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Flame Retardant Properties of Fiber-Based Decorative Wallboard

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Abstract. In this study, bamboo pulp is utilized as the main raw material for the production of compression-molded, fiber-based decorative wallboard panels which have three-dimensional geometric structure and possess environmentally compatible "green" flame retardant properties. The effectiveness of several flame retarding agents, including the $Al(OH)_3$ single component system, the $Al(OH)_3/Mg(OH)_2$ mixed system and the $Al(OH)_3/Mg(OH)_2$/Zinc Borate mixed system are examined in terms of the resulting flame resistance, physical properties and oxygen indexes of the fiber-based decorative wallboard. The results show that the $Al(OH)_3/Mg(OH)_2$/Zinc Borate multicomponent mixed system is the most ideal flame retardant system for such applications. Results indicate that the optimal formulation consist of: 30% $Mg(OH)_2$/25% $Al(OH)_2$ /15% Zinc borate (relative mass ratio). Under such conditions, the oxygen index of the fiber decorates wallboard is 34.4, and the level of formaldehyde release reaches a value of E0.

Introduction

Environmental protection and flame retardant properties have become increasingly important factors in the development of "green" building material products. To date, building materials made primarily from plant fiber as the raw material have used viscous materials in the production process, and have produced harmful by-products, such as formaldehyde [1]. In addition, such wooden or fibrous materials generally have the important detrimental characteristic of high flammability. These two factors represent significant potential threats to human life and safety, and to the safety and stability of the corresponding products, and also limit the application range of such products [2].

The introduction of flame retardant properties to molded fiber products in China has occurred only relatively recently. Flame retardant brine is currently widely used for this purpose; however, its decomposition and burning characteristically produces a large amount of smoke and toxic gases [3]. Inorganic flame retardants have properties such as good stability and flame retardant performance, and do not easily precipitate during processing, and thus have undergone wider use [4, 5]. Aluminum hydroxide and magnesium hydroxide are now commonly used halogen-free, inorganic flame retardants which have triple functions as filling agent, flame retardant and smoke inhibitor [6]. It has been shown from research that zinc borate blended with magnesium and other inorganic flame retardants has a cooperative or enhancement effect; after its addition, the resulting mechanical properties of the materials suffer less deterioration [7-10].

The present study utilizes bamboo pulp as the main raw material for automated hydraulic compression molding technology production of environmentally safe, flame retardant fiber-based decorative wallboard panels (abbreviated to wallboard herein) which have a three-dimensional decorative design. Comparative analyses of the effects of an $Al(OH)_3$ single-component flame-retardant system with an $Al(OH)_3/Mg(OH)_2$ two-component blended system and an $Al(OH)_3/Mg(OH)_2$/Zinc Borate multi-component system on the flame resistance, physical properties and oxygen indexes of the decorative wallboard panels are also presented.

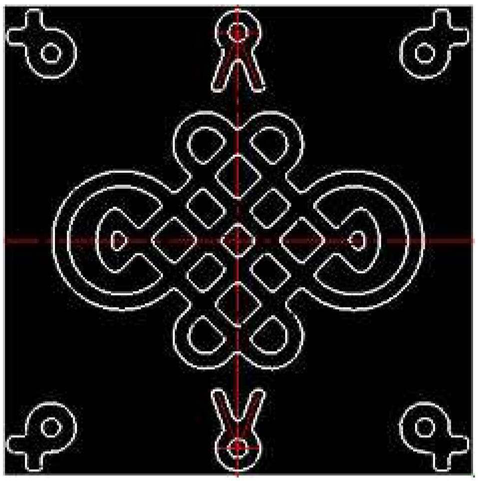
Experimental

Materials. Raw fibrous materials consisted of bamboo pulp, with a beating degree of 16 SR as determined using a PN-SDJ100 beating degree instrument test. Flame retardant components consisted of zinc borate, magnesium hydroxide (800 mesh) and aluminum hydroxide (800 mesh) (Gold Surplus Thai Chemical Co., Ltd., Jinan, China)

