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Impact of the Mixture of Hexa(N-hydroxymethyl)amidocyclotriphosphazene and Partially Methylated Melamine Formaldehyde Resin on the Flame Retardancy of Paper

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Abstract

The flame retardancy of the mixture of hexa(N-hydroxymethyl)amidocyclotriphosphazene and partially methylated melamine formaldehyde resin (HHMATP/PMMM) in paper was proposed by limiting oxygen index measurement (LOI), the vertical burning test and cone calorimetry test (CCT). In our research, the LOI of washed FR-paper could still be up to 33.5%; the after flame time , and burning time were reduced to 4.8 s & 0 s, and the char length was only 12.0 mm. While the results of CCT imply that compared with non-flame retarded paper, the heat release rate (HRR) of FR-paper with HHMAPT/PMMM increases gently; the mass loss becomes significantly slow, and the prolonged maximum heat release rate (PHRR), average heat release rate (MHRR), average effective heat of combustion (MEHC) and total heat release (THR) drop greatly. According to the experimental results, HHMATP/PMMM has not only excellent flame retardancy in paper but also good water resistance, with HHMATP/PMMM playing a flame retardant role mainly by means of the condensed phase mechanism.

Key words: *hexa(n-hydroxymethyl)amidocyclotriphosphazene, partially methylated melamine formaldehyde resin, flame retardancy, paper.*

Introduction

Cellulose obtained from plant fibers is the most abundant natural polymer. It is widely used but flammable. Being a typical example, paper and paper products as a three-dimensional fibrous network are extremely easy to burn. Growing environmental concern and fire safety have drawn increasing attention to the need for flame retardant properties of paper and its products [1]. Due to the properties of biodegradable, recyclable and cheap material, paper products have been used in many fields such as packaging materials, building decoration, high-voltage transformers, and automobile exhaust emissions, where paper products must have good flame retardant properties [2]. Adding flame-retardant additives to paper products is the main way to reduce flammability. Currently flame retardants may be based on halogens [2, 3], phosphorus [4 - 7], nitrogen [5, 6], and boron system flame-retardants as well as metal compounds (such as metal hydroxide [7], oxide [8 - 10] and its silicate [11, 12], etc.). The halogen-based compounds, which are the most effective and cost-efficient flame retardants, have been criticised for both environmental and safe reasons [13]. They can be leached from the polymer into the environment and can accumulate inside human and animal bodies. Moreover they release toxic gases during combustion [14, 15]. Phosphorus-containing flame retardants are more suitable than halogen-based compounds. Phosphorus-based compounds favour the formation of char instead of combustible volatile species [16]. The char, a multilamellar carbonaceous structure, acts as a thermal insulator and protects the surrounding polymer from further decomposition and thus has a flame-retardant effect [17, 18]. However, the disadvantages of char, such as low fire-retardant efficiency, in large amounts make the physical properties of paper poor. Moreover nitrogen-based compounds and metal compounds have the same effect. Phosphazene flame retardants have some advantages such as being halogen-free, more efficiency, as well as emitting less smoke and non-toxic and non-corrosive gas formed during combustion; hence it is considered the development direction for flame retardants [19]. Some literatures report that hexaamidocyclotriphosphazene (HACTP) and its derivative- hexa(N-hydroxymethyl)amidocyclotriphosphazene (HHMAPT) have good flame retardancy in textile fiber [20, 21]. Based on the similarity between paper and textile composition, the authors studied the flame retardant effect of HACTP and HHMAPT in paper, and found that they had good flame retardancy in paper; but the water resistance and strength of the flame retarded paper with them were poorer [22 - 24]. Melamine formaldehyde resin is often used as a wet strength agent and a nitrogen based flame retardant for paper, and has a synergistic effect with phosphorus based flame retardant. Therefore the authors studied the synergistic flame retardant effect of HHMAPT and partially methylated melamine formal-

