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Combustion and thermal properties of paper honeycomb

Treatment of phosphorus-based flame retardant agents

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Abstract The honeycomb structure has superior compressive strength so that it is being utilized in various fields. In addition, the paper honeycomb has excellent economic feasibility because of its low production cost and has an environment-friendly advantage because its recycling is possible. Securing of flame retardant performance is essential to use it as interior materials of buildings and fireproof doors using the advantage like this. The present research has evaluated combustion and thermal properties according to flame retardant treatment in terms of two kinds of specimens when flame retardant film is attached to paper honeycomb, and when paper honeycomb is impregnated to flame retardant agents. As a result of evaluating flame retardant performance utilizing a cone calorimeter, the case impregnated into flame retardant agents showed the most superior flame retardant performance. Through this result, it was confirmed that the paper honeycomb can be utilized as interior materials of buildings though improvement of flame retardant performance.

Keywords Cone calorimeter · Combustibility test · Paper honeycomb · Flame retardant

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Introduction

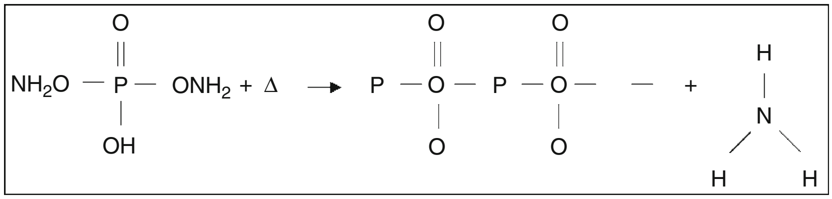
High-rise buildings are in the steadily increasing trend as a result of urbanization due to rapid development of the industries. In addition, the population density was also continuously increased. The case that connects to massive disaster in case of fire occurrence in economic life due to this is also in the increasing trend [1]. According to this, a research on fireproofing and resistance to flame for preventing fast fire spread and destruction of structures in case of fire occurrence for securing of the escape time of occupants is being actively progressed [2, 3].

The honeycomb structure has excellent rigidity and strength so that it is being used and applied in various fields, such as aviation, machine facilities, space engineering, building structures, marine engineering, and mechanical engineering, etc. requiring lightweightness. Especially, the honeycomb with paper material is being used in various fields due to economic efficiency, recycling possibility, and lightweight property. The paper honeycomb is being usually utilized as corrugated board or box forms for protecting products from vibration and impact, and is being also utilized as walls of a building, a trunk mat of a car, and sun shade by being manufactured as a sandwich panel form. But it is vulnerable to a fire according to a property of paper, so if proper flame retardant performance is not secured, securing of fire resistance of sandwich panels and doors might be impossible [4].

Accordingly, the present research has performed basic research on a recycling possibility of building's interior materials by analyzing combustion and thermal properties according to flame retardant treatment of paper honeycomb and evaluating flame retardant performance according to the flame retardant treatment using phosphorus-based flame retardant agents.

Table 1 Mechanism of phosphorus-based flame retardant agents

Diammonium phosphate + Δ → Polyphosphate + NH_3



Experimental methods

Flame retardants

The WEEE/RoHS legislated by EU was legislated to remove a legal gap of signatory countries on use restrictions of hazardous substances being used in electrical/electronic devices and contribute to health protection of the mankind and environment-friendly recovery and disposal of WEEE. Owing to this environment-friendly regulation of EU, it is being prescribed that the use of heavy metals, such as lead (Pb), mercury (Hg), cadmium (Cd), and hexavalent chromium (Cr), as well as PPB and PBDE which are bromine-based flame retardant agents in products being previously produced is prohibited [5].

Bromine-based flame retardant agents form a carbonaceous layer in a surface by promoting carbonization of wood and paper, and this layer can get flame retardant effects by intercepting oxygen. In addition, it has an advantage that includes less toxic substances and does not receive environmental regulation. Table 1 shows a mechanism of phosphorus-based flame retardant agents.

Accordingly, the present research has evaluated flame retardant performance using phosphorus-based flame retardant agents to replace bromine-based flame retardant agents.

Cone calorimeter test

For combustion tests, a cone calorimeter test (ISO 5660 standards, manufacturing by ASTM E 1354 [6], Cone Calorimeter 2006, Festec International Co., Ltd.) was executed according to ISO 5600 standards [7] using specimens of 100 × 100 × 26 mm^3. The test compared and analyzed flame retardant performance according to flame retardant treatment conditions of honeycomb paper materials in heat flux conditions of 50 kW m^{-2}.