Instrumentation and equipment. Wallboards were produced using an AE automatic paper pulp molding machine (Eurasian Machinery Manufacturing Co., Ltd., Hangzhou, China). The wallboard was dried using a DHG-9070 type A electrothermal constant temperature draught drying cabinet (Shanghai Precision Laboratory Equipment Co., Ltd). Oxygen indexes were measured using an HC-2 oxygen index locator (Instrument Analysis Factory, Jiangning County, China). A 756 type UV-Vis spectrophotometer (Spectral Instrument Co., Ltd, Shanghai, China) and SPX intelligent biochemical incubator (Jiangnan Instrument Plant in Ningbo) were also utilized. Wallboard properties were measured using an MW-10A computer controlled board universal testing machine (Jinan Tianchen test machine manufacturing Co., Ltd). [11]

Experimental process and process parameters. The detailed wallboard preparation process is described in the patent of reference [11]. The basic process parameters of this experiment are as follows: thin slurry time, 25 min; suck filtration time, 24 s; cold pressing time, 1 s; hot pressing time, 45 s; hot pressing duration, 15~90 s; cold mold merged pressure, 30 KN; hot pressing mold merged pressure, 132 KN; the hot molding temperature, 160~170℃; the hot under mold temperature, 180~200℃. Parameters were adjusted according to the specific parameters of the actual operation, such as requirements of the experiment, paper pulp molding machine specifications; mold preparation, barbed wire limited resistance and cost.

The wallboard mold design is shown in Figure 1. The corresponding dimensions are: length x width is 460×460 mm, the protruding length and sunken depths of the surface design are 5 mm. The dimensions of the blank wallboard without flame retardant (Grain board) are 460×460×1.5 mm, the default density is 6.5 g/cm^3.



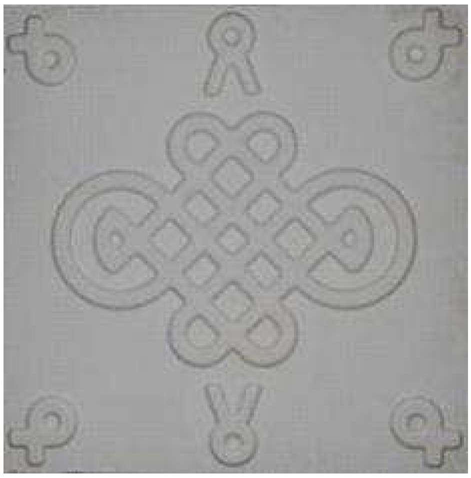


Figure 1. Mold design (left) and the resulting wall panel product from bamboo pulp (right)

Flame retardant study. The application levels of the $Al(OH)_3$ single-component flame retardant system are: 50%, 60%, 70% and 80%; the application levels of the $Al(OH)_3$ /$Mg(OH)_2$ two-component blended system are: 20%/20%, 25%/25%, 30%/30% and 35%/35%. The application level of the $Al(OH)_3$/$Mg(OH)_2$/Zinc borate multi-component blended system was determined using orthogonal design, and an organized optimization test to compare the application levels of the three flame retardants. The orthogonal factors and levels are shown in Table 1, and wallboard was prepared using L9 (34) orthogonal grid board. Among these factors and levels, the percentage of the application level of the flame retardant is just the dry weight ratio of the bamboo pulp raw material.

Table 1. Orthogonal test factors and levels of multi-component system

Level	Factors		
	Al $(OH)_3$	Zinc Borate	Mg $(OH)_2$
1	20%	5%	20%
2	25%	10%	25%
3	30%	15%	30%

Property testing methods Fiber-based wallboard is a relatively new type of interior wall decoration material. Properties of the wallboards were determined according to <<The method to test the physiochemical properties of GB/T 17657-1999, man-made board and decorative man-made board>>. This test specifically checks the internal combinative strength, moisture, content density, 2 h bibulous inflation and the quantity of formaldehyde released. The measurement of flame retardant properties (oxygen index), was determined using<<GB/T 2406-93 Plastic Combustion Property Oxygen Index Testing Method>>.[11]