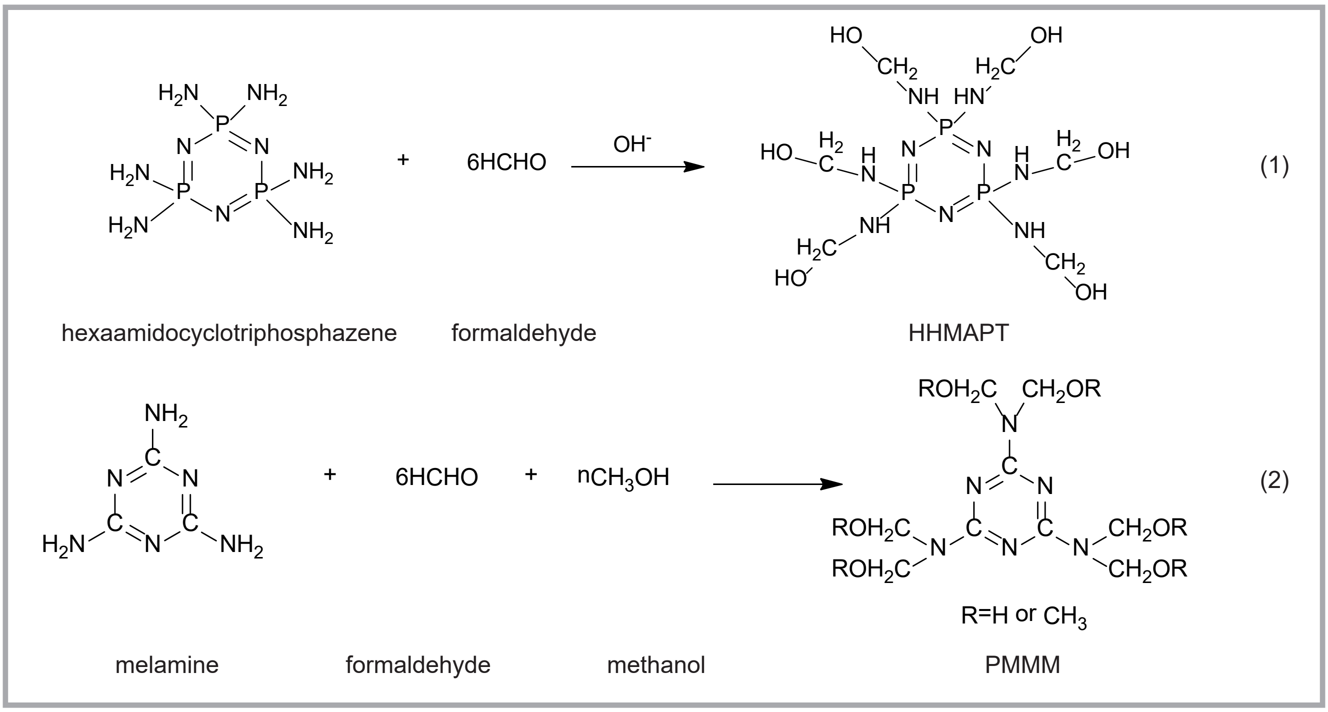


Figure 1. *Equations of reactions 1 & 2.*

dehyde resin (PMMM) in paper. In this paper, the results are presented.

Experimental part

Canada dolphin softwood papers with a weight of 1000 g/m^2 and thickness of 1.0 mm as well as 70 g/m^2 and 0.09 mm, respectively, were provided by Qingdao Tianfeng Makepaper Co. LTD., China. Hexachlorocyctriphosphazene was provided by Zibo Lanyin Chemical Co. LTD., China. Ammonia was supplied by Qingdao Pengxin Gas Manufacturing Co.LTD., China. Other materials were analytical reagents purchased from Tianjin Kemiou Chemical Reagent Co.LTD., China. All materials were used without further purification in this work.

Preparation of hexa(N-hydroxymethyl)amidocyclotriphosphazene (HHMAPT)

HHMAPT was prepared according to literature [20]. The process is as follows: aa mixture of hexaamidocyclotriphosphazene and ammonium chloride (40.0 g, which contain 0.067 mol of hexaamidocyclotriphosphazene) and 50 ml of deionized water were placed in a 250 ml four-necked round-bottomed flask equipped with a reflux condenser, thermometer and mechanical stirrer. The pH of the dissolved mixture was adjusted to about 9 with triethanolamine, then 37 wt.% formaldehyde solution (37.3 g, 0.46 mol HCHO) was added dropwise over a period of 40 min at room temperature. In the following, the contents were reacted at 70 °C for 3 h. 128 g of the product was obtained by cooling the contents to room temperature. The product is a colourless and transparent solution with of about 7 pH, 21.5 wt.% of HHMAPT and 6.89 mPa·s viscosity.

The chemical reaction equation for HHMAPT is presented in ***Figure 1***.

Preparation of partially methylated melamine formaldehyde resin (PMMM)

PMMM was prepared according to literature [25]. The process is as follows: 29.0 g of 37 wt.% formaldehyde solution, 4.1 g of 95 wt.% paraformaldehyde and 40.0 g of methanol were placed in a 250 ml four-necked round-bottomed flask equipped with a reflux condenser, thermometer and mechanical stirrer. The pH of the dissolved mixture was adjusted to 8.0 - 9.0 with 20 wt.% sodium hydroxide solution, then the contents was heated to 50 °C and 11.2 g of melamine was added. Subsequently the content was heated to 60 °C and maintained for 4 - 5 h, then 14.0 g of methanol was added. When the content was cooled to 35 - 40 °C, the pH was adjusted to 3.0 - 4.0 with concentrated sulfuric acid, and then the content was maintained at 35 - 40 °C till transparent, followed by adjusting of the pH to 9.0 - 10.0 with 20 wt.% sodium hydroxide solution. 38 g of the product was obtained by vacuum distillation for removal of volatile compounds. The product is a colourless and transparent solution with of about pH 10, 75.0 wt.% PMMM and 243.5 mPa·s viscosity.

The chemical reaction equation for PMMM is as follows (see ***Figure 1*** Equation of reaction 2).

Preparation of flame-retardant paper (FR-paper) sheets

First the solution of flame retardants was sprayed evenly on paper by a manual sprayer, then the paper was dried in a natural environment for 1 - 2 h. During the process, the flame retardants were further uniformly distributed on the paper because of the permeability. Next the paper was dried in a ZY-GZQ paper dryer (Jinan Zhongyi Instrument Co. Ltd, China) at about 100 °C for 1 h and at 140 - 150 °C for 10 min. The dried sheets were then cut into standard samples for flammability tests.

The amount of flame retardants can be calculated from the concentration and weight of the solution (half weight of the paper) sprayed onto the paper.

Flammability tests

The limiting oxygen index (LOI) was measured according to ASTM D 2863 with a JF-3 oxygen index meter (Jiangning Analytical Instrument Company, China). The specimens used for the LOI test were of dimensions 100 × 6.5 × 1.0 mm. The vertical burning test was carried out according to TAPPI T461 OS79 on a CZF-3 horizontal and vertical burning tester (Jiangning Analytical Instrument Company, China) with specimens of 210 × 70 × 1.0 mm. The cone calorimeter test (CCT) was conducted with a FTT standard cone calorimeter (FTT Company, British) in external heat fluxes of 50 kW/m^2 with specimens of 100×l00×1.0 mm according to ISO 5660. The paper in the amount of 1000 g/m^2 and of a thickness of 1.0 mm was used for the flammability tests above.

