

# Preparation and Characterization of Ammonium Polyphosphate/Diatomite Composite Fillers and Assessment of their Flame-retardant Effects on Paper

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Ammonium polyphosphate (APP) was synthesized by heating a mixture of phosphoric acid and urea, and APP/diatomite composite flame-retardant fillers were prepared by two methods: mixing and *in situ* polymerization. Flame-retardant paper was made by adding the prepared composite fillers to paper. The APP and APP/diatomite composite fillers were characterized by XRD, <sup>31</sup>P NMR, SEM, FTIR, and TG. The flame retardation of paper containing these composite fillers was determined. Results showed that the prepared APP had a minimum solubility when the molar ratio of phosphoric acid to urea was 1:1.8. Under these conditions, its degree of polymerization was 91.21. After mixing and *in situ* polymerization, a large amount of APP was adsorbed into the surface of the diatomite. These two APP/diatomite composite fillers had similar thermal stabilities, but the flame retardation of paper containing *in situ* polymerized composite filler was better than that of paper containing the composite filler obtained by mixing.

*Keywords:* Ammonium polyphosphate; Diatomite; In situ polymerization; Composite flame-retardant filler; Flame retardation

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## INTRODUCTION

Paper made from plant fibers is a flammable material. However, fire resistance is desirable for many paper products, such as auto filters, building materials, and decoration materials (Chang and Hung 2003; Hong *et al.* 2011; Rie *et al.* 2012; Yang *et al.* 2002). Therefore, the improvement of flame retardation in paper has become an important research topic for specialty paper. The present methods for retarding immolation of paper include impregnation, surface coating, and the addition of flame retardants to paper pulp (Cui *et al.* 2010; Nassar *et al.* 1999; Shang and Yang 2010; Shen *et al.* 2011; Wang *et al.* 2012; Zhou *et al.* 2009). Flame retardants can be applied by impregnation, but that usually decreases the strength, dimensional stability, and moisture resistance of the paper. Flame retardants can also be applied with water-based coating formulations, but such coatings typically contain combustible starch and latexes, which limit the efficiency of the flame retardant.

Aluminium hydroxide and magnesium hydroxide filler particles are usually used in paper products that are intended to be flame-retardant. Adding these inorganic flame retardants to papermaking furnish is simple, but a large amount of inorganic flame retardants are required for such an application, which adversely affects the physical

properties of paper. The objective of our work was the development of an efficient, flame-retardant filler, capable of retarding paper immolation at lower filler content.

Ammonium polyphosphate (APP) is an efficient, inorganic flame retardant. APP contains phosphorus and nitrogen and is widely used in polymers, coatings, wood products, and various fibrous materials (Fan *et al.* 2013; García *et al.* 2009; Guo *et al.* 2013; Tian *et al.* 2013; Zhang *et al.* 2013). Diatomite is a non-metallic mineral with a vesicular structure, strong adsorption capabilities, and a large specific surface area. Because of its low cost and wide availability, it is sometimes used as papermaking filler (Li *et al.* 2008). Therefore, it appeared feasible to prepare an effective composite flame-retardant filler by combining diatomite and APP and using a small amount of this product in the preparation of high-quality, flame-retardant paper. APP/diatomite composite flame-retardant fillers were prepared by two methods: mixing and *in situ* polymerization. The structures and properties of these products were characterized, and their flame-retardant effects on paper were investigated.

## EXPERIMENTAL

### Materials

Laboratory reagent-grade phosphoric acid (Bioreagent, 85%), urea, and diatomite were all supplied by Sigma-Aldrich (USA) and were used without further purification, aluminium hydroxide was purchased from market.

### Synthesis of APP

The desired amount of phosphoric acid was poured into a three-neck flask and heated to 70 °C in an oil bath. The required amount of urea was then added into the agitated flask and the mixture was heated to 130 °C at a rate of 2~3 °C /min. The temperature was kept at 130 °C for 15 min, and the product was poured onto a small tray and placed, for 2 h, in a 210 °C oven to solidify. The solid product was ground into APP powder. The molar ratios of phosphoric acid to urea were adjusted to obtain different grades of APP, and the optimal APP was chosen for later use.

