.58 MJ^{·m⁻²}, showing a difference of 91.94%. This demonstrated that plywood with fire retardant treatment a small THR during the combustion process, which reflected the very significant had flame retardant efficiency. Fire retardant treatment decelerated the growth of surrounding temperature of ignition point in fire accidents significantly, and thereby delayed time and speed of fire spreading effectively.



Fig. 2: The THR curves of plywoods.

Effective heat of combustion (EHC) analysis

Effective heat of combustion (EHC) refers to the ratio between heat release and mass loss at a moment, which reflects the burning degree of volatile gases in meteorological flames. The THR curves of plywoods at combustion are shown in Fig. 3.

As shown in Fig. 3 that average EHC of plywood with fire retardant treatment was 5.44 MJ⁻kg⁻¹, which was 53.70% lower than that of plywood without fire retardant treatment (11.75 MJ⁻kg⁻¹). That was because the fire retardant could inhibit pyrolysis of wood effectively and decrease the output of combustible volatiles, thus decreasing EHC significantly.



Fig. 3: The EHC curves of plywoods.

Mass loss (ML) and residual mass (Mass) of plywoods

Mass changes before and after the combustion of plywood are shown in Tab. 1. The ML of plywood without fire retardant treatment was 52.04 g, which decreased to 8.97 g for plywood with fire retardant treatment. This reflected that fire retardant could inhibit plywood combustion effectively and made it difficult for plywood to develop pyrolytic reactions, thus decreasing ML. The Mass of plywood without fire retardant treatment was 18.17%, which amounts to 85.92% for plywood with fire retardant treatment. This indicated that fire retardant inhibited combustion of plywood and accelerated the char-forming rate, thus increasing Mass. As a result, fire retarding plywood also could maintain strength in fire for a long period and it was difficult to collapse.

Tab. 1: The	combustion i	mass change	of plywoods.
-------------	--------------	-------------	--------------

Plywoods	ML (g)	Mass (%)
Control group	52.04	18.17%
Experimental group	8.97	85.92%

Smoking properties analysis

Total smoke release (TSR), CO yield (COY), CO₂ yield (CO₂Y) and total oxygen consumption (TOC) of plywoods during combustion are shown in Fig. 4 and Tab. 2.

TOC of plywood with fire retardant treatment was 3.6974 g, which was 91.86% lower than that of plywood without fire retardant treatment (45.4428 g). It was because fire retardant accelerated char-forming rate of plywood, decreased the formation of combustible volatiles and inhibited combustion.

TSR, COY and CO₂Y of plywood with fire retardant treatment were 25.99 m²·m⁻², 0.0178 kg·kg⁻¹ and 0.6036 kg·kg⁻¹, which were decreased by 76.81%, 84.99% and 38.70% compared to those of plywood without fire retardant treatment (112.09 m²·m⁻², 0.1186 kg·kg⁻¹ and 0.9847 kg·kg⁻¹). TSR, COY and CO₂Y of plywood with fire retardant treatment were

decreased to different extents, which could be explained as follows. Borides and magnesium sulfate in fire retardant had excellent smoke suppression performances and decreased the possibility of smoke asphyxia or toxicity-induced deaths during the occurrence of fire accidents.



Fig. 4: Smoking effect and oxygen consumption of plywoods.

1 ab. 2. The gas emission and total oxygen consumption of prywoods.								
	Plywoods	$TSR (m^{2} m^{-2})$	COY (kg.kg ⁻¹)	$CO_2Y (kg kg^{-1})$	TOC (g)			
	Control group	112.09	0.1186	0.9847	45.4428			
	Experimental group	25.99	0.0178	0.6036	3.6974			

Tab. 2: The gas emission and total oxygen consumption of plywoods.

Evaluation of potential fire hazard of plywoods

Fire performance index (FPI) and fire growth index (FGI) were applied to evaluate potential fire hazards comprehensively. FGI reflects the fire spreading capability of plywoods when they are exposed to high-heat environment. The higher value of FGI indicates the greater risks of fire accidents (Fig. 5). FPI reflects the tendency of combustion of plywoods. The smaller value of FPI indicates the smaller fire hazards (Cao 2019, Zhang et al. 2015, Huang et al. 2019).