Physical property test

The folding strength of the paper was measured according to the Chinese national standard GB/T 23843-89 with a ZZD-25B paper folding strength tester (Changchun Small Test Machine Factory, China) and specimens of 20 × 15 × 0.09 mm. The tearing strength of the paper was measured according to the Chinese national standard GB/T 455-2002 with a ZSE-1000 paper tear strength tester (Changchun Yueming Small Test Machine Co. Ltd, China) and specimens of 76 × 63 × 0.09 mm with a 20 mm incision. The tensile strength of the paper was measured according to GB/T 12914-1991 with a TTM-500A computer tensile strength tester (Hangzhou Boke Automation Technology Co., Ltd, China) and specimens of 90 × 15 × 0.09 mm. The whiteness of the paper was measured according to the Chinese national standard QB/T 2804-2006 with a WSB-2A automatic brightness meter (Shanghai Pingxuan Scientific Instruments Co., Ltd, China).

Paper with a weight of 70 g/m^2 and thickness of 0.09 mm was used for the tests above.

Washing test of the FR- paper

A washing test of the FR- paper was carried out according to GB/T 14656-2009. First the FR-paper specimen was put into a 2000 ml beaker, a glass tube with an inner diameter of 6 mm inserted into the bottom of the beaker, into which 24 - 25 °C deionized water was injected continuously at a speed of 12 l/h for about 4 h, and finally the specimen was removed from the beaker, the water on its surface wiped off, which was followed by drying at 105 °C for about 1 h for testing.

Morphology analysis of residues

The morphology of residues obtained in the CCT was observed by scanning electron microscopy (SEM, S-4800 Hitachi High-Tech Corporation, Japan).

^{31}P NMR spectra measurement

^{31}P NMR spectra were acquired on an Advance 500 MHz spectrometer (Bruker Corporation, Germany) and D_2O was used as a solvent. The sample was dissolved with 10% sodium hydroxide solution using phosphoric acid as an internal standard; ^{31}P chemical shifts were referenced against phosphoric acid (δ = 0 ppm).

Phosphorous content analysis

The content of phosphorous was measured by the quimociac gravimetric technique according to ISO6598. A 0.5000 g sample was placed in a 100 ml iodine flask, equipped with a reflux condenser, containing 15 ml 10% nitric acid solution. The content was boiled for a few minutes using a heating jacket, to which 35 ml of a quimoc reagent was then added, subsequently cooled to room temperature, and left to stand for 30 min for precipitation. Then the precipitation was followed by the procedure of filtration, drying and weighing. The content of phosphorous was calculated according to the formula presented in ISO 6598.

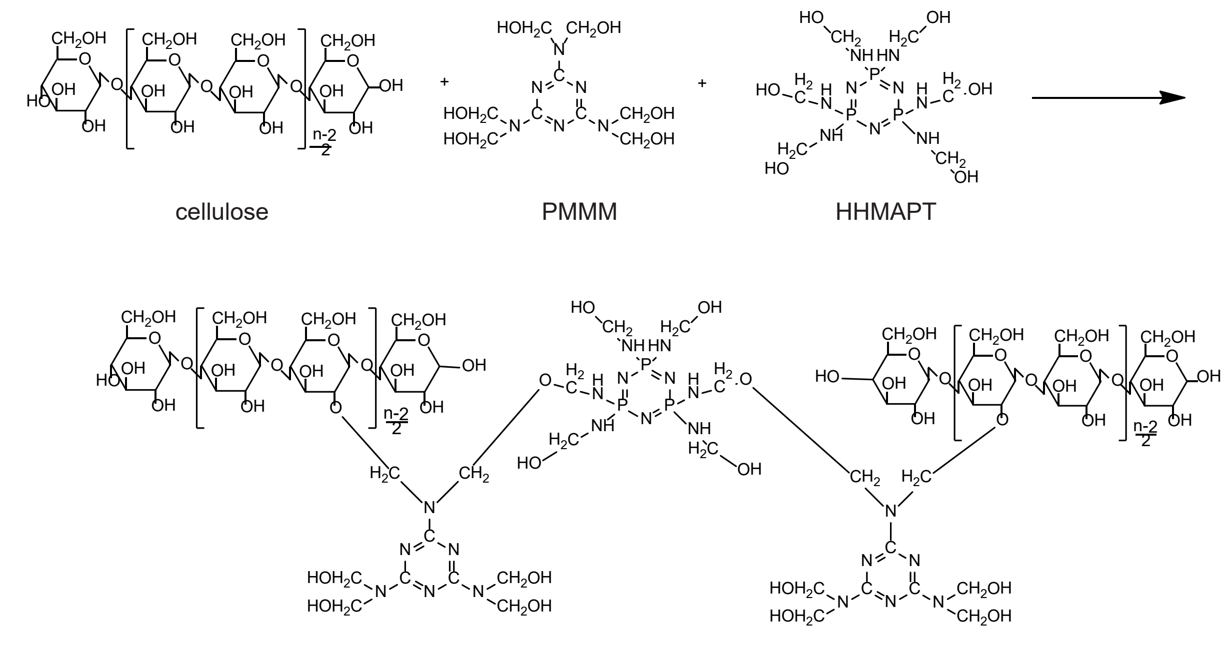
*Table 1. Influence of the Dosage of Flame Retardants on Paper flammability. *Here, the after flame time is related to the flameless combustion time after the flame goes out, and the burning time is related to te flaming time.*