Experimental results and analysis

The effects of $Al(OH)_3$ single-component flame retardant system on wallboard properties.Table 2 shows the experimental results for the properties of the flame retardant wallboard and grain boards containing different levels of $Al(OH)_3$. It may be seen that the oxygen index of the flame retardant wallboard increases with increasing amount of $Al(OH)_3$, while the bibulous inflation and the internal combinative strength tend to decrease. Compared to the grain board without flame retardant, its internal combinative strength decreases 58.9% at most, and decreases more rapidly. At the 50% $Al(OH)_3$ level, good flame retardant effects are exhibited, because $Al(OH)_3$ has good stability, and will strongly absorb heat and decompose to alumina and water at temperatures above 200 ^oC. The alumina and water can both assume a flame retardant role[12]. Meanwhile, the interior combinative strength decreases noticeably, probably because $Al(OH)_3$ and the bamboo pulp fiber have a lower compatibility. Only some of the inorganic material may combine directly with the cellulose of the fibers, with the remainder filling in the micropores between the fibers, but not combining permanently with the fibers. As a result, it may destroy the hydrogen bond network between the fibers, thereby reducing the internal combinative strength of the material.

Table 2. Results for the single-component $Al(OH)_3$ flame retardant system

Wt. % $Al(OH)_3$	Density [g/cm^3]	Water ratio %	(2h) %	Water absorption	Inside combinative strength [MP]	Oxygen Index	Formaldehyde Release
50%	0.708	5.9	61.0	1.53	0.089	30.0	E0
60%	0.720	6.1	59.6	1.49	0.075	31.8	E0
70%	0.744	5.7	55.9	1.47	0.068	33.0	E0
80%	0.761	6.1	50.1	1.10	0.053	34.4	E0
Blank control	0.645	7.7	70.5	1.76	0.129	24.4	E0

With increasing amount of $Al(OH)_3$, the bibulous ply inflation rate of the flame retardant wallboard decreases, but decreases less than that of the grain board. This may be because the bibulous ply inflation rate is mainly determined by the absorption ability of the raw material bamboo fiber. However, the bibulous rate of $Al(OH)_3$ is less than that of bamboo fiber raw materials, which leads to the result that with the increasing amount of $Al(OH)_3$, its percentage in the wallboard increases and the corresponding thickness swelling rate of water absorption effect correspondingly decreases.

3.2 The effects of $Mg(OH)_2$/$Al(OH)_3$ mixed flame retardant system on wallboard properties. The results of the $Mg(OH)_2$/$Al(OH)_3$ mixed fire retardant system are shown in Table 3. We can see from Table 3 that the oxygen index increases with increasing amount of composite flame retardant additive. The combined use of $Mg(OH)_2$ and $Al(OH)_3$ appears to have a certain synergistic effect on the flame retardant ability of bamboo fiber raw materials. This synergistic effect may due to both $Al(OH)_3$ and $Mg(OH)_2$ absorbing a considerable amount of heat after being heated, but the thermal decomposition temperature of $Mg(OH)_2$ is 140 ℃ higher than that of $Al(OH)_3$. Two absorption peaks surround the main decomposition exothermic reaction area of the new wall materials. Thus, the two components may work with each other over a wide temperature range to control the heating and decomposition of fiber board materials, compared to that of a single-component fire retardant system. In addition, the two-component system can successively release steam over a wider range of temperatures, dilute the surrounding oxygen concentration, thereby placing the whole fiber board continuously in an environment of low oxygen concentration for a relatively long time before and after ignition [14-15], making it more difficult to burn.