### Preparation of Composite Flame-retardant Fillers

*Filler 1:* First, 5.00 g of APP was dissolved in 30 mL of distilled water in a heated and agitated beaker. Then, 2.50 g of diatomite was added to the APP solution and the mixture was stirred by a magnetic stirrer at 90 °C to form a slurry. The slurry was placed into an oven at 105 °C for 24 h to solidify. The solid product was ground to powder and screened to obtain composite filler 1.

*Filler 2:* In the process of APP synthesis, 2.50 g of diatomite (about half of the production of APP) was added when the temperature reached 130 °C. The mixture was stirred rapidly and the temperature was kept at 130 °C for 15 min. The product was poured onto a small tray and placed in an oven to solidify at 210 °C for 2 h. The solid product was then ground into powder and screened to obtain composite filler 2.

### Preparation of Flame-retardant Papers and Measurements of their Physical Properties

Softwood pulp was refined to about 40 degrees Schopper-Riegler (°SR) in a Valley beater and disintegrated in a standard fiber disintegrator (LABTECH). Then, 25%

composite filler and 0.03% cationic polyacrylamide (CPAM) (by weight of paper) were added to the fiber suspension, which was used to prepare 90 g/m<sup>2</sup> handsheets. The handsheets were pressed with a pressure of 245 kPa for 5.5 min and dried at the temperature of 105 °C using a flat plate dryer.

For comparison, paper without filler, paper loaded with only diatomite, APP, and aluminium hydroxide were also prepared.

Tensile strength and bursting strength were evaluated according to TAPPI standard methods, and the tensile index and burst index of papers were calculated to account for small differences in basis weights. Constant temperature and humidity chamber was used to determine the equilibrium moisture regain of the prepared papers.

## Characterization

### *X-ray diffraction (XRD) analysis*

The XRD pattern of the APP powder was recorded with a Bruker D8 ADVANCE X-ray diffractometer (Germany) using Cu Ka radiation ( $\lambda_{\text{Cu Ka}}=1.5148 \text{ \AA}$ , 40 kV, 30 mA) in a  $2\theta$  range of 5° to 60°. The acquisition parameters were as follows: a step size of 0.02° and a step time of 17.7 s.

### *Solubility measurement (Li et al. 2012)*

A batch of 4.00 g of APP powder was dispersed well in 100 mL of distilled water at room temperature and oscillated in an oscillator (150 rpm) for 40 min; the supernatant was then transferred to a centrifugal tube. After 30 min of centrifugal separation at 2000 rpm, 20 mL of supernatant was transferred to a beaker, pre-dried to a constant weight, and weighed with an analytical balance ( $m_1$ , the beaker weight is not included); then, the beaker was placed in an oven at 110 °C and dried to a constant weight ( $m_2$ , the beaker weight is not included). The solubility ( $S$ ) of APP was calculated according to the following equation:

$$S = m_2/(m_1-m_2) \times 100\% \quad (1)$$

### *Solid state nuclear magnetic resonance (NMR) measurement (Chen et al. 2008; Wang et al. 2012)*

Measurements of <sup>31</sup>P NMR were performed with a Bruker Advance 400 spectrometer. APP and D<sub>2</sub>O were mixed in a nuclear magnetic tube. The mixture was heated in a boiling water bath and, when APP was dissolved, the solution was cooled to room temperature. The resonance peak areas of terminal phosphorus ( $A_2$ ) and middle phosphorus ( $A_1$ ) were measured and the degree of polymerization ( $DP$ ) of APP was obtained by calculating the ratio of the peak area of middle phosphorus to that of terminal phosphorus. The following equation was used:

$$DP = 2A_1/A_2+2 \quad (2)$$

### *Fourier transform infrared (FTIR) spectroscopy*

FTIR spectra of APP, diatomite, and composite flame-retardant fillers were obtained using a KBr disk and FTIR-8400S spectrometer (Shimadzu, Japan) in the range of 400 to 4000 cm<sup>-1</sup>.

### Thermogravimetric analysis (TGA)

TG analysis of APP, diatomite, and composite fillers was carried out using an SDT-600 (TA Co., USA). Samples of approximately 10 mg were heated from 20 °C to 800 °C at a heating rate of 10 °C /min under a nitrogen atmosphere, and the flow of nitrogen was 50 mL/min.