Dosage, wt.%		Washing conditions	Vertical burning test*			LOI, %
HHMAPT	PMMM		After flame time, s	Burning time, s	Char length, mm	
0	0		73.4 ± 1.0	140.4 ± 1.0	-	22.1 ± 1.0
3.0	0	Unwashed	16.5 ± 1.0	0	12.0	32.0 ± 1.0
		Washed	62.4 ± 1.0	0	210.0	22.1 ± 1.0
4.5	0	Unwashed	3.2 ± 0.1	0	6.0	34.9 ± 1.0
		Washed	74.2 ± 1.0	0	210	23.8 ± 1.0
6.0	0	Unwashed	1.5 ± 0.1	0	4.5	47.5 ± 1.0
		Washed	108.3 ± 1.0	0	210	24.9 ± 1.0
9.0	0	Unwashed	0.7 ± 0.1	0	2.7	>5 2.0
		Washed	24.0 ± 1.0	0	89	27.6 ± 1.0
0	6.0	Unwashed	71.4 ± 1.0	149.4 ± 1.0	-	22.3 ± 1.0
0	10.0	Unwashed	80.5 ± 1.0	204.3 ± 1.0	-	23.2 ± 1.0
0	14.0	Unwashed	105.3 ± 1.0	232.2 ± 1.0	-	23.5 ± 1.0
0	18.0	Unwashed	109.6 ± 1.0	311.9 ± 1.0	-	24.0 ± 1.0
6.0	6.0	Unwashed	1.5 ± 0.0	0	5.0	47.6 ± 1.0
		Washed	119.9 ± 1.0	0	98.0	27.2 ± 1.0
6.0	10.0	Unwashed	0.5 ± 0.1	0	5.4	48.2 ± 1.0
		Washed	4.8 ± 1.0	0	12.0	33.5 ± 1.0
6.0	14.0	Unwashed	0.4 ± 0.1	0	4.5	49.0 ± 1.0
		Washed	4.2 ± 1.0	0	8.3	34.8 ± 1.0
6.0	18.0	Unwashed	0.4 ± 0.1	0	4.4	49.3 ± 1.0
		Washed	3.9 ± 1.0	0	6.5	36.1 ± 1.0

Results and discussion

LOI tests and UL94 classification

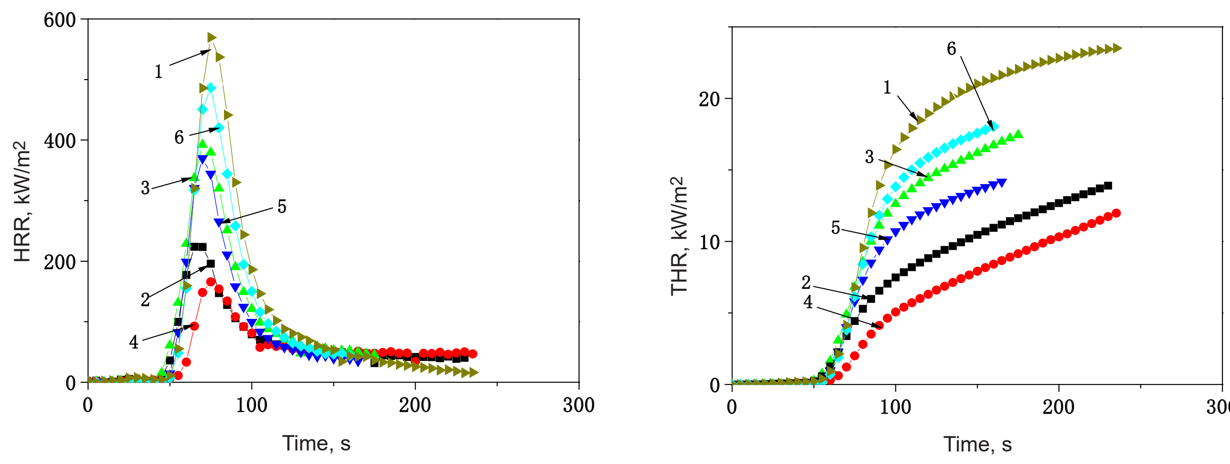
The effect of the dosage of HHMAPT, PMMM and HHMAPT/PMMM on the LOI and vertical burning property of the paper was investigated. As can be seen in ***Table 1***, HHMAPT shows good flame retardancy in paper, and the LOI of which is increased with an increase in its dosage, while the vertical burning property is decreased. The LOI of the non-flame retardant paper is 22.1%, and burns completely. But the LOI of FR-paper with HHMAPT can be up to 47.5%, and the nonflammable level can be passed. Moreover the after flame time of the vertical burning is reduced to 1.5 s, with the burning time being 0 s and the char length only 4.5 mm as the dosage of HHMAPT increases to 6.0 wt.% based on the weight of paper. The LOI is equal to or greater than 52.0% as the dosage of HHMAPT is more than 9.0 wt.%. However, the FR-paper with HHMAPT has poor water resistance, and flame retardancy decreases significantly after washing, for example when the dosage of HHMAPT is 6.0 wt.%, the LOI of



(3)

__Figure 2.__ Equation of reaction 3.

the washed FR-paper decreases from 47.5% to 24.9%; after the flame time it increases from 3.2 s to 108.3 s, and the char length increases from 6 mm to 210 mm. PMMM has a poor flame retarded effect on paper, where the LOI of the FR-paper increases slightly with an increase in the amount of PMMM, and the after flame time and burning time continue to increase significantly. When the amount of PMMM increases up to 18 wt.%, the LOI of the FR-paper is still



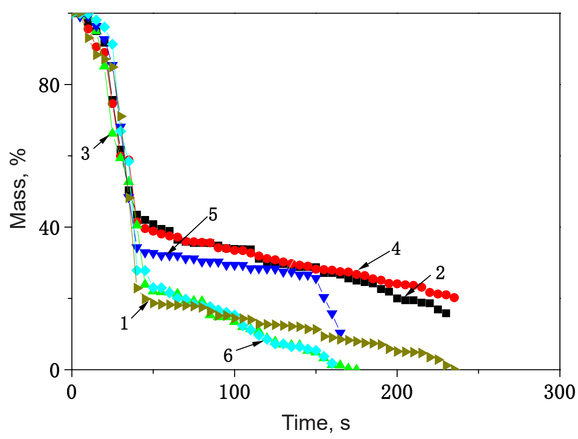


__Figure 3.__ HRR(a),THR(b) and ML(c)curves of the paper and the FR-paper. 1 - Base paper; 2 - Unwashed FR-paper with HHMAPT, 3 - Washed FR-paper with HHMAPT; 4 - Unwashed FR-paper with HHMAPT/HMMM, 5 - Washed FR-paper with HHMAPT/HMMM; 6 - Unwashed FR- paper with HMMM.

