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Flame Retardation Modification of Paper-Based PVC Wallcoverings

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Abstract. The flame-retarded paper-based polyvinyl chloride (PVC) wallcoverings were successfully prepared, using plant fiber paper as base material and adding inorganic flame retardants and flame-retarded plasticizer as additives. Flame retardancy, thermostability, smoke suppression and mechanical properties were tested regarding to the prepared wallcoverings. The results showed that $2ZnO\cdot 3B_2O_3\cdot 3.5H_2O$ could improve flame retardancy and thermostability of paper-based PVC wallcoverings; plasticizer tricresyl phosphate increased flame retardancy of the prepared materials auxiliarily. Also, flame-retarded paper-based PVC wallcoverings with higher flame retardancy, smoke suppression and mechanical property was prepared using plant fiber paper with fix quantity of 90 g/m^3 as base material, using $2ZnO\cdot 3B_2O_3\cdot 3.5H_2O$ as inorganic flame retardant, and using tricresyl phosphate as plasticizer. For the flame-retarded paper-based PVC wallcoverings in this study, the limit oxygen index (LOI) reaches 32.3, maximal smoke density is 16.91 %, and the horizontal and longitudinal wet tensile strength reaches 1.38 kN·m^{-1} and 1.51 kN·m^{-1} respectively. Meanwhile, its flame retardancy meets the requirements about flame retardancy for material Class B_1 listed in Chinese National Standards GB 8624-2012, *Classification for burning behavior of building materials and products*. This research creates an effective path to prepare paper-based PVC wallcoverings with high flame retardancy.

1 Introduction

According to *Wallcoverings Sales Statistics* of International Wallcovering Manufacturers Association which was operated in 2013, the total home sales of wallcoverings in Chinese market reached 186.7 million rolls, occupying 29 % of the world total consumption.[1] On the other hand, according to Chinese National Standard *Classification for burning behavior of building materials and products* (GB 8624-2012), the flame retardancy of wallcoverings must reach Class B_1, namely the values of limit oxygen index (LOI) must larger than 32.[2] Unfortunately, over 70 % wall coverings products in China are paper-based PVC wallcoverings,[3] which the values of LOI are less than 20.[4] At this low-level of LOI, such wallcoverings are deemed as flammable materials and would trigger a severe fire hazard, threatening people's lives and assets possibly. Therefore, the study of flame-retarded paper-based PVC wallcoverings not only takes great effects of architecture fire protection, fire extinguishment and person evacuation, but also assists to improve the added value of products.

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The improvement of flame retardancy regarding to paper-based PVC wallcoverings consists of the flame retardation modification of paper-based materials[5-6] and PVC compound pastes.[7-8] Due to the low costs, flame retardation modification of PVC compound paste is one of the most popular research hotspots. In this paper, the most appropriate inorganic flame retardant was selected out, and optimized the dosage through parallel experiments that adding three types of inorganic flame retardants into PVC compound pastes according to the results of LOI test and thermal gravity analysis of paper-based PVC wallcoverings. Then the flame-retarded paper-based PVC wallcoverings were prepared, replacing traditional flammable plasticizer with flame-retarded plasticizer and the inorganic flame retardant. The flame retardancy, thermostability, smoke suppression and mechanical property of the prepared wallcoverings were investigated.

2Experimental

2.1 Materials

Plant fiber based paper (90 g/m^3), polyvinyl chloride (PVC) resin powder with a polymerization degree of 1000 and plasticizer dioctyl phthalate (DOP) was generally provided by Sunreal Pro-environmental Wallpaper Co., Ltd in Fujian province in China.

Magnesium hydroxide ($Mg(OH)_2$), aluminium hydroxide ($Al_2(OH)_3$) and hydrous zinc borate ($2ZnO\cdot 3B_2O_3\cdot 3.5H_2O$, abbreviated as ZB-2335) were purchased from Aladdin Industrial Co., Ltd (China).

Plasticizer tricresyl phosphate (TCP) was got from Sinopharm Chemical Reagent Co., Ltd (China).

2.2 Specimen Preparation

The modification of paper-based PVC wallcoverings was carried out as the following steps. Firstly, 50 g of plasticizer DOP or TCP was added into 100 g of PVC resin to produce two types of PVC compound premixes by stirring with high speed. Then three kinds of inorganic flame retardants ($Mg(OH)_2$, $Al_2(OH)_3$ and ZB-2335) were respectively added into the PVC compound premixes with the mass fraction of 1 %, 3 %, 5 %, 8 % and 10 % to form compound paste. Finally, the PVC compound paste were coated on the surface of plant fiber paper (90 g/m^2) through 60 mesh screen, foamed and molded at 200 °C for 40 seconds, preparing paper-based PVC wallcoverings (250 g/m^2).