Selection of test materials

The paper honeycomb being utilized in architectural interior materials and packing materials mainly uses liner boards that have strong durability and that need cheap production expenses. The paper used for manufacturing of specimens is paper honeycomb core for doors, and the present test has used the paper with the basis weight of 200 and 210 g m^{-2}. For its objective performance evaluation, the flame retardant paper honeycomb being commercialized in Japan was selected as a control group. Sample 1 is paper with the basis weight of 200 g m^{-2}, and Sample 2 is paper with the basis weight of 210 g m^{-2}. Table 2 shows properties of the targeted paper.

Impregnation and strength measurement of flame retardant agents

The impregnation of phosphorous-based flame retardant agents for securing flame retardant performance of honeycomb deduced proper impregnation time by varying impregnation time of flame retardant agents through basic tests. In order to measure the impregnation amount of flame retardant agents, the water content was sought by recording mass before and after impregnation. Table 3 shows the water content of paper honeycomb in case of impregnation of flame retardant agents.

It was reported that the proper time for impregnating flame retardant agents into paper honeycomb does not make heat release rate's suppression effects go up after impregnation time of 2 s, and it was confirmed that when impregnation time lengthens, deformation of paper occurs due to

Table 2 Properties of paper

	Sample 1	Sample 2
Thickness/mm	0.29	0.30
Moisture/%	7.5	7.3
Bursting/kg cm^{-2}	3.1	5.38
Ring crush-CD/kg f	30.0	32.8

Table 3 The water content's measurement

Test piece	Times			Average
	1	2	3	
Sample 1	39.83	42.08	39.32	40.41
Sample 2	41.92	37.05	43.36	40.78

Table 4 Strength of paper honeycomb before/after flame retardant treatment

Test items	Before treatment/ N cm^{-2}	After treatment/ N cm^{-2}	Strength degradation rate/%
Sample 1			
Compressive strength	8.38	7.03	16.11
Wet compressive strength	2.82	2.95	−4.61
Sample 2			
Compressive strength	11.62	9.87	15.06
Wet compressive strength	5.26	4.51	14.26

weakness to moisture, and that when impregnation time is short, flame retardant performance is not secured properly because flame retardant agents are not deeply penetrated into paper honeycomb. According to these results, the impregnation time used in the present test was set as 2 s [8, 9].

In order to quantitatively measure strength deterioration of paper honeycomb after impregnation treatment of flame retardant agents, the compressive strength and wet compressive strength before and after the treatment of specimens were measured according to the standard of KS F 3517:2006 (Paper cores for panel) [10], so its result is shown in Table 4.

Like the result of Table 4, the strength deterioration of 16.11% occurred in Sample 1, and the strength deterioration of 14.26% occurred in Sample 2 after flame retardant treatment.

Classification of specimens

Specimens were manufactured according to five kinds of conditions, such as Case A (untreated), Case B (case that a flame retardant film is attached to a surface), Case C (case impregnated into phosphorus-based flame retardant agents), Case D (case that a flame retardant film is attached to a surface after impregnation of flame retardant agents), and Case E (flame retardant paper honeycomb that is a control group) and executed flame retardant performance evaluation on the respective specimen.

Result

Flame retardant performance test of Sample 1 (weight 200 g m^{-2})

The present research utilized a cone calorimeter to grasp flame retardant performance according to the flame retardant treatment, compared a heat release rate of each specimen through Figs. 1 and 2 and showed it.

Figure 1 shows a total heat release of Sample 1 (basis weight 200 g m^{-2} paper), and the total heat release of Case A, which is paper honeycomb that flame retardant treatment is not executed, appeared as 14.54 MJ m^{-2}. Especially, its ignition was most fast as 8 s, and its heat release rate was rapidly decreased by being burned mostly after 120 s. Ignition of Case B appeared as 14 s, so ignition time's delay effects could be confirmed, compared with the Case A. But the peak heat release's value after ignition was 155.62 kW m^{-2} per 80 s and appeared as most highly among all the specimens, so the total heat release was eventually the highest as 14.57 MJ m^{-2}. Case C was not ignited singly, and its total heat release's value was the lowest as 2.30 MJ m^{-2}. The ignition time of Case D was 12 s, so it was ignited similar to Case B, but its combustion time was 9 s so that the combustion time of Case A was just 3% of combustion time of Case A. Its total heat release was 3.30 MJ m^{-2}, so that it appeared as being lower by about 77% than Case A. Case E was burned while showing a similar propensity to Case D, but its total heat release