only 24.0%, with the paper undergoing complete combustion in the vertical combustion test. When the amount of HHMAPT is 6 wt.%, the combination of HHMAPT and PMMM has little influence on the flame retardant properties of unwashed FR-paper, but a significant effect on those of washed FR-paper. With an increasing amount of PMMM, the LOI of unwashed FR-paper increases slightly, and after the flame time decreases slightly, with the burning time and char length showing no significant change. However, the LOI of washed FR-paper has a significant increase, and the after flame time and char length decrease significantly. When the amount of PMMM is more than 10 wt.%, the LOI of the washed sample is more than 33.5%; the after flame time and average char length of vertical combustion are less than 4.8 s and 12 mm, respectively, and the burning time was 0 s. The above results reveal that FR-paper with HHMAPT/PMMM has good water resistance. The poor water resistance of FR-paper with HHMAPT is ascribed to physical adsorption, and hence it is easily washed by water. PMMM is a wet strength agent for paper. N-CH_2OH or N-CH_2OCH_3 of the PMMM molecule could be etherified or transetherified by the -OH of paper cellulose molecules, which make the cellulose molecules crosslinked, thus improving the strength of the paper [26]. The N-CH_2OH or N-CH_2OCH_3 of PMMM could also be etherified or transetherified by the N-CH_2OH of HHMAPT, which make HHMAPT bond chemically to cellulose molecules (presented in ***Figure 2***), and hence it could not easily be washed off by water, thereby increasing the strength and water resistance of the FR-paper. Phosphorus content analysis confirms the conjecture above. The phosphorus residual rate of washed FR-paper with 6 wt.% HHMAPT alone is 51%, while the phosphorus residual rate of washed FR-paper with a mixture of 6 wt.% HHMAPT and 10 wt.% PMMM is 76%.

Table 2. *Important cone calorimeter data.*

Argument*	Base paper	HHMAPT/ unwashed	HHMAPT /Washed	HHMAPT/PMMM/ Unwashed	HHMAPT/ PMMM/Washed	PMMM/ Unwashed
THR, kW/m^2	23.51	13.90	17.44	13.57	14.17	18.03
PHRR, kW/m^2	569.3	223.7	392.4	165.8	369.8	486.5
PHRR, time, s	75	70	70	75	70	75
MHRR, kW/m^2	98.17	59.60	97.56	49.75	83.89	109.9
PEHC, MJ/kg	80	80	80	44.00	80	80
MEHC, MJ/kg	8.719	9.841	17.70	4.529	19.09	13.41
MMLR, g/s	0.04	0.0301	0.0570	0.0429	0.0702	0.0462
TTI, s	55	55	50	65	45	50
COM, time, s	235	230	175	270	165	160

Cone calorimeter analysis

In order to further reveal the flame retardancy of HHMAPT, PMMM and HHMAPT/ PMMM in the paper, a CCT was carried out, in which the heat release rate (HRR), total heat release (THR) and mass loss (ML) were analysed. The results are presented in ***Figure 3*** and some important data listed in ***Table 2***. As can be seen from the data, non-flame retardant paper burns very quickly after ignition, and the HRR increases rapidly up to a maximum of 569.3 kW/m^2 in 75 s. Meanwhile the THR also increases rapidly; the weight decreases quickly, and the