3 Characterizations

3.1 Limit Oxygen Index (LOI)

According to the ISO 4589-2: 1996, the prepared materials were cut into strip-shaped specimens with size of 52 mm width and 140 mm length. The specimens were measured on an oxygen index testing apparatus (JF-3, Nanjing Jionglei instrument equipment Co. Ltd., China). The LOI of the specimens was the average value determined from 5 specimens.

3.2 Thermal Gravity Analysis (TGA)

Material mass losses vs. temperature were determined with a TG-DTA instrument (Netzsch STA 449 F3) at the heating rate of 10 °C/min under oxygen with allow rate of 20 mL/min. Approximately 5 mg of three kinds of inorganic flame retardants, two kinds of plasticizers and the prepared materials were weighed and heated from 25 °C to 800 °C.

3.3 Combustion Simulation Test

The prepared materials were cut into square shape with side length of 20 mm. Place samples into box type resistance furnace (SX2-5-12, Shanghai Bomedical Equipment Industrial Co., LTD) at 300 °C for a prescribed time period under environment of air to simulate the combustion process.

3.4 Smoke Densityt

According to the ASTM D2843-1999, the prepared materials were cut into square shape with side length of 25.4 mm. The specimens were measured on a building materials smoke density apparatus (JCY-1, Nanjing Jiangning Analytical Instrument Co. Ltd., China). Smoke density data was recorded with the interval time of 15 seconds. The smoke density of the specimens was the average value determined from 5 specimens.

3.5 Wet Tensile Strength

According to the ISO 1924-2: 1994, the prepared materials were cut into strip-shaped specimens with size of 15 mm width (longitudinal direction) and 250 mm length (transverse direction). The specimens were immersed in deionized water for 5 minutes and absorbed superficial water using quantitative filter paper. The specimens were measured on a universal tensile tester (CMT 6104, Shenzhen SANS Test Machine Co. Ltd., China). The longitudinal and transverse wet tensile strengths of the specimens were the average value determined from 10 specimens.

4 Results and Discussion

4.1 The Comparison of Inorganic Flame Retardants

Using plant fiber paper as base material, three types of inorganic flame retardants, $Mg(OH)_2$, $Al_2(OH)_3$ and ZB-2335 were added into PVC compound paste (PVC resin and plasticizer DOP) to prepare PVC wallcoverings successfully. LOI and TG of the specimens were determined and the carbonization results were observed after simulating combustion in resistance furnace at 300 °C. Results are shown in figure 1 - figure 4.

LOI values of paper-based PVC wallcoverings with different content of inorganic flame retardants were shown in figure 1. The results showed that LOI of specimens without retardants was 23.4, and the LOI increased with the addition of retardants. LOI values of the wallcoverings adding ZB-2335 were obviously higher than other inorganic flame retardants ($Al_2(OH)_3$, $Mg(OH)_2$). LOI values of the wallcoverings increased with the content of ZB-2335. When the content of ZB-2335 was 5 %, the LOI values of the wallcoverings was 26.9, while the LOI values of $Al_2(OH)_3$ and $Mg(OH)_2$ were 23.8 and 24.0, respectively.

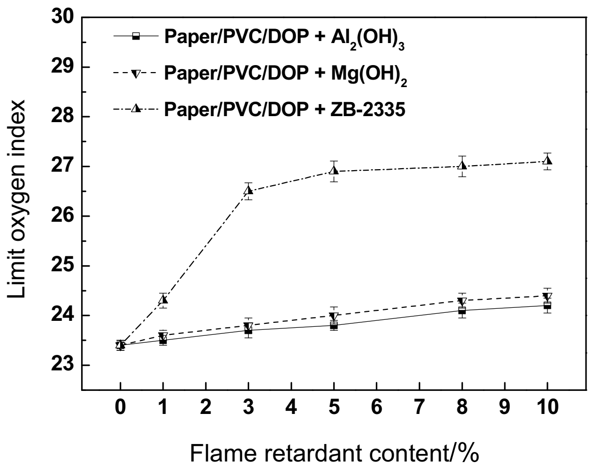

Fig. 1. Effect of amount of inorganic flame retardants on LOI of paper-based PVC wallcoverings