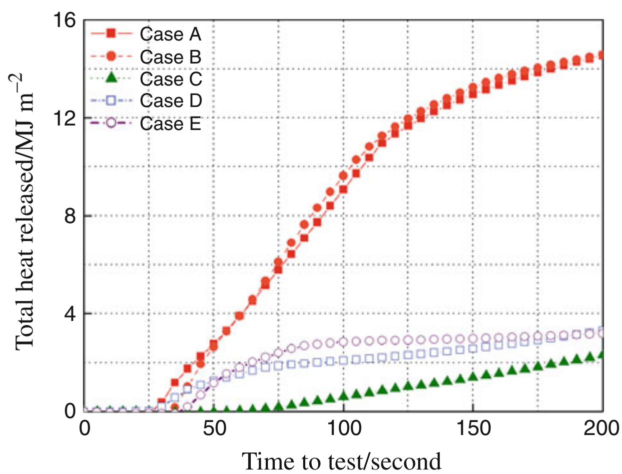


Fig. 1 Graph of the total heat release (Sample 1)

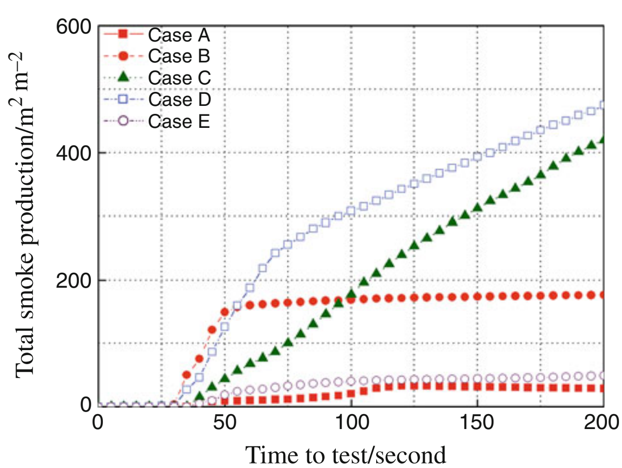


Fig. 2 Graph of the total smoke production (Sample 1)

appeared as 3.19 MJ m^{-2} so that it appeared more highly by 0.89 MJ m^{-2} than Case C.

As a result, it is judged that although the flame retardant film delays ignition time, it does not deteriorate the total heat release amount, and it is judged that the phosphorous-based flame retardant agents executed a function preventing ignition and lowering the heat release.

Figure 2 shows total smoke production of Sample 1 (basis weight 200 g m^{-2} paper). Total smoke production of Case A appeared the lowest as 28.32 m^2 m^{-2}. In case of Case B, the smoke production increased for about 30 s after ignition, but afterward, smoke was not generated anymore. In case of Case B, the smoke was continuously generated after ignition time of Case A, and its total smoke production appeared as 534.72 m^2 m^{-2}, and the smoke was continuously generated even after completion of tests. In case of Case D, it generated the most smoke of 593.67 m^2 m^{-2}, recorded a higher value by 20.96 times than Case A and generated smoke continuously. Case E generated smoke of 49.18 m^2 m^{-2} and recorded a higher value by about 1.74 times than Case A, but it showed a relatively lower value than Case B, C, and D.

As a result, it is judged that the flame retardant film and phosphate-based flame retardant agents all act as a factor increasing smoke production.

Flame retardant performance test of Sample 2 (weight 210 g m^{-2})

Figure 3 is a result of a total heat release of Sample 2 (paper with basis weight of 210 g m^{-2} paper). The total heat release of Case A appeared as 15.38 MJ m^{-2}. Its ignition time was 9 s and was first ignited among all the Cases like Case 1 of Sample 1. The ignition time of Case B was delayed by 5 s compared with the Case A. Its heat release rate's generation timing was also later by about 10 s than Case A. But the total heat release highly appeared as 0.03 MJ m^{-2}. Case C which is specimens impregnated with flame retardant agents did not ignite even in this test, and its total heat release appeared the lowest as 2.49 MJ m^{-2}. Case D ignites at 13 s and burned for 12 s, and its total heat release was 3.12 MJ m^{-2} and more highly appeared by around 25% than Case C. As a result of comparing it on the graph, Case D and E showed a similar propensity in an aspect of ignition time and total heat release.

As a result, it is judged that although the flame retardant film delays ignition time, it does not have an impact on the total heat release. The phosphorus-based flame retardant agents acted to suppress the total heat release by preventing ignition.