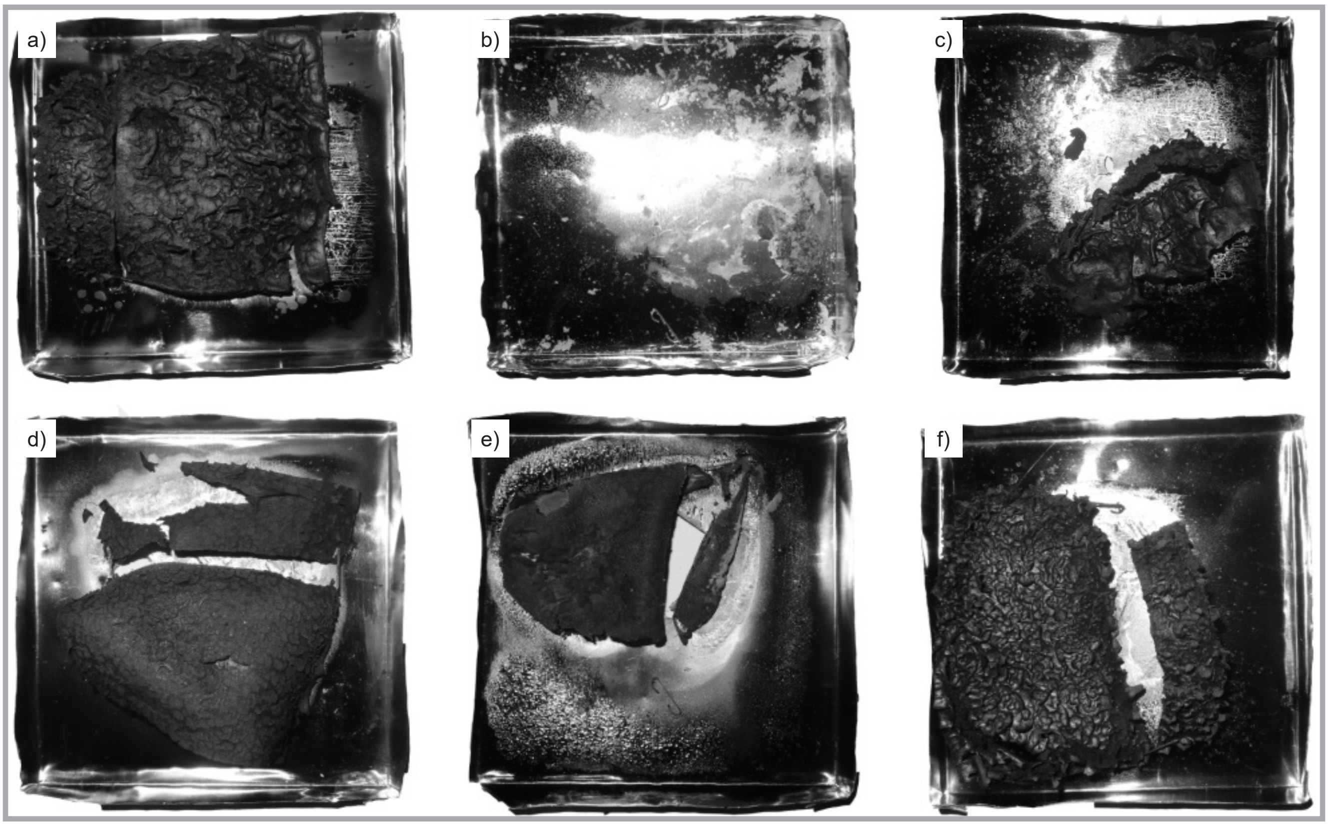


Figure 4. *Photos of residues of the paper and FR-paper. a - Base paper;d b - Unwashed FR-paper with HHMAPT, c - Washed FR-paper with HHMAPT, d - Unwashed FR-paper with HHMAPT/PMMM, e - Washed FR-paper with HHMAPT/PMMM, f - Unwashed FR- paper with PMMM.*

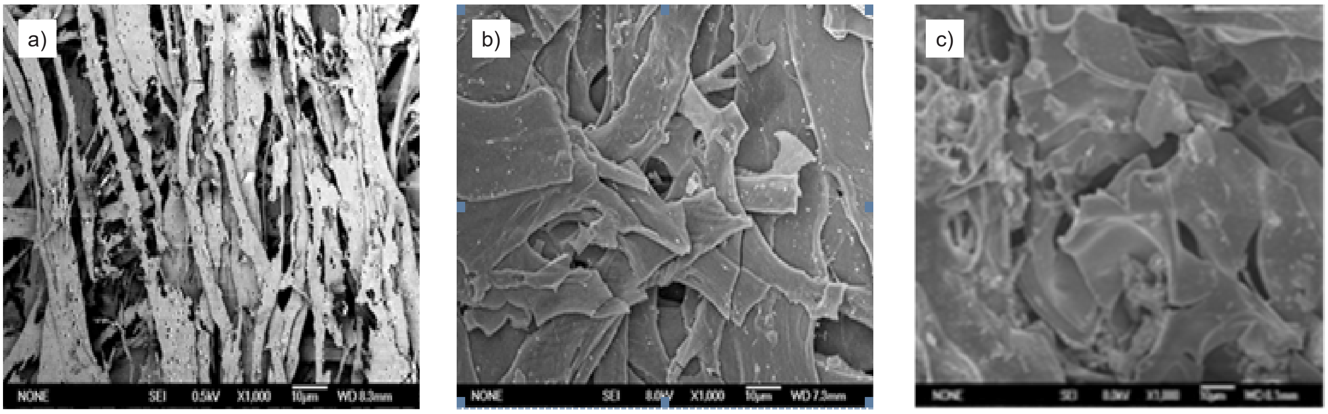
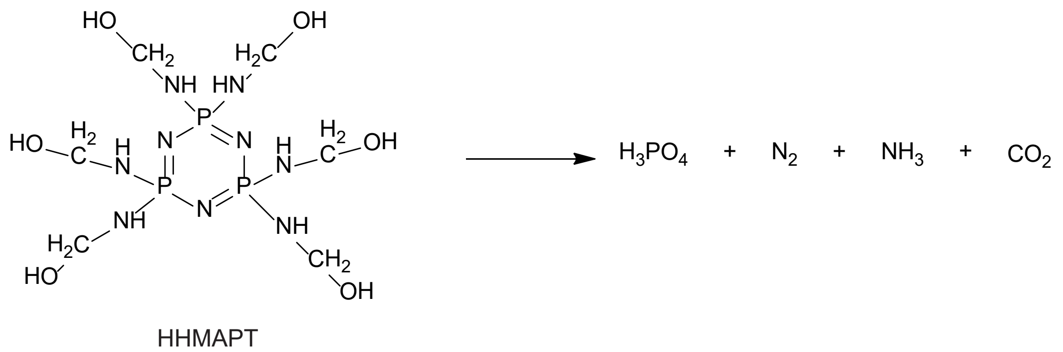


Figure 5. *SEM of the residues. a) Base paper; b) FR-paper with HHMAPT, c) FR-paper with HHMAPT/ PMMM.*



(4)

Figure 6. *Equation of reaction 4.*

time required for complete combustion is about 235 s. However, the HRR of FR-paper with 6 wt.% HHMAPT increases slowly; the mass is slowly lost after igniting; time of complete combustion is prolonged, and the maximum heat release rate (PHRR), average heat release rate (MHRR), average effective heat of combustion (MEHC) and the THR obviously decrease. While the burning behaviour of the washed FR-paper with HHMAPT is similar to that of non-flame retardant paper, and that of FR-paper with 6 wt.% HHMATP/10 wt.% PMMM is similar to that of FR-paper with HHMAPT; but the THR, PHRR, MHRR, peak effective heat of combustion (PEHC) and MEHC are smaller, and the time required for complete combustion is longer. Although the washing increases significantly, the HRR, PHRR, MHR and THR of FR-paper with HHMATP and HHMATP/ PMMM, the data above are still significantly lower than for non-flame retardant paper. Moreover the data with HHMATP /PMMM are lower than with HHMATP, which shows that FR-paper with HHMATP/PMMM has better flame retardant properties and water resistance than with HHMAPT. The burning behaviour of FR-paper with 10 wt.% PMMM is similar to that of base paper, which indicates that PMMM has a poor flame retarded effect in paper. The conclusion above is basically consistent with that of the limiting oxygen index (LOI) and vertical combustion test.