### Scanning electron microscopy (SEM)

The surface morphologies of diatomite and composite fillers were observed with a JEOL 6400 scanning electronic microscope (Japan). Samples were sputter-coated with a gold layer before observation.

### Combustion test

After conditioning with constant temperature and humidity, the flame-retardant papers were cut into rectangles of 150 mm × 20 mm (length × width) and weighed. Then, the rectangular paper strips were lit in a combustor and weighed after the flame was extinguished. The weights of the rectangular paper strips both before and after combustion were specified as  $w_1$  and  $w_2$ , respectively. The weight loss ratio ( $W$ ) of paper strips during combustion was used as a measure of the flame retardation of paper. The following equation was used:

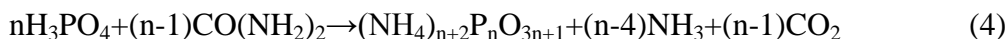
$$W = (w_1 - w_2) / w_1 \times 100\% \quad (3)$$

The less weight loss ratio of paper, the better flame retardation.

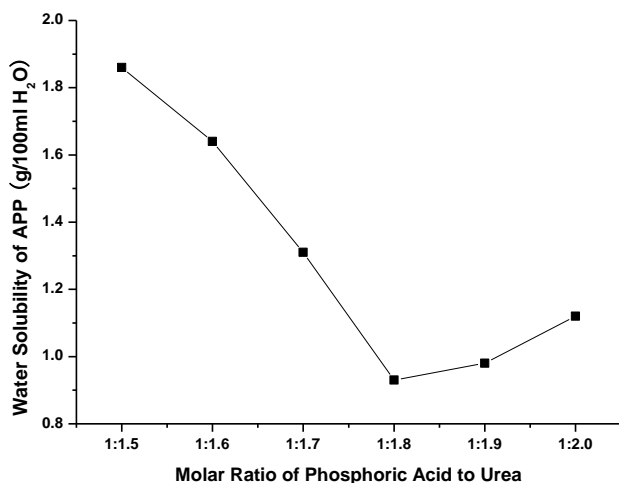
## RESULTS AND DISCUSSION

### Properties of APP

The APP was synthesized by a condensation reaction using phosphoric acid and urea. The relevant equation is:

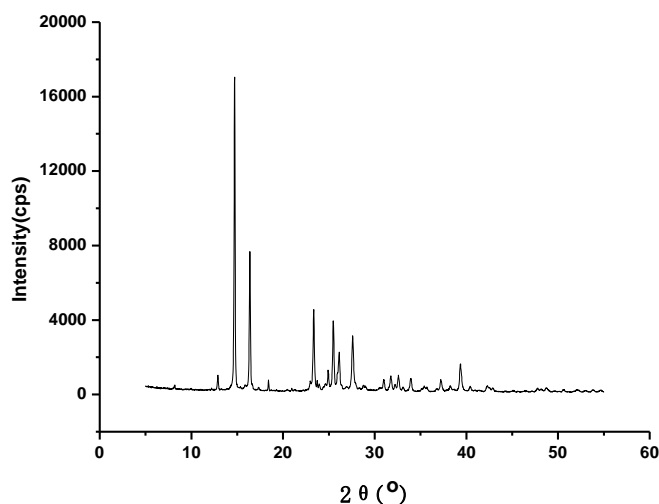


Low water solubility of APP is essential for its application in composite fillers because high water solubility reduces retention in composite fillers and papers. Water solubility of synthesized APP is also influenced by molar ratio of phosphoric acid to urea, reaction temperature, reaction time, and some other factors (Liu *et al.* 2009; Wu *et al.* 2004). In this work, we studied the effect of molar ratio of phosphoric acid to urea on the water solubility of APP. Curing temperature and time were set at 210 °C and 2 h, and the molar ratio of phosphoric acid to urea was adjusted to 1:1.5, 1:1.6, 1:1.7, 1:1.8, 1:1.9, and 1:2.0. The water solubility of APP synthesized with different molar ratios of phosphoric acid to urea is shown in Fig. 1. It is apparent from the figure that APP had the lowest water solubility when the molar ratio of phosphoric acid to urea was 1:1.8. In the process of APP synthesis, too little urea cannot provide sufficient ammonia for complete condensation reaction, while too much urea can cause a loss of ammonia and the generation of biuret at high temperature. Also the synthesized APP solidifies with more difficulty (Jiao *et al.* 2009). Therefore, the optimal molar ratio of 1:1.8 was used in the subsequent experiments.