Figure 4 shows total smoke production of Sample 2 (basis weight 210 g m^{-2} paper). Total smoke production of Case A and Case E appeared the lowest as 58.32 and 49.18 m^2 m^{-2}, respectively. In case of Case B, smoke production increased for 30 s after igniting at 14 s, but afterward, smoke was not generated anymore. In case of Case C, smoke is continuously generated after ignition time, and its total smoke production appeared as 534.72 m^2 m^{-2}, and smoke production increased even after completion of tests. In case of Case D, its total smoke production appeared the highest as 593.67 m^2 m^{-2}, and highly appeared by 12.07 times compared with the Case E that total smoke production is the lowest.

In case of smoke production, smoke was continuously generated even after completion of tests.

As a result, it is judged that the flame retardant film and phosphorus-based flame retardant agents all became a factor increasing total smoke production.

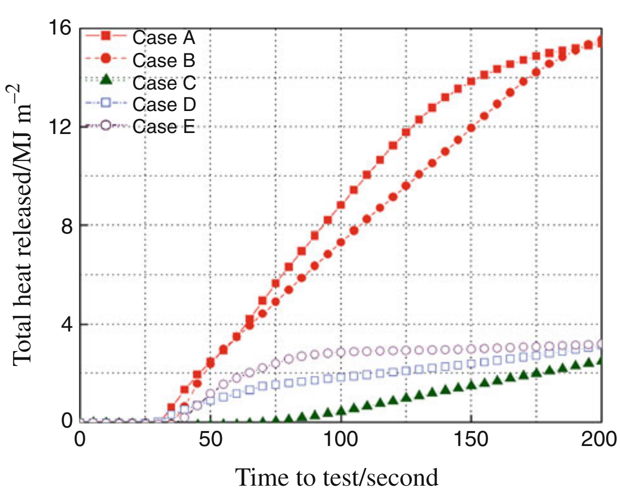


Fig. 3 Graph of the total heat release (Sample 2)

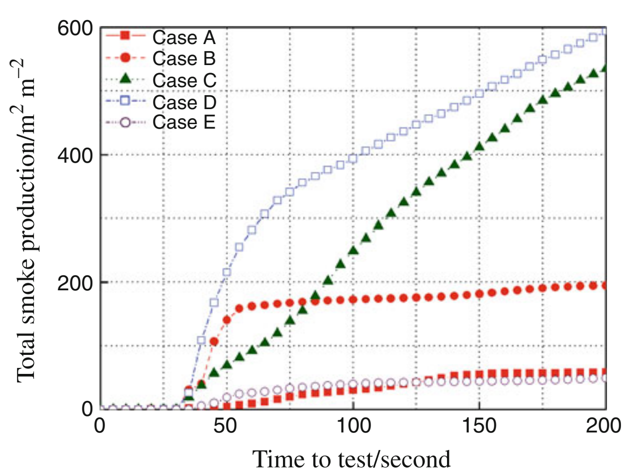


Fig. 4 Graph of the total smoke production (Sample 2)

Conclusions

As a result of analyzing properties on Combustion and thermal properties according to flame retardant treatment of paper honeycomb, the following conclusion was deduced:

1. The paper with the basis weight of 200 and 210 g m^{-2} shows a similar heat release rate, and it was confirmed that it is the same even after flame retardant treatment.
2. The flame retardant film was confirmed to have effects delaying ignition time, but it does not have a big impact on the heat release rate after ignition. But the total smoke production significantly increased due to the combustion of flame retardant films.
3. The impregnation effect of phosphorus-based flame retardant agents for 2 s showed performance that is not ignited in heat flux of 50 kw, but its total smoke production increased by an average of 11.86 times.
4. When attachment of a flame retardant film and impregnation of flame retardant agents are carried out side by side, its total heat release increases by 1.34 times and total smoke production increases by 1.12 times, so that its performance appeared to lower than specimens impregnated with flame retardant agents.
5. The impregnation effect of flame retardant agents showed a decrease effect of 24.9% in case of a total heat release compared with Japan's flame retardant honeycomb being commercialized, but its total smoke production increases by 9.70 times so although its performance was improved in an aspect of a heat release rate, it appeared that improvement of smoke production is necessary.
6. The phosphorus-based flame retardant agents has excellent flame retardant performance on paper and short treatment time, so it is thought that it can be utilized as interior or exterior materials inside a building requiring fire resistance.
7. As a result of analyzing properties on combustion and thermal properties according to flame retardant treatment of paper honeycomb obtained through the present test, the case impregnated with flame retardant agents showed the most superior flame retardant performance, so it is judged that these results could be utilized and applied to interior materials of a building using the honeycomb structure.

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