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An experimental study on the ignition and emissions characteristics of wallpapers †

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Abstract

The combustion characteristics of wallpaper and the toxicity of gas produced from wallpaper fires were analyzed to evaluate the fire risk of wallpaper used in living spaces. Ash content was measured with a high-temperature electric furnace, and thermal analysis was carried out with thermogravimetric analysis (TGA). Combustion time and smoke concentration were measured with a cone heater and a combustion gas analyzer. The smoke density of samples was measured using the smoke chamber ASTM E 662. Pyrolysis in silk wallpaper began at a lower temperature than the other samples. This means that silk wallpaper can be ignited at a low heat flux and will have a greater fire risk than other kinds of wallpaper. Heat by radiation flux caused silk wallpaper to ignite in the shortest time compared to the other samples, so the time for evacuation in this situation may also be reduced. Silk wallpaper also released the highest carbon monoxide concentration, so the toxicity and harmful effects to consciousness were stronger than any other wallpaper. The smoke densities of silk wallpaper and fire retardant-treated silk wallpaper were very high due to their vinyl coatings.

Keywords**:** Combustion; Combustion gas; Fire risk; Toxicity; Wallpaper

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1. Introduction

Recently, fire safety has become a major social issue in Korea. Huge fires in public and private places — for example, Sealand Youth Training Center in Hwaseong-gun, Gyeonggido; The Amazon Bar in Seongnam City, Gyeonggido; and Daegu Subway Station — resulted in many casualties and substantial damage to property [1]. In all of these cases, highly combustible interior materials were used. Large-scale damage to human life and property was caused because flames spread rapidly and large amounts of smoke and toxic gas were emitted [2]. In Korea, wallpapers are commonly used as interior finishing materials. A fire risk analysis of wallpapers needs to be carried out to help prevent future calamities as a result of fires. Fire risk analysis of wallpapers consists of analyzing the combustion characteristics of wallpapers and analyzing the composition of smoke emitted during combustion [3].

Despite this urgency to analyze the fire risk of buildings, the state of research on the toxicity of materials emitted by the combustion of interior wallpapers and flooring materials has been patchy and inadequate [2-4]. However, the recent revision of regulations on fire prevention that mandates the assessment of the characteristics of smoke emitted from interior materials has stimulated increased research in

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this field.

To identify the combustion characteristics of wallpapers, it is necessary to review the speed of combustion and the speed of heat emission. In the case of smoke, which affects evacuation efforts in the early phase of a fire, the major variables in risk assessment are concentration, emitted ingredients, and toxicity influenced by the amount of emissions [5]. Most of the casualties in domestic fire incidents are found to be due to suffocation caused by combustion gases; therefore, the concentration and toxicity of combustion gases are important factors to be assessed [4, 7]. For these reasons, quantitative risk assessment data about wallpapers, which are interior materials, must be gathered. This kind of data, however, is not readily or sufficiently available.

The studies of assessment methods on combustion gas toxicity can be useful sources of reference. In the United States, New York became the first state to regulate combustible products in 1986. The most representative method for the relative assessment of the lethality of concentration, LC_{50}, is provided for CO, HCN, and CO_2 involving building materials, plastic products [8, 9], and textile products by the National Institute of Standards and Technology (NIST) [10]. It is important to determine the combustion chara teristics and assess the fire risk of wallpaper.

The aim of this paper is to investigate the ignition properties, emissions characteristics and toxicity index of various wallpapers. Seven wallpaper types were investigated: two types of wallpapers that are commonly used, three types of wallpapers that have been developed to be environment-friendly, and two types of wallpapers with a fire-retardant function. To obtain the ignition and emission data for fire risk assessment from the combustible properties of the wallpapers, thermogravimetric analysis was performed, and ignition time by radiation heat flux and combustion gas components was measured.

2. Experiments

2.1 Test wallpapers

Many types of wallpapers are used on the inside walls of buildings. The wallpapers selected for this study are commonly used wallpapers (silk wallpaper and Hapji wallpaper), environment-friendly wallpapers designed to prevent “new apartment syndrome” (green tea-coated wallpaper, char-coated wallpaper, and ocher- and char-coated wallpaper), and wallpapers designed to reduce fire risk (fire retardant-treated silk wallpaper and vermiculite-coated wallpaper). We attempted to obtain the ingredients of the selected samples, which are produced by four companies, from the manufacturers, but the data was not released because the information was considered confidential. Samples were cut into appropriate amounts and sizes and were dried for 24 hours in a dryer at 100 ± 2℃.