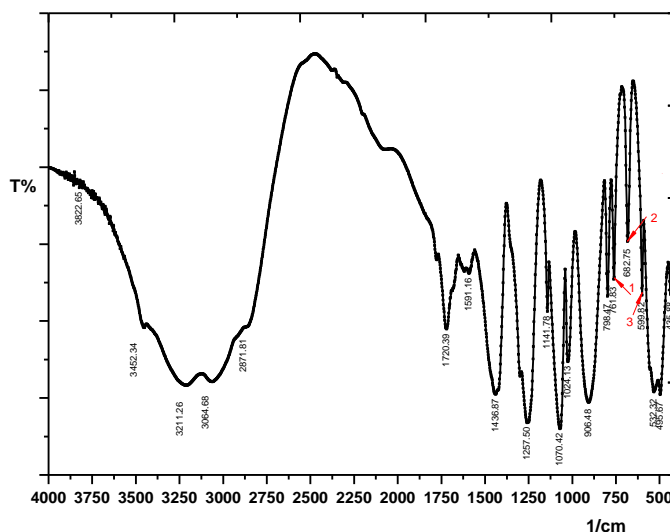
**Fig. 1.** Effect of molar ratio of phosphoric acid to urea on water solubility of APP

To identify the crystal form of synthesized APP, the XRD spectrum of APP was recorded, as shown in Fig. 2. It can be seen that the maximum intensity XRD peak appeared in a  $2\theta$  range of  $14^\circ$  to  $18^\circ$ . Compared with standard XRD data of APP (Sun *et al.* 2004), the characteristic diffraction peaks of synthesized APP were consistent with that of APP-I, so it can be determined that APP synthesized in the experiment was APP-I.



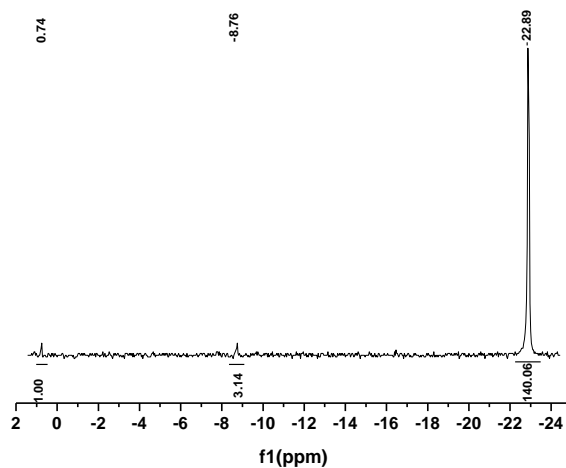
**Fig. 2.** XRD spectrum of synthesized APP

The FTIR spectrum of APP is shown in Fig. 3. The synthesized APP has absorption peaks at  $760\text{ cm}^{-1}$ ,  $680\text{ cm}^{-1}$ , and  $600\text{ cm}^{-1}$ . The observed absorption peak at  $760\text{ cm}^{-1}$  can be assigned to stretching vibration of O=P-O, and the peaks at  $680\text{ cm}^{-1}$  and  $600\text{ cm}^{-1}$  can be assigned to stretching vibration of -OH and O-P-O, respectively. These absorption peaks are the characteristic absorption peaks of APP-I (Liu *et al.* 2010), which confirms that the synthesized product was indeed APP-I.



**Fig. 3.** FTIR spectrum of synthesized APP

The  $^{31}\text{P}$  NMR spectrum of the optimal APP is shown in Fig. 4. The signal at -8.76 ppm was assigned to the terminal phosphorus, and the signal at -22.89 ppm was assigned to the middle phosphorus of APP-I. The resonance peak area of terminal phosphorus is 3.14, and the peak area of middle phosphorus is 140.06. According to Eq. (2), the  $DP$  of the synthesized APP is 91.21 when the molar ratio of phosphoric acid to urea is 1:1.8.