Table 3. Results of $Mg(OH)_2/Al(OH)_3$ mixed system

Mixed system composition[1]	Density [g/cm^3]	Water ratio %	(2h) %	Water absorption	Internal combinative strength [MP]	Oxygen Index	Formaldehyde Release
20%+20%	0.688	6.7	62.6	1.59	0.081	30.0	E0
25%+25%	0.715	6.1	61.3	1.52	0.098	32.0	E0
30%+30%	0.735	6.2	63.2	1.51	0.101	32.6	E0
35%+35%	0.789	6.2	61.7	1.49	0.072	33.4	E0
Blank control	0.645	7.7	70.5	1.76	0.129	24.4	E0

[1] Ratio of $Mg(OH)_2$ to $Al(OH)_3$

The $Mg(OH)_2/Al(OH)_3$ two-component system may also produce a synergistic effect on the internal combinative strength of the fiberboard walls. When the two components are used together, the internal combinative strength of fiberboards are stronger than with the single-component $Al(OH)_3$. These effects become increasingly evident, especially at the 30% $Mg(OH)_2$/30% $Al(OH)_3$ composition level. The differences of the absorption expansion rate of $Al(OH)_3/Mg(OH)_2$ two-component blended system are not obvious. Under the condition of adding the same amount of flame retardants, the thickness swelling rate of water absorption of $Al(OH)_3/Mg(OH)_2$ two-component blended system is greater than that of the single- component $Al(OH)_3$ flame retardant system, which is probably because $Mg(OH)_2$ has a tendency to become more easily bibulously damp relative to $Al(OH)_3$.

Orthogonal design optimization of the $Al(OH)_3$ / $Mg(OH)_2$ / Zinc Borate multi-component system

Results of the orthogonal design experiment. The results of the orthogonal experimental design to carry out optimization of the addition of relative amounts of $Al(OH)_3$, $Mg(OH)_2$ and Zinc Borate for this multi-component system, and the corresponding resulting properties of the wallboard, are shown in Table 4.

Table 4. Orthogonal test results of $Al(OH)_3/Mg(OH)_2$/Zinc Borate multi-component system

Number	Factors and levels A	B	C	Density [g/cm^3]	Water ratio %	(2h) %	Water absorption	Internal combinative strength [MP]	Oxygen Index	Formaldehyde release
1	1	1	1	0.718	6.0	56.9	1.42	0.094	30.8	0.17
2	1	2	2	0.720	5.7	56.9	1.44	0.090	31.6	0.12
3	1	3	3	0.729	5.7	50.4	1.37	0.102	33.2	0.15
4	2	1	2	0.710	6.1	61.5	1.48	0.099	33.2	0.12
5	2	2	3	0.723	5.5	48.6	1.37	0.101	33.4	0.13
6	2	3	1	0.700	5.9	54.8	1.39	0.095	32.0	0.14
7	3	1	3	0.715	5.9	54.3	1.48	0.105	32.8	0.12
8	3	2	1	0.697	5.7	60.5	1.50	0.097	32.4	0.12
9	3	3	2	0.721	5.5	60.8	1.54	0.091	34.0	0.11
Blank control	----			0.645	7.7	70.5	1.76	0.129	24.4	0.14

Analysis of orthogonal test results. From Table 5 we can see that the extreme difference of factor 4 is the greatest; in other words, the added amount of $Mg(OH)_2$ is the key factor influencing the multi-component system. This can be shown from the fact that it has the greatest influence on the comprehensive quality of wallboard, and it is good on level 3. However, for the factors A and B, that is, $Al(OH)_3$ and Zinc Borate, their extreme difference is almost the same; both are smaller than factor C. $Al(OH)_3$ (A) is good on level 2, while Zinc Borate is good on level 3. From this comprehensive evaluation, we draw the conclusion that with the function of the three flame retardants, the optimum combination to use for studies should be A2 B3 C3. According to the influence of the factors on the experiment, this corresponds to a formulation of 30% $Mg(OH)_{2,}$ 25% $Al(OH)_{3,}$ and 15% Zinc Borate.

Table 5. Orthogonal experimental extreme difference analysis of comprehensive evaluation for multi-component fire retardant system

Number	Factors and levels A	B	C	Comprehensive evaluation
1	1	1	1	0.5829
2	1	2	2	0.5852
3	1	3	3	0.7594
4	2	1	2	0.5236
5	2	2	3	0.7822
6	2	3	1	0.6467
7	3	1	3	0.7047
8	3	2	1	0.5393
9	3	3	2	0.5351
Average 1	0.642	0.604	0.590	
Average 2	0.651	0.636	0.548	
Average 3	0.593	0.647	0.749	
Extreme difference	0.058	0.043	0.201	
Ideal composition	A2	B3	C3	

Repetitive experiments for group optimization and contrast analysis. We obtained the optimum theoretical formulation of the three-component fire retardant system from the above analysis of the orthogonal test results, but repeated experiments were undertaken, in order to confirm the results. In addition, comparative tests were performed on wallboard using the fifth group from the orthogonal design experiment, the single component $Al(OH)_3$ flame-retardant system, and the $Mg(OH))_2/Al(OH)_3$ two-component mixed system. These test results are shown in Table 6.