Table 1. Lists of wallpaper samples.

Sample name	Sample symbol	Density (g/m^3)	Main component parts
Hapji wallpaper	S1	7.7600	Paper
Silk wallpaper	S2	7.1069	Paper+PEC*
Char-coated wallpaper	S3	7.2363	Char+Paper
Vermiculite-coated wallpaper	S4	8.8688	Vermiculite+ Paper
Ocher- and char-coated wallpaper	S5	7.4050	Ocher+Char+ Paper
Fire retardant-treated silk wallpaper	S6	8.2736	Paper +PEC
Green tea-coated wallpaper	S7	7.3198	Green tea + Paper

*PEC: Polyethylene Chloride

2.2 Experimental apparatus and procedure

To measure the amount of ash, an electric furnace which can attain temperatures of up to 1300 °C was used and a coal ash measurement method was applied. The samples were dried for 24 hours at 100 °C. Then, 1 g of each sample was placed in a silica crucible. The crucibles were put into electric furnaces and heated for four hours at 600 °C.

Thermogravimetric analysis measures changes in sample weight and temperature caused by temperature change. The character istics of decomposition and combustion of wallpaper due to temperature change can be verified by the temperature-weight characteristic curve [11]. Measurements were made in an aerobic environment at a heating rate of 6 °C /min, and the samples reached temperatures of up to 500 °C.

Fig. 1 shows the device for testing the combustion characteristics of the wallpaper. The experimental setup was composed of a cone-shaped radiation electric heater, a holder to fix the specimen, a combustion gas analyzer, a heat flux measurement device, a spark ignition circuit, and a data collection and analysis system

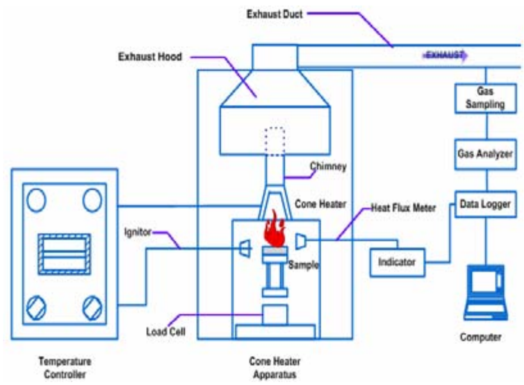

Fig. 1. Schematic diagram of experimental apparatus.

a) Sample b) Heating c) Burning d) Ash

Fig. 2. Combustion processes of test wallpapers.

Fig. 2 shows the combustion process from the sample to ash for the test wallpaper. Dried samples were fixed to specimen holders with diameters of 11.3 cm. Using a cone heater, 20 kW/m^2 of radiation heat flux was applied to measure ignition time and ignition phenomena. Using a combustion gas analyzer, the concentrations of HCN, HCl, CO_2, CO, NO_x, and SO_2 were analyzed during heating. The smoke concentration in the combustion chamber was measured with the optical density measuring system based on the testing method of ASTM 662. The assessment of toxicity for the combustion gas was made by the N-gas model of NIST [3].

3. Results and discussion

Table 2 shows the results from the measurement of changes in mass and ash amount by wallpaper type. Table 2 lists the ash content of the tested wallpapers. The ash content of the char-coated wallpaper (S3) is highest among the wallpapers and the reduction rate is in order of green tea-coated wallpaper (S7), Hapji wallpaper (S1), ocher and char wallpaper (S5), fire retardant-treated wallpaper (S6) , silk wallpaper (S2) , and vermiculite wallpaper (S3).

The greater amount of mass loss is associated with products that had greater potential for pyrolysis and were therefore more combustible. In general, the amount of ash was influenced by the composition of

Table 2. Ash content of samples.

Sample	Weight loss (g)	Ash (%)
S1	0.8589	14.6223
S2	0.7969	20.6591
S3	0.9521	4.9900
S4	0.7070	29.9723
S5	0.855	14.9300
S6	0.825	17.5000
S7	0.8884	11.9000

materials. In other words, wallpaper that was composed of fibroid materials formed small amounts of ash, whereas wallpapers with large amounts of additives tended to yield larger amounts of ash.