Thermal gravimetric analysis (TGA) curves for three inorganic flame retardants were shown in figure 2. According to figure 2, the initial thermal decomposition temperature of $Al_2(OH)_3$, $Mg(OH)_2$ and ZB-2335 were found at 234 ^oC, 203 ^oC, and 297 ^oC, respectively. The flame-retardant mechanisms about $Al_2(OH)_3$ and $Mg(OH)_2$ were similar. Their thermal decomposition performance began at 200 ^oC, losing crystal water gradually. The released water vapor can dilute the oxygen concentration and adsorb radiation energy of flame, thus decrease the surface temperature and the speed of thermal decomposition of PVC.[9] Weight loss of ZB-2335 started at 300 °C, losing 3.5 crystal water per molecule and playing a performance with the same as $Al_2(OH)_3$ and $Mg(OH)_2$. With the increase of temperature, heat decomposition of ZB-2335 was continued and $ZnCl_2$ and B_2O_3 were generated, covering the surface of PVC. The generated $ZnCl_2$ and B_2O_3 were covered with the surface of PVC, prevented from further oxidation reactions and heat decomposition. Additionally, some BCl_3 released during heat decomposition and reacted with water steam, generating HCl gas. Then, free radical halogen atoms were generated from HCl gas in flame, preventing from chain reaction and flame retardant.[10-12]

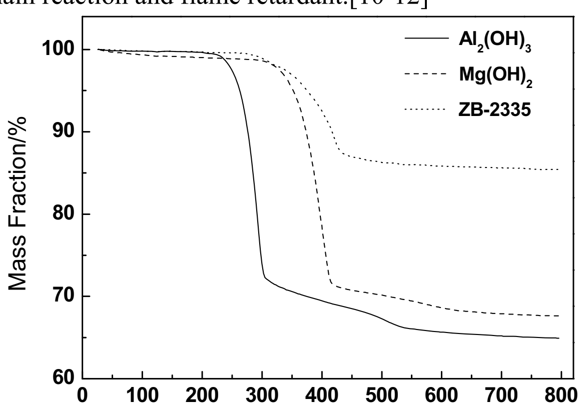

Fig. 2. TGA of different inorganic flame retardants

TGA curves of paper-based PVC wallcoverings were shown in figure 3. The thermal decomposition process of paper-based PVC wallcoverings was found for two stages in figure. 3. The thermo gravity rate was rapid at the first stage (200 °C - 300 °C) where the HCl was released from PVC, resulting the loss of total weight. At the second stage (300 °C - 800 °C), the thermo gravity rate was slow where the structure of conjugation polyene changed and carbon-containing compound combusted to decompose.[13] In figure 3, significant change of TGA curves for the parallel experiments were not found until 297 °C, which was close to the initial thermal decomposition temperature of ZB-2335. After adding 5 % ZB-2335, the thermal decomposition rate of specimens was found slower than the specimens with no additive. The final thermo gravity of specimens with ZB-2335 was found 83.19 %, while the other one was found 79.66 %. According to the results, thermostability performance of paper-based PVC wallcoverings was improved by adding ZB-2335.

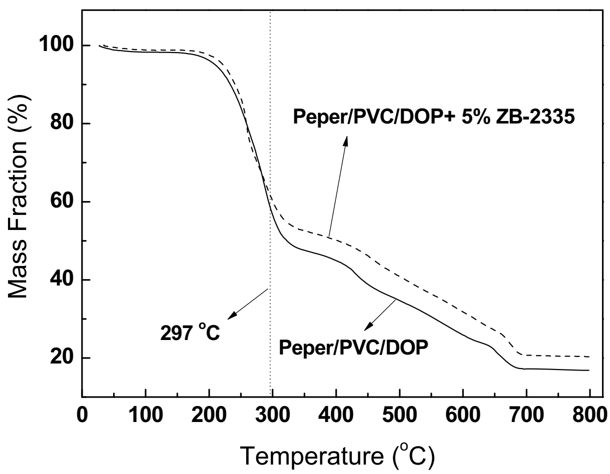

Fig. 3. TGA of paper-based PVC wallcoverings

In order to obtain flame retardancy performance, prepared paper-based PVC wallcoverings was placed in a constant high-temperature environment to simulate combustion to observe the morphology after burning. The morphologies of paper-based PVC wallcoverings with 0 % and 5 % ZB-2335 were shown in figure 4. The specimen without any flame retardant was found surface carbonization after combustion for 2 minutes. However, the surface carbonization of the specimens with 5 % ZB-2335 began with 5 minutes after combustion. The flame retardant of ZB-2335 can extend the process of carbonization of species, and improve the thermostability and flame retardancy of wallcoverings.