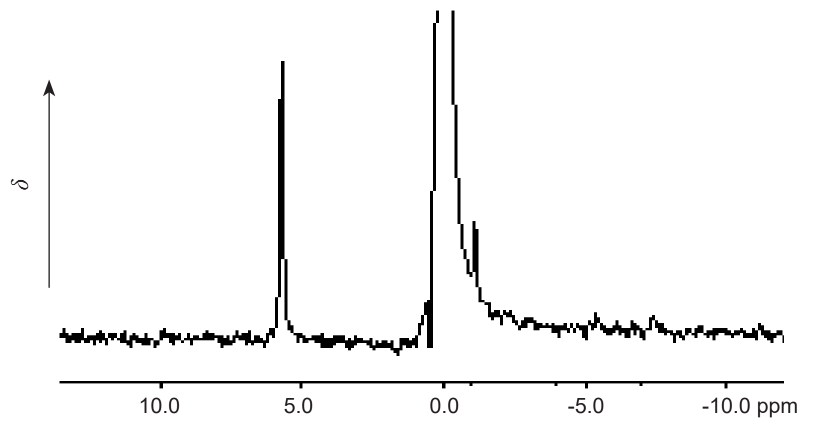


Figure 7. *^{31}P NMR of the residue of the FR-paper with HHMAPT/PMMM.*

Fire retardancy mechanisms

The flame retardancy mechanism of HHMAPT/PMMM in paper was discussed by analysis of the residue obtained in the CCT. Photos of residues of the paper and FR-papers are presented in ***Figure 4*** (see page 157).

As can be seen in the photos of residues shown in ***Figure 4***, the residue of the non-flame retardant paper is very little, only 0.14 wt.% based on the weight of paper before burning, while those of the FR-paper with 6 wt.% HHMAPT and 6 wt.% HHMAPT/10 wt.% PMMM are much more, about 15 wt.%, and appear intumescent. And the residue of the washed FR-paper with HHMAPT is reduced to 3.47 wt.%, while that of the washed FR-paper with HHMAPT/ PMMM is still up to 12.67 wt.%. The residue of the FR-paper with PMMM is just 3.63%.

An SEM of the residue section presented in ***Figure 5*** shows that the residue appears to be of a sheet structure, while that of the FR-paper with HHMAPT and HHMAPT/PMMM is wider, more compact and smoother, which results in better flame retardancy due to the greater barrier effect on heat and air, as well as prevention of the volatilisation of the pyrolysis products of paper.

The structure of the phosphorus compound in the residues of the FR-paper with HHMAPT/PMMM and HHMAPT (the residues were dissolved in 10 wt.% sodium hydroxide solution) was characterised by ^{31}P NMR. Both ^{31}P NMR are the same, shown in ***Figure 7***, with the main chemical shift around 5.5 ppm, which indicates that the dominant phosphorus compound is sodium phosphate (phosphoric acid compounds are converted into sodium phosphate in the presence of sodium hydroxide). The result above reveals that HHMAPT is converted into phosphoric acid compounds such as phosphoric acid, metaphosphoric acid and the polyphosphoric acid in the process of combustion, which is consistent with the thermal degradation behaviour of poly(diphenoyphosphazene) [27], seen in ***Figure 6*** Equation of reaction 4.

Based on the results above, it can be concluded that HHMAPT plays a flame retardant role mainly by condensed-phase mechanisms. In the process of combustion, HHMAPT is decomposed into non-volatile phosphoric acid compounds which promote the carbonisation of paper, with inert gases such as CO_2, and N_2 released from the decomposition of HHMAPT, PMMM and paper making the char foam. The intumescent layer formed results in flame retardancy by means of the barrier effect on heat, air and decomposition products.

Physical properties of the paper

Physical properties of the papers were tested according to the standard, the results of which are shown in ***Table 3***. The data shows that the folding strength and tensile strength of the FR-paper with 6 wt.% HHMAPT are obviously reduced, while that of the FR-paper with 6 wt.% HHMAPT/10 wt.% PMMM is slightly decreased and the tensile strength is obviously increased. In addition, the whiteness of the FR-paper is slightly decreased.

Table 3. *Physical properties of papers.*

Term	Folding strength	Tearing strength, mN	Tensile strength, N·m·g^{-1}	Whiteness, %
Non-flame retardant paper	33	392	40.58	91
FR-paper with 6 wt.% HHMAPT	27	394	33.3	88
FR-paper with 6 wt.% HHMAPT/10 wt.% PMMM	30	392	42.0	88

Conclusions

HHMAPT/PMMM not only has excellent flame retardancy in paper, but also has good water resistance. The LOI of the non-flame retardant paper is 22.1%, and burns completely in the vertical burning test. However, when the dosages of HHMAPT and PMMM are 6 wt.% and 10 wt.%, respectively, based on the weight of paper, the LOI of the FR-paper can be up to 42.0%; the after flame time is reduced to 0.5 s, the burning time to 0 s, and the char length is only 5.4 mm in the vertical combustion test. While the LOI of the washed FR-paper can still be up to 33.5%; the after flame time is reduced to 4.8 s, the burning time to 0 s, and the char length is only 12.0 mm. The results of CCT reveal that compared with the non-flame retarded paper, the heat release rate (HRR) of the FR-paper with HHMAPT/PMMM increases slowly; the mass loss becomes obviously slow, and the PHRR, MHRR, MEHC and THR decrease significantly. Although the HRR, PHRR, MHRR, MEHC and THR are increased by washing, the data of the washed FR-paper above are still obviously lower. Analysis of the residues obtained from the CCT shows that HHMAPT/PMMM plays a flame retardant role mainly by means of the condensed phase mechanism. The HHMAPT is decomposed into phosphoric acid compounds in the process of combustion, which promotes the carbonisation of paper, and inert gases such as CO_2, N_2, NH_3 released from the thermal decomposition of HHMAPT, PMMM and paper make the char foam. The intumescent layer formed results in flame retardancy by means of the barrier effect on heat and air as well as prevention of the volatilisation of pyrolysis products of the paper.