Fig. 3 shows the characteristics of thermogravimetric analysis (TGA) of the various wallpapers. For example, an analysis of the Hapji wallpaper's TGA graph showed that the initial temperature of pyrolysis was about 260 ℃ and that rapid weight loss caused by pyrolysis occurred at temperatures between 260 and 350 ℃. In this case, the combustion began at a heating temperature around 330 ℃ and the maximum reduction of mass was 74.5% at the temperature range between 330~350 ℃. In the same manner, the various wallpapers were investigated for the TGA.

Fig. 4 shows the temperature of pyrolysis onset for each sample. As illustrated in Fig. 4, the initial pyrolysis temperature of the fire retardant-treated silk wallpaper was lowest among the samples, and thus it was expected to be faster than the other samples.

In spite of the treatment with fire retardant, the pyrolysis temperature is low (about 150 °C) compared to the other wallpapers due to the initial decomposition of the flame retardant. The experimental results show that the process of decomposition in the high-temperature field is fast in silk wallpaper (S2) and fire retardant-treated silk wallpaper (S6), whose surfaces are vinyl-coated. Pyrolysis takes place easily in wallpapers such as green tea-coated wallpaper (S7) and ocher and char wallpaper (S5) that have a smooth surface because of low density paper. Pyrolysis is relatively slower in high density cellulose wallpapers such as Hapji wallpaper (S1) and char-coated wallpaper (S3). In the case of the vermiculite wallpaper (S4), the initial temperature for decomposition seems to be high because of incombustible ingredients.

Using a cone heater as illustrated in Fig. 1, the phenomenon of ignition for wallpaper was investigated when heat flux was 20 kW/m^2. In this case, an electric spark was given as the ignition source.

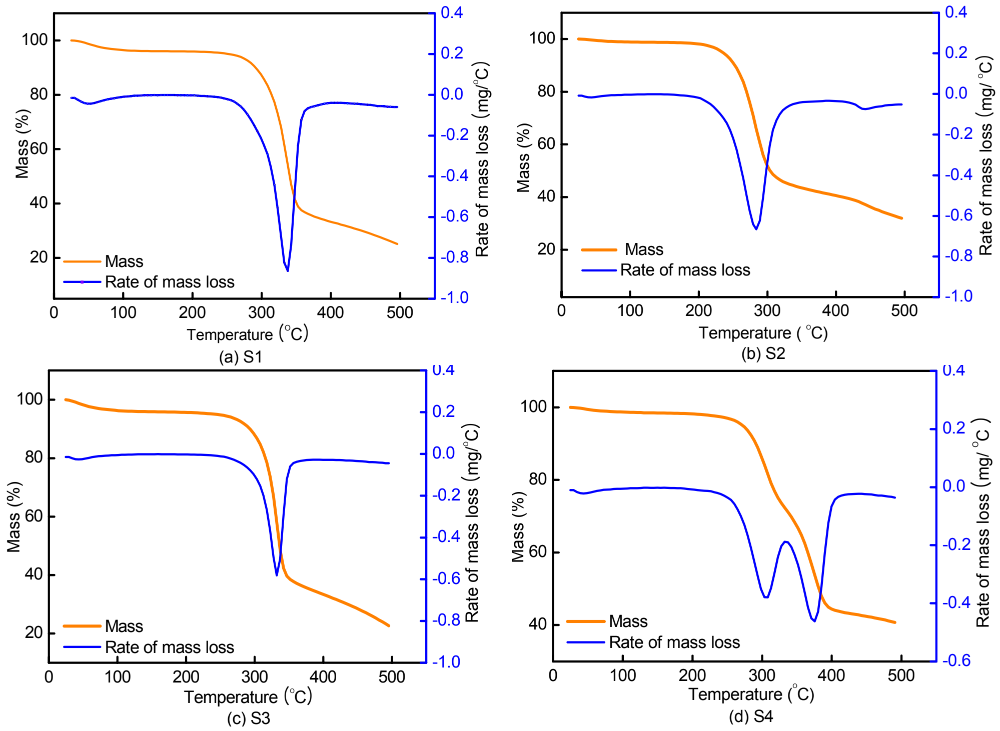

Fig. 3. TGA analysis of mass reduction and temperature difference of wallpapers.