FGI values of plywoods with and without fire retardant treatment were 3.454 kW·m⁻²·s⁻¹ and 6.148 kW·m⁻²·s⁻¹, indicating that fire retardant could decrease pk-HRR of plywoods, prolong the time to reach the pk-HRR and decelerate fire spreading. FPI values of plywoods with and without fire retardant treatment are 0.136 s·m²·kW⁻¹ and 0.106 s·m²·kW⁻¹, resp. This reflects that fire retardant prolonged the ignition time of plywoods and increased the time for escaping from fire accidents. In a word, plywood with fire retardant treatment had relatively high FPI and relatively low FGI, showing a high safety level.



Fig. 5: FPI and FGI of plywoods.

CONCLUSIONS

A high-efficiency fire retardant composition was prepared with dicyandiamide, phosphoric acid, boric acid, borax, urea and magnesium sulfate and it was used to process veneers which were then to prepare the plywood. Meanwhile, heat release and smoke release from combustion of plywood were tested by a cone calorimeter. Results showed that: (1) The plywood with fire retardant treatment had the better flame-retardant performance and smoke suppression effect as well as the stronger char-forming capability compared to plywood without fire retardant treatment. (2) The average heat release rate, total heat release, average effective heat of combustion, total smoke release, CO yield and oxygen consumption of the plywood with fire retardant treatment were decreased by 63.72%, 91.94%, 53.70%, 76.81%, 84.99% and 91.86%, respectively. (3) The fire growth index of plywood treated by fire retardant was relatively low (3.454 kW·m⁻²·s⁻¹) and it took longer time to reach the peak heat release rate, accompanied with slow fire spreading. (4) The fire performance index was relatively high (0.136 s·m²·kW⁻¹) and it took longer time to be ignited, thus leaving a long time for escaping at fire accidents. (5) The fire hazard of plywood with fire retardant treatment was low, and its safety level was high.

ACKNOWLEDGMENTS

This work was supported by Science-technology Support Foundation of Guizhou Province of China (Nos. [2019]2308, [2020]1Y125 and NY[2015]3027), National Natural Science Foundation of China (No. 31800481), Cultivation Project of Guizhou University of China (No. [2019]37).

REFERENCES

1. Altun, S., Ozcifci, A., Senel, A., 2010: Effects of silica gel on leaching resistance and thermal properties of impregnated wood. Wood Research 55(4): 101-112.