Table 6. Contrast results of repeated group optimization experiments

Experimental Group		Density [g/cm^3]	water ratio %	(2h) %	water absorption	Internal combinative strength [MP]	Oxygen Index	level	Comprehensive Evaluation
1■		0.729	5.9	46.1	1.32	0.112	34.4	E0•	0.8083
2■		0.734	5.4	41.8	1.28	0.105	34.0	E0	0.8193
3▲		0.723	5.5	48.6	1.37	0.101	33.4	E0	0.7822
$Al(OH)_3$ Single flame retardant System	50%	0.708	5.9	61.0	1.53	0.089	30.0	E0	0.4595
	60%	0.720	6.1	59.6	1.49	0.075	31.8	E0	0.4732
	70%	0.744	5.7	55.9	1.47	0.068	33.0	E0	0.5147
	80%	0.761	6.1	50.1	1.10	0.053	34.4	E0	0.3857
$Al(OH)_3/Mg(OH)_2$ Mixed system	20%+20%	0.688	6.7	62.6	1.59	0.081	30.0	E0	0.3818
	25%+25%	0.715	6.1	61.3	1.52	0.098	32.0	E0	0.5100
	30%+30%	0.735	6.2	63.2	1.51	0.101	32.6	E0	0.4403
	35%+35%	0.789	6.2	61.7	1.49	0.072	33.4	E0	0.4246
Blank Control		0.645	7.7	70.5	1.76	0.129	24.4	E0	

Notes: ■No. 1 and 2 are the wallboards combined and suppressed by orthogonal flame retardant

▲No. 3 is the wallboard combined and suppressed by No. 5 which is the optimum result from the orthogonal design experiment

•Level E0 represents the amount of formaldehyde released ≤0.5 mg/L (man-made board)

The results of Table 6 prove that the comprehensive quality of wallboard containing the flame retardant combination A2B3C3 is better than that of the best experimental group No. 5 from the orthogonal design. Additionally, its comprehensive evaluation is better those of both the single-component $Al(OH)_3$ flame-retardant system and of the two-component $Mg(OH)_2/Al(OH)_3$ mixed system. After addition of the optimized flame retardant group, the internal combinative strength changes less, and the physical and mechanical performances are improved. In addition, when compared with the blank control board, the thickness swelling rate of water absorption and rate of water absorption have undergone a certain amount of decrease. The corresponding oxygen index of the flame retardant property is 34.4. This value exceeds the minimum oxygen index restrictions for required burning difficulty of level 1 of the Japanese industry specification JIS A1322, which is the test method for burning difficulty of building materials. The amount of formaldehyde released also reaches the E0 level.

Conclusions

From a study of the effects of three flame retardant systems on the comprehensive quality of new interior decorative fiber-base wallboard, the best inorganic flame-retardant system appears to be the 30% $Mg(OH)_2$, 25% $Al(OH)_3$, 15% Zinc Borate multi-component system. This flame retardant system has little influence on the internal combinative strength, while providing the best physical and mechanical properties of the wallboard products, compared to the other tested flame retardants. In addition, when compared to the blank control board, the thickness swelling rate of water absorption and rate of water absorption decrease to some extent in the presence of this multi-component flame retardant system. The oxygen index for the corresponding flame retardant property is 34.4, which exceeds the minimum oxygen index restrictions of required burning difficulty for level 1 of the Japanese industry specification JIS A1322. In addition, the amount of formaldehyde released reaches E0 level, rendering this combination of materials safe for both the environment and human use..

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