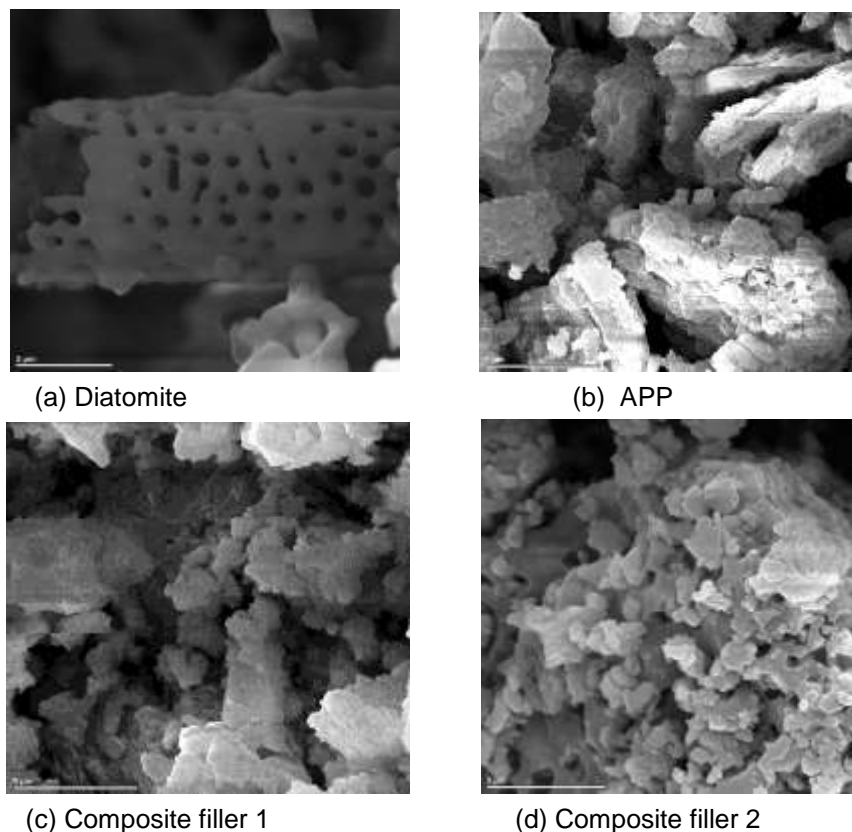


**Fig. 4.**  $^{31}\text{P}$  NMR spectrum of synthesized APP

### SEM Images of Diatomite and Composite Flame-retardant Fillers

Figures 5(a) and 5(b) are the SEM images of diatomite and APP, and Figs. 5(c) and 5(d) are the SEM images of composite fillers 1 and 2, respectively. Figure 5(a) shows that diatomite is a porous material with plenty of macropores on its surface. During preparation of the composite flame-retardant fillers, the large specific surface area of diatomite is conducive to the adsorption and deposition of APP. Figure 5(c) shows that a

large amount of APP particles are deposited on the surface of diatomite, and the particle size of APP is nearly unchanged compared with the pure APP. Figure 5(d) shows that part of the APP particles are distributed on the surface of diatomite and part of the APP particles are penetrated into the macropores of diatomite, and the particle size of APP is smaller than that in Fig. 5(c). During the preparation of filler 2, diatomite was added prior to the formation of APP from phosphoric acid and urea. In this manner, the two reagents could be adsorbed and react with each other on the surface and inside of the macropores of diatomite, perhaps forming strong bonds between APP and diatomite (Yang and Li 2013).