- 2. Cao, J.Z., 2019: A review on wood protectant dispersion systems and their liquid penetration. Journal of Forestry Engineering 4(3): 1-9.
- 3. Cao, Y., Wang, X., Li, Y., Shen, D., Dai, Y.P., Zhang, S.Z., Zhang, W.G., 2020: Effect of high temperature oil heat treatment on the starch content and mold-resistant property of bamboo. Journal of Forestry Engineering 5(2): 109-115.
- 4. Chu, D., Mu, J., Zhang, L., 2017: Promotion effect of NP fire retardant pre-treatment on heat-treated poplar wood. Part 2: hygroscopicity, leaching resistance, and thermal stability. Holzforschung 71(3): 217-223.
- 5. Chung, Y.J., 2010: Comparison of combustion properties of native wood species used for fire pots in Korea. Journal of Industrial and Engineering Chemistry 16(1): 15-19.
- 6. Dong, W.R., Xu, M., 2019: Effect of nano copper-zinc preservative combined with phenolic resin on properties of rubber wood. Journal of Forestry Engineering 4(1): 39-44.
- 7. Fateh, T., Rogaume, T., Luche, J., Richard, F., Jabouille, F., 2014: Characterization of the thermal decomposition of two kinds of plywood with a cone calorimeter-FTIR apparatus. Journal of Analytical and Applied Pyrolysis 107: 87-100.
- 8. Huang, X.D., Huang, J.K., Hse, C.Y., Todd, F.S., Lin, J.G., Li, S.J., 2019: Study on the mold-resistant properties of moso bamboo treated with starch amylase. Journal of Forestry Engineering 4(3): 60-65.
- 9. Kartal, S.N., Hwang, W.J., Imamura, Y., 2007: Water absorption of boron-treated and heat-modified wood. Journal of Wood Science 53(5): 454-457.
- 10. Kim, J., Lee, J.H., Kim, S., 2012: Estimating the fire behavior of wood flooring using a cone calorimeter. Journal of Thermal Analysis and Calorimetry 110(2): 677-683.
- 11. Li, C.Y., Lv, C.Y., Yu, L.L., 2019: Flame retardant treatment of bamboo and its effect on bamboo properties. World Bamboo and Rattan 17(6): 16-20, 24.
- Mo, T.C., Wang, H.W., Chen, S.Y., 2007: Synthesis and characterization of polyimide-silica nanocomposites using novel fluorine-modified silica nanoparticles. Journal of applied polymer science 104(2): 882-890.
- 13. Nicholas, D.D., Siau, J.F., 1973: Factors influencing the treatability of wood, in: wood deterioration and its prevention by preservative treatment. New York: Syracuse University Press.
- Pan, J., Mu, J., Wu, Z., Zhang, X., 2014: Effect of nitrogen-phosphorus fire retardant blended with Mg(OH)₂/Al(OH)₃ and nano-SiO₂ on fire-retardant behaviour and hygroscopicity of poplar. Fire and Materials 38(8): 817-826.
- 15. Qu, H.Q., Wu, W.H., Wu, H.J., Xie, J.X., Xu, J.Z., 2011: Study on the effects of flame retardants on the thermal decomposition of wood by TG-MS. Journal of Thermal Analysis and Calorimetry 103(3): 935-942.
- Son, D.W., Kang, M.R., Kim, J.I., Park, S.B., 2012: Fire performance of the wood treated with inorganic fire retardants. Journal of the Korean Wood Science and Technology 40(5): 335-342.
- 17. Xue, S.Q., Li, B., Feng, K.X., 2006: Characteristics and application of water-based fire retardants. Fire Technique and Products Information 8: 25-27.
- 18. Yu, L.P., Tian, M.F., Li, L.F., Wu, Z.G., Chen, S.C., Chen, J., Xi, X.D., 2020: Study of nano

colloidal silica sol based protectant on the prevention of Masson pine. Wood Research 65(5): 797-808.

- 19. Zhang, X., Li, D., Xie, H., Wang, D., 2014: Preparation and application of water-based fire retardant of ammonium phosphate. Advanced Materials Research 1015: 287-290.
- Zhang, X.T., Mu, J., Chu, D.M., Zhao, Y., 2015: Synthesis of fire retardants based on N and P and poly (sodium silicate-aluminum dihydrogen phosphate) (PSADP) and testing the flame-retardant properties of PSADP impregnated poplar wood. Holzforschung 70(4): 341-350.
- Zhang, X.T., Mu, J., Chu, D.M., Zhao, Y., 2016: A study on the fire performance and hygroscopicity of poplar treated with melamine modified N-P fire retardant. Journal of Central South University of Forestry & Technology 36(2): 119-124.
- 22. Zhou, Z.X., Du, C.G., Yu, H.L., Yao, X.L., Huang, Q.L., 2020: Promotion effect of nano-SiO₂ on hygroscopicity, leaching resistance and thermal stability of bamboo strips treated by nitrogen-phosphorus-boron fire retardants. Wood Research 65(5): 693-704.

ZHIGANG WU, XUE DENG, LIFEN LI, LIPING YU*, JIE CHEN GUIZHOU UNIVERSITY COLLEGE OF FORESTRY GUIYANG 550025 GUIZHOU P.R. CHINA *Corresponding author: wzhigang9@163.com, ylpgzu@163.com

BENGANG ZHANG, XUEDONG XI UNIVERSITY OF LORRAINE IUT-LERMAB 88000 EPINAL FRANCE

QIAOYAN ZHANG ZHAZUO STATE-OWNED FOREST FARM OF GUIZHOU PROVINCE GUIYANG 550299 GUIZHOU P.R. CHINA