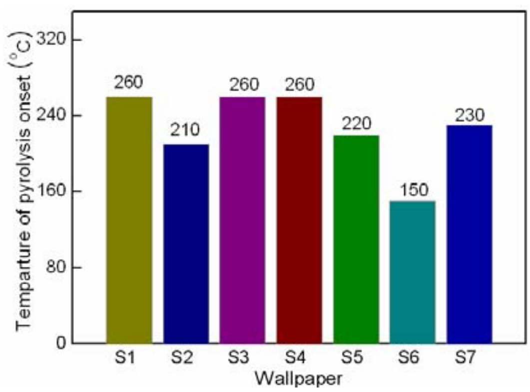

Fig. 4. Pyrolysis temperature of wallpapers.

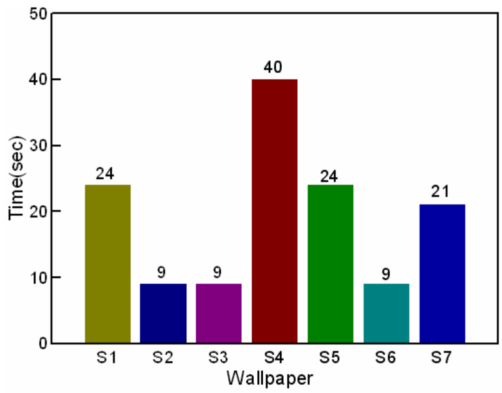

Fig. 5. Ignition characteristics of wallpapers.

Fig. 5 shows the characteristics of ignition time when heat flux of 20 kW/m^2 was applied to samples with an electric spark. The experimental results show that the silk wallpaper (S2), char-coated wallpaper (S3) and fire retardant-treated silk wallpaper (S6) had shorter ignition times than those of samples S4, S1, S5 and S7. This means that the pyrolysis begins at a low temperature and it facilitates the production of combustible gas. The ignition times ranged from 21 to 40 seconds for S4, S1, S5 and S7.

In general, solid combustible materials are known to ignite when radiation heat is 10-20 kW/m^2 [12]. In the case of wallpaper, the thickness is less than 1 mm and the wallpaper is composed of thin combustible materials. With a heat flux of 20 kW/m^2, ignition limits are higher than those of cellulose combustible materials.

Fig. 6 shows the CO concentration released by the samples when heat flux of 20 kW/m^2 is applied with an electric spark. As can be seen in the distribution of

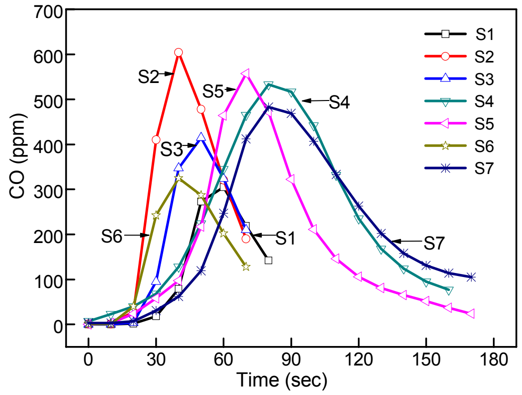

Fig. 6. CO generation from the wallpapers.

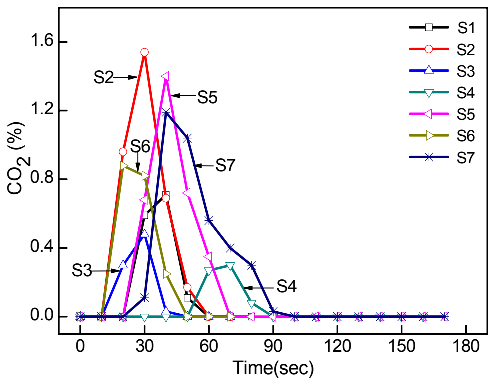

Fig. 7. CO_2 generation from the wallpapers.

CO concentrations, larger amounts of CO were generated by silk wallpaper (S2), ocher- and char-coated wallpaper (S5), vermiculite wallpaper (S4) and green tea-coated wallpaper (S7). As shown in Fig. 6, the ignition times of wallpapers S2, S3, S6 and S1 were completed within 80 seconds, whereas the wallpapers S5, S7 and S4 were finished within 170 seconds of ignition time. The main reason for the higher concentrations of CO emission from sample combustion by heat flux seems to be due to smoldering in the heating process of the smoldering wallpapers such as the ocher- and char-coated wallpaper, green tea-coated wallpaper, and so on. Combustion gas analysis showed that vinyl-coated silk wallpaper generates greater amounts of CO in comparison with the other wallpapers, and that vinyl-coated silk wallpaper thus increases the risk of suffocation by smoke during a fire.