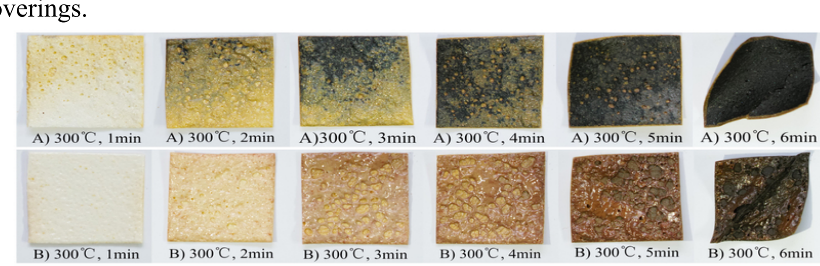

Fig. 4. photographs of paper-based pvc wallcoverings combusting at 300 oc (a. Without inorganic flame retardants, b. With 5 % zb-2335)

4.2 Influence of plasticizer on paper-based PVC wallcoverings

DOP was adopted as plasticizer in conventional paper-based PVC wallcoverings with mass fraction of 50 % of PVC resin. In figure 1, the LOI was less than 32 if the inorganic flame retardant was not added into the wallcoverings. The LOI of DOP and TCP were 23.4 and 26.4, respectively. This indicated that TCP not only was a plasticizer but also had potential advantage on flame retardancy. Thus improve fire retardation performance of paper-based PVC wallcoverings, flame-retarded specimens with TCP as plasticizer and 5 % ZB-2335 were prepared. Flame retardancy of plasticizer determined by LOI value, and TGA value was shown in table 1 and figure 5.

Table 1. Effect Of Plasticizer And Flame Retardant On Limited Oxygen Index Of Paper-Based Pvc Wallcoverings

Types of plasticizer	Types and contents of flame retardant	Limited oxygen index	Increasing range of LOI (%)
DOP	None	23.4	None
TCP	None	26.4	12.8
TCP	5 % ZB-2335	32.3	38.0

From table 1, LOI of paper-based PVC wallcoverings adding TCP plasticizer was increased by 12.8 % compared with the one adding DOP plasticizer. LOI value was increased by 38.0 % after adding 5 % ZB-2335. The results showed that TCP and ZB-2335 played the important role in flame retardancy. DOP was a flammable plasticizer, while TCP was flame-retardancy plasticizer. Combusting TCP can release polymetaphosphate to cover the surface of PVC and isolate oxygen, preventing combustion.[14] Flame-retarded paper-based PVC wallcoverings with plasticizer TCP and 5 % ZB-2335 was also found that LOI value was up to 32.3, satisfying the class B_1 of flame retardancy of the Chinese National Standards (GB 8624-2012)

TGA of two different plasticizers were shown in figure 5. From figure 5, initial thermal decomposition temperature of DOP and TCP were found at 155 ^{o}C and 206 ^{o}C, respectively. Roughly parallel thermal decomposition of two plasticizers was found in the two curves between 155 ^{o}C and 265 ^{o}C, crossing at 307 ^{o}C. It was indicated that, thermostability of TCP was better than DOP before 307 ^{o}C, while no significant difference of thermostability was found between TCP and DOP after 307 ^{o}C. This explained that the poor thermostability of C-O bond of ester group in DOP, which was easily broken after heating.[15]