**Fig. 5.** SEM images of diatomite, APP, and two composite fillers

### FTIR Spectra of Diatomite and Composite Flame-retardant Fillers

Figure 6 shows the FTIR spectra of diatomite, composite filler 1, and filler 2. Diatomite has absorption peaks at  $3467.77\text{ cm}^{-1}$ ,  $1087.78\text{ cm}^{-1}$ , and  $476.38\text{ cm}^{-1}$ . The absorption peak at  $3467.77\text{ cm}^{-1}$  is ascribed to the absorption of  $-\text{OH}$ , while absorption peaks at  $1087.78\text{ cm}^{-1}$  and  $476.38\text{ cm}^{-1}$  are respectively assigned to the antisymmetric stretching vibration and antisymmetric bending vibration of  $\text{Si-O}$ . The FTIR spectrum of composite filler 1 is similar to that of composite filler 2. The peaks at  $1076.21\text{ cm}^{-1}$  and  $489.89\text{ cm}^{-1}$  for composite filler 1 and the peaks at  $1074.28\text{ cm}^{-1}$  and  $497.60\text{ cm}^{-1}$  for composite filler 2 are the absorption peaks of  $\text{Si-O}$ , showing a corresponding displacement compared with that of diatomite. Sharp absorption peaks at  $760\text{ cm}^{-1}$ ,  $680\text{ cm}^{-1}$ , and  $600\text{ cm}^{-1}$  in composite filler 1 and composite filler 2 are assigned to the absorption of  $\text{O=P-O}$ ,  $-\text{OH}$ , and  $\text{O-P-O}$ . Composite filler 1 and composite filler 2 therefore both contain a certain amount of APP.

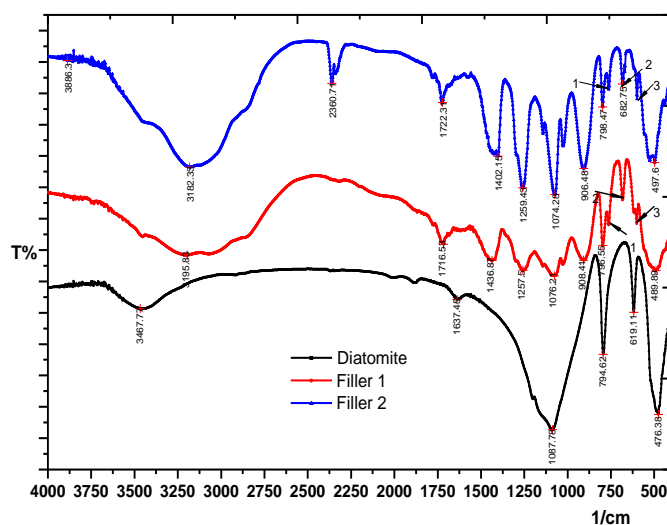


Fig. 6. FTIR spectra of diatomite and composite fillers

### TG Curves of APP, Diatomite, and Composite Fillers

TG analysis of synthesized APP, diatomite, and composite fillers are shown in Fig. 7. It can be seen that only of 3.3% weight was lost from APP before 250 °C. This weight loss can be attributed to the release of a limited amount of  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , mainly from thermally unstable structural groups or chain ends. However, weight loss rapidly increased in the temperature range of 250 to 550 °C. By the time the temperature reached 550 °C, about 24.6% of the APP weight was lost. This weight loss was also attributed to the release of  $\text{H}_2\text{O}$  and  $\text{NH}_3$ ; however, this thermal degradation leads to a cross-linked -P-O-P- structure, which has better thermal stability (Camino *et al.* 1985). The second important thermal degradation stage occurred over the range of 550 to 700 °C and about 65% weight loss occurred by the time the temperature reached 700 °C. The weight loss at this stage is contributed to the release of phosphoric acid, polyphosphoric acid, and metaphosphoric acid with APP decomposition (Gu *et al.* 2007).