Fig. 7 shows the CO_2 concentrations of the wallpapers according to the elapsed time after the heating of radiation heat flux of 20 kW/m^2. As shown in this

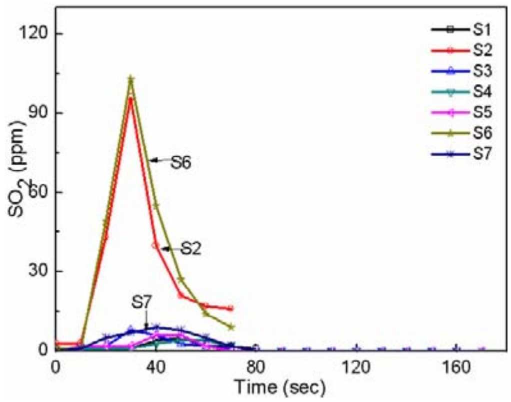

Fig. 8. SO_2 generation from the wallpapers.

figure, all samples were ignited and rapidly burned at the same time. Especially, somewhat high concentration of CO_2 was produced in silk wallpaper (S2), ocher- and char-coated wallpaper (S5), green tea-coated wallpaper (S7), and fire retardant-treated silk wallpaper (S6) in the decreasing order of concentration. The cause was the difference in organic content. Semiconductor had the most production of organic matters among synthetic silk (organic) + PEC (organic) samples, and for ocher- and char-coated wallpaper (S5), CO_2 emissions decreased by retarding the combustion reaction by adding ocher, or inorganic compound. For fire retardant-treated silk wallpaper (S6), addition of flame retardants decreases heat transfer rates and production of combustible gas, and also, it does not participate in combustion reaction. That is emission of CO_2 gas can decrease depending on the content of flame retardants.

Fig. 8 illustrates the SO_2 concentration of combustion gas of the wallpaper. As illustrated in Fig. 8, SO_2 concentration was generated in a large quantity in the combustion of fire retardant-treated silk wallpaper (S6) and silk wallpaper (S2). In the other samples, nearly 10ppm was generated when a radiation heat flux of 20 kW/m^2 was applied with an electric spark.

Fig. 9 shows the relation between NO_X concentration and elapsed time for various wallpapers at constant heat flux. NO_X emission was generated in small quantities in all of the samples. As shown in S7 wallpaper, NO_X emission of the green tea-coated wallpaper S7 emitted higher concentrations in comparison with the other wallpapers because of the higher temperature of the combustion gas. As illustrated in Fig. 9, the silk wallpaper S2, ocher- and char-coated wallpaper S5, fire retardant-treated silk wallpaper S6 and

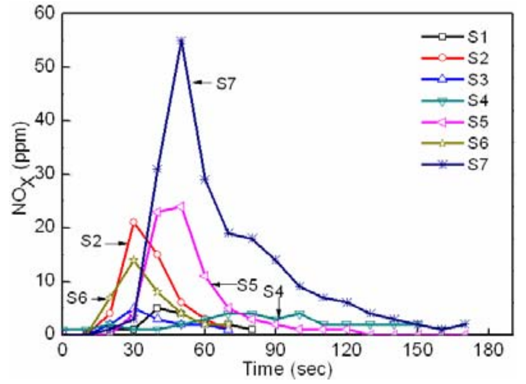

Fig. 9. NOx generation from the wallpapers.

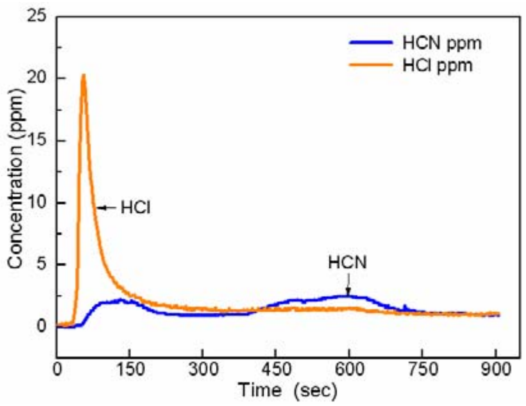

Fig. 10. HCl and HCN generation from fire retardant treated silk wallpaper under 20kW/m^2 heat flux.

green tea-coated wallpaper S7 emitted a greater extent of nitric oxide than the other samples. Green tea-coated wallpaper, as mentioned above, generated a large amount of NO_X emission because it was ignited with a flame. The maximum concentration of NO_X appears at 50 seconds after the elapsed time after the heating with ignition source.