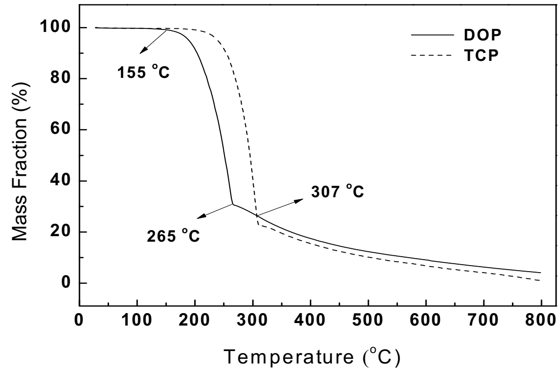

Fig. 5. tga of pvc plasticizers

4.3 Smoke Suppression of Flame-retarded Paper-based PVC Wall coverings

Large amount of black smoke in combustion was released by conventional paper-based PVC wall coverings, which threatened and endangered people's lives. Smoke suppression performance was found from inorganic flame retardant along with the effect of flame retardancy.[16] Smoke suppression performance was determined by the results of smoke density test. Smoke density images of the prepared flame-retarded specimen with TCP plasticizer and 5 % ZB-2335 against the conventional specimen with DOP plasticizer and without inorganic flame retardant were shown in figure 6. From figure 6, maximum smoke density of flame-retarded specimen was 16.91 %, which were decreased by 6.1 % compared with conventional specimen. During whole combustion smoke period, smoke densities of flame-retarded specimens were throughoutly less than conventional specimen, which indicated the better smoke suppression performance of flame-retarded paper-based PVC wall coverings.

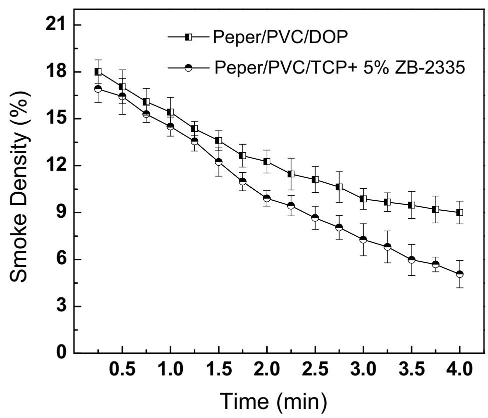

Fig. 6. The smoke density of paper-based PVC wallcoverings

4.4 Mechanical properties of Flame-retarded Paper-based PVC Wall coverings

Any mixing behavior of inorganic flame retardant was not allowed to decrease the mechanical property of paper-based PVC wallcoverings. Horizontal and longitudinal wet tensile strength of the prepared flame-retarded specimen with TCP plasticizer and 5 % ZB-2335 were shown in table 2.

Table 2. The Wet Tensile Strength Of Paper-Based Pvc Wallcoverings

Types of plasticizer	Types and contents of flame retardant (%)	Horizontal wet tensile strength (kN·m^{-1})	Longitudinal wet tensile strength (kN·m^{-1})
DOP	None	1.36	1.45
TCP	5 % ZB-2335	1.38	1.51

From table 2, the horizontal and longitudinal wet tensile strength increased by 9.7 % and 10.1 %, respectively. Due to the effect of tensile force, partial plastic deformation and orientation may be found in some weak area, leading the phenomenon of "crazing" at the surface or inside of the species. Inorganic fillers were found to compensate such deficiency, increasing the mechanical properties of species.[17] In table 2, longitudinal wet tensile strength was larger than the horizontal one regardless of inorganic flame retardants because the base material was plant fiber paper with the same property. Therefore, wet tensile strength of paper-based PVC wallcoverings was related to the properties of plant fiber paper.

5 Conclusions

1. It was found that the flame retardancy performance of paper-based PVC wallcoverings was improved by $Mg(OH)_2$, $Al_2(OH)_3$ and $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ (ZB-2335), respectively, and ZB-2335 had the best performance of flame retardancy. The initial thermal decomposition of ZB-2335 was found at 297 ^oC, releasing H_2O steam, $ZnCl_2$ and B_2O_3 to cover the surface of PVC and restrain the combustion of species.
2. Flammable material DOP was adopted in conventional process as plasticizer which the effect of flame retardancy of paper-based PVC wallcoverings was suppressed. However, the TCP was found to have better performance of both plasticizer and flame retardancy. LOI of paper-based PVC wallcoverings with plasticizer TCP was increased by 12.8 % comparing with DOP.
3. Flame-retarded paper-based PVC wallcoverings was prepared as the following method: 90 g/m^3 plant fiber paper as base material, $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ with the mass fraction of 5 % as inorganic flame retardant and TCP as plasticizer. After testing, LOI of wallcoverings was 32.3, maximum smoke density was 16.91 %, horizontal and longitudinal wet tensile strength were 1.38 $kN{\cdot}m^{-1}$ and 1.51 $kN{\cdot}m^{-1}$, respectively. These results conformed to flame retardancy of class B_1 of the Chinese National Standard GB 8624-2012.

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