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References

1. Köklükaya O, Carosio F, Grunlan J C and Wågberg L. Flame-Retardant Paper from Wood Fibers Functionalized via Layerby-Layer Assembly. *ACS Appl. Mater. Interfaces* 2015; 7: 23750−23759.
2. Li C, Hui LF and Liu Z. Development status and trend in flame retardant paper. *China Pulp Paper Industry* 2010; 23: 62-66.
3. Cui JF, Guo JH and Yang BP. Investigation and preparation of sizing agent with waterborne epoxy bromine carbon resin for flame retardant paper. *Journal of Lanzhou University of Technology* 2010; 36: 62-65.
4. Katovic D, Vukusic SB, Grgac SF, Lozo B and Banic D. Flame retardancy of paper obtained with environmentally friendly agents. *Fibres and Textiles in Eastern Europe* 2009; 17, 3(74): 90-94.
5. Guo DD and Li YT. Synthesis of Halogen-Free Flame Retardant Agent and Its Application in the Paper making. *Paper and Paper Making* 2012; 31: 54-57.
6. Ma ML. Modified amidine urea phosphate flame retardant impregnated paper research. *Fire Science and Technology* 2012; 28: 932-933, 940.
7. Zhou H, Liu Z and Wei YJ. Research on the preparation of flame retardant magnesium hydroxide as fire retardant in paper. *China Pulp & Paper* 2009; 28: 13-16.
8. Liu YJ, Hao ZX and Liu YW. Multiple layered double hydroxyl metal composite oxide is used as flame retardant filler preparation of flame retardant in paper. *China Pulp & Paper* 2012; 31: 17-21.
9. Wang SL and Huang JL. Silicon doping effect on the properties of flame retardant filler magnesium aluminum hydrotalcite. *China Pulp & Paper Industry* 2012; 33: 40-43.
10. Wang SL, Huang JL, Shao XJ and Chen FS. Doped zinc magnesium aluminum water talc in the paper for application of the flame retardant. *China Pulp & Paper Industry* 2012; 33: 38-41.
11. Hu F, Nie SX and OuYang CL. Research on Sodium aluminum silicate coating properties of flame retardant paper combined systems. *China Pulp & Paper* 2012; 31: 22-25.
12. Yang SS. The development of sepiolite flame retardant in paper. *Transactions of China Pulp & Paper* 2005; 20: 153-155.
13. Liagkouridis L, Cousins IT and Cousins AP. Emissions and fate of brominated flame retardants in the indoor environment: A critical review of modeling ap-

proaches. *Science of the Total Environment* 2014; 491-492: 87-99.

14. Alongi J, Carletto RA, Di Blasio A, Carosio F, Bosco F and Malucelli G. DNA: a novel, green, natural flame retardant and suppressant for cotton. *J. Mater. Chem. A* 2013; 1: 4779-4785.
15. Cain AA, Nolen C R, Li Y C, Davis R and Grunlan J C. Phosphorous-filled nanobrick wall multilayer thin film eliminates polyurethane melt dripping and reduces heat release associated with fire. *Polym. Degrad. Stab.* 2013; 98: 2645-2652.
16. Alongi J, Carletto R A, Bosco F, Carosio F, Di Blasio A, Cuttica F, Antonucci V, Giordano M, Malucelli G. Caseins and hydrophobins as novel green flame retardants for cotton fabrics. *Polym. Degrad. Stab.* 2014; 99: 111-117.
17. Camino G, Costa L, Luda di Cortemiglia M P. Overview of fire retardant mechanisms. *Polym. Degrad. Stab.* 1991; 33: 131-154.
18. Alongi J, Di Blasio A, Cuttica F, Carosio F and Malucelli G. Bulk or surface treatments of ethylene vinyl acetate copolymers with DNA: Investigation on the flame retardant properties. *Eur. Polym. J.* 2014; 51: 112-119.
19. Qian LJ. The current research and development status quo of phosphorus-containing flame retardants. *Chinese Journal of Flame Retardant* 2011; 3: 2-4.
20. Hebeish A, Waly A and Abou-Okeil AM. Flame retardant cotton. *Fire and Materials* 1999; 23: 117-123.
21. Shizuo K. Fireproofing Method of fibers by aminophosphazenes derivatives. Patent JP0104074A2, JP, 1989.
22. He W, Liu YJ and Tang LS. Preparation of high performance flame retardant paper. *Paper Science & Technology*, 2014; 33: 46-49.
23. He W, Bi W, Ke Y, Liu YJ and Tang LS. Flame retarded paper with hexaadimocyclotriphosphazene. *Paper Science & Technology* 2015; 34: 24-26.
24. He W, Liu YJ, Li T and Tang LS. The flame retardancy of hexahydroxymethyladimocyclotriphosphazene on paper. *Paper Science & Technology* 2015; 34: 34-38.
25. Coating Process Board. Coating process board (the first volume). Beijing: Chemical Industry Press 1997; 553-555.
26. Yang KJ, Su WQ, Shen J. Mechanism and progress of wet strength agent for paper making. *Paper Science & Technology* 2006; 25: 58-62.
27. Maynard SJ, Sharp TR and Haw JF. Thermal degradation chemistry of poly-(diphenoyphosphazene). *Macromolecules* 1991; 24: 2794-2799.

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