Fig. 10 shows the HCN and HCl concentrations of the fire retardant-treated silk wallpaper at heat flux of 20 kW/m^2. As shown in Fig. 10, emissions of HCl were concentrated in 40 to 100 seconds of the time but HCN emissions were at the same concentration of 4ppm for the duration of combustion. Both toxic component gases arise from coated vinyl and fire retardants. As shown in Table 3, other wallpapers generated smaller amounts or none at all.

As shown in Table 3, a comparison of HCI and HCN in wallpaper samples shows that HCl and HCN generation in fire retardant-treated silk wallpaper (S6) occurred in larger quantities than in other samples.

Table 3. Peak HCl and HCN concentrations (ppm).

Gas	Samples						
	S1	S2	S3	S4	S5	S6	S7
HCl	3	3	2	2	3	20	7
HCN	0	0	0	1	2	3	1

Table 4. Toxicity index of the samples (20 kW/m^2 heat flux with spark ignition).

Samples	Combustion Gases						
	CO (ppm)	CO_2 (ppm)	SO_2 (ppm)	NO x (ppm)	HCN※ (ppm)	HCl※ (ppm)	Toxicity index (Tx)
S1	305	0.71	5	5	3	3	0.11
S2	604	1.54	96	21	3	0	0.35
S3	415	0.48	8	5	2	2	0.12
S4	533	0.3	4	4	2	1	0.13
S5	557	1.4	6	24	3	3	0.26
S6	325	0.88	103	15	20	3	0.38
S7	483	1.19	9	55	7	1	0.46

※ Without ignition.

This probably stems from the use of chemical components as fire retardants. The HCl value of green tea-coated wallpaper (S7) was high because of the adhesives used to attach green tea particles onto the paper.

To assess the combustion gas toxicity of wallpaper samples, the method proposed by the NIST of the United States was used [13, 14]. In this method, toxicity is expressed by LC_{50}, Cco, Cco$_2$, C_{SO2}, C_{NOx}, C_{HCN}, and C_{HCl}, which are analytical concentrations (ppm) of combustion products. The toxicity index of emissions is given by

$$T_X = \frac{C_{CO}}{(LC_{50})_{CO}} + \frac{C_{CO_2}}{(LC_{50})_{CO_2}} + \frac{C_{SO_2}}{(LC_{50})_{SO_2}} + \frac{C_{NO_X}}{(LC_{50})_{NO_X}} + \frac{C_{HCN}}{(LC_{50})_{HCN}} + \frac{C_{HCl}}{(LC_{50})_{HCl}}$$

where LC_{50} (lethal concentration 50) is the level of concentration at which 50% of a test population died from the introduction of this airborne chemical and C denotes the concentration of each component.

The toxicity index of the samples is summarized in Table 4. The toxicity index shows that the green-tea coated wallpaper (S7) had the highest toxicity. Toxicity of the remaining samples, in descending order, was silk wallpaper (S6), silk wallpaper (S2), ocher- and char-coated wallpaper (S5), vermiculite-coated

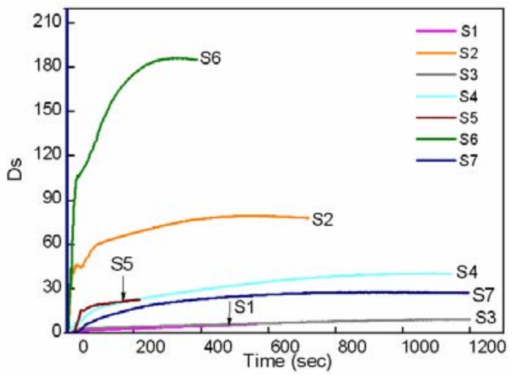

Fig. 11. Specific optical density of retardant coated silk wallpapers.

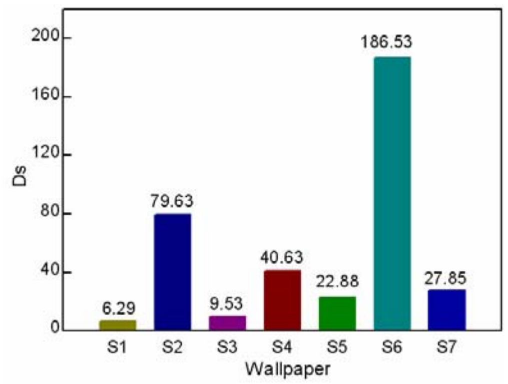

Fig. 12. Optical smoke density of wallpapers.

wallpaper (S4), char-coated wallpaper (S3), and Hapji paper wallpaper. A toxicity value of more than 0.4 is known to be dangerous [13, 14].

Figs. 11 and 12 show the relation between smoke concentration and elapsed time of heating and the comparison of smoke density of the various wallpapers, respectively. The smoke indices of the wallpaper samples were investigated with the ASTM E 662. In Fig. 11, the smoke density of the combustion gas of fire retardant-treated silk wallpaper (S6) was highest and S6 had the shortest time of combustion. Green tea-coated wallpaper (S7) had low the smoke density and had the longest combustion time. The Hapji wallpaper and char-coated wallpaper showed the lowest smoke density, whereas the char-coated wallpaper had the longest duration, as illustrated in Fig. 11. Measurement of smoke concentration by ASTM E 662 showed that vinyl-coated silk wallpaper and fire retardant-treated silk wallpaper, which are beautiful and highly decorative, generate a large amount of toxic smoke that impedes the rapid evacuation of people.

As shown in Fig. 12, the maximum smoke density value was 186.53 for the fire retardant-treated silk wallpaper (S6), and the next largest smoke density was 79.63 for the silk wallpaper (S2). The smoke densities of the Hapji wallpaper (S1) and char-coated wallpaper (S3), which are almost purely composed of cellulose, were low. These results mean that smoke concentration is high in the case of silk wallpaper (S2) and fire retardant-treated silk wallpaper (S6) because of the polyester carbonate coating on the wallpaper surface, and that smoke concentration is relatively higher for wallpapers that were coated to prevent other harmful factors for environmental hygiene.

4. Conclusions

This study investigated by thermogravimetric analysis, the ignition and emissions characteristics of the various wallpapers that are commonly used as interior finishing materials. The experiments were carried out on the different kinds of wallpapers such as commonly used wallpapers, environment-friendly wallpapers, and fire retardant treated wallpapers. The results obtained from this investigation are as follows:

(1) Thermogravimetric analysis showed that silk wallpaper was more dangerous during a fire than other wallpapers. Pyrolysis began at a relatively lower temperature and silk wallpaper could be ignited at a lower level of radiation heat flux.

(2) The combustion experiment using a cone heater showed that silk wallpaper and fire retardant-treated silk wallpaper had faster ignition at low heat flux in comparison with the other wallpapers. The difference in ignition time occurs by the chemical structure of combustion reactants. Therefore, as a result of this study, ignition times of vinyl-coated silk wallpaper (S2) and fire retardant-treated silk wallpaper (S6) which both exhibit characteristics of organic materials, turned out to be short. Such a phenomenon is caused by the difference in materials characteristics, which is influenced by the different contents of organic matters. The S2 sample had the shortest ignition time because the PEC used in silk materials and glues consisted of organic matters. The S6 sample contained some fire-retardants, but it had the second-shortest ignition time because of high organic content. Also, higher concentration of organic matters (or organic compounds) means faster burning velocity as well as easier igni-

tion. As a result of measuring pyrolysis temperatures of samples, pyrolysis temperatures of S2 and S6 were lower than the other samples. This phenomenon is that a pyrolysis temperature brings about easier production of pyrolysis gas, faster pyrolysis rate, and consequently shorter arrival time to concentration range of flammable gas onto surface of samples.

(3) Combustion gas analysis showed that vinyl-coated silk wallpaper generates a greater amount of CO in comparison with other wallpapers and increases the risk of suffocation by smoke during a fire.

(4) Measurement of smoke concentration showed that vinyl-coated silk wallpaper and fire retardant-treated silk wallpaper, which are beautiful and highly decorative, generate a large amount of toxic smoke that impedes the rapid evacuation of people.

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