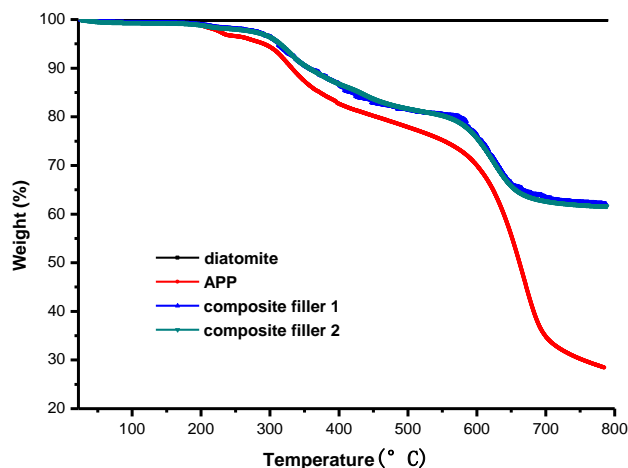


Fig. 7. TG curves of APP, diatomite, and composite fillers



Figure 7 also shows that diatomite had a residual weight of 99.8% at the end of the heating, indicating that it has good thermal stability and does not contribute to the observed thermal degradation of APP. The TG curve of composite filler 1 looks exactly like that of composite filler 2 due to their similar content of APP. Composite filler 1 had 3.47% weight loss and filler 2 had 3.61% weight loss before 300 °C, but their weight loss sped up over the range of 300 to 550 °C (the first key weight loss stage) and reached about 20% at 550 °C. In the second thermal degradation stage, composite fillers had a residual weight of 60% over the range of 550 to 650 °C, and the weight loss in both stages resulted from the decomposition of APP. Compared with composite fillers, the weight loss in the case of pure APP in both stages was higher because the APP content in composite fillers was lower than when using pure APP. Furthermore, the TG curve of APP powder was steeper and the initial thermal degradation temperature of APP was lower than that of composite fillers, which indicates that thermal decomposition of composite flame-retardant fillers lagged behind that of APP powder.

### Flame Retardation of Papers

Combustion tests were performed on paper without filler, paper with only diatomite, APP, aluminium hydroxide, and paper with composite flame-retardant fillers. The results are given in Table 1.

**Table 1.** Weight Change of Various Paper Samples

No.	Paper samples	Basis Weight (g/m <sup>2</sup> )	Weight (g)	Ash (g)	Weight Loss (%)
1	Without filler	91.8	0.2890	0.0005	99.83
2	Diatomite (25%)	88.2	0.2699	0.0623	76.92
3	APP (25%)	90.0	0.2763	0.0744	73.07
4	Composite filler 1 (25%)	89.3	0.2744	0.0942	65.67
5	Composite filler 2 (25%)	91.2	0.2834	0.1258	55.61
6	Aluminium hydroxide (50%)	90.5	0.2716	0.0910	66.49

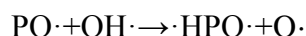
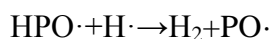
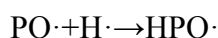
Table 1 shows that the weight loss of paper without filler was 99.83%, as practically all of the paper was burned. The weight loss of paper with only diatomite was 76.92% and a small amount of gray ash was left, indicating that diatomite itself has some flame-retardant effect, but its effect was not very good. When the amount of APP was 25 wt%, the residual weight of paper was only 26.93%, meaning that the flame-retardant effect of paper with the application of only APP was not very good. When 50 wt% aluminium hydroxide was added into paper pulp, the flame retardation of paper was still inferior to paper with the application of 25 wt% composite fillers. After being burned, papers with composite filler 1 and filler 2 had weight losses of 65.67% and 55.61%, respectively, and their residues contained a lot of carbide, as shown in Fig. 8.



(a) Residue of paper with filler 1      (b) Residue of paper with filler 2

**Fig. 8.** Combustion residue of papers filled with composite flame-retardant fillers

The residual weights of paper with filler 1 and paper with filler 2 were much higher than those of paper samples either without filler, with only diatomite, or with aluminium hydroxide and APP, indicating that composite fillers have good flame-retardant effect. Because APP adsorbed by diatomite can decompose at high temperature, the generated phosphoric acid can promote dehydration and carbonization of paper and cut off the further spread of temperature and flame. Furthermore, solid polyphosphoric acid or polymetaphosphate can be further generated at high temperature, together with the release of  $\text{NH}_3$ , water vapor, and other non-flammable gases, which dilute air and retard combustion. At the same time, free radical termination reactions can also happen at high temperature. The equations are as follows:



The above reactions capture the free radical of  $\text{O}\cdot$  and stop combustion (Zhang and Mei 2004), resulting in a flame-retardant effect.

It can be seen from Table 1 and Fig. 8 that paper with filler 2 left the most residue, while paper with filler 1 left less residue. Therefore, it can be reasonably concluded that paper with filler 2 was more flame-retardant than paper with filler 1. Paper with filler 2 contained more effective APP than paper with filler 1. Because P-O-Si bonds might be formed by combining P-OH on the surface of APP with Si-OH on the surface of diatomite in the process of in situ polymerization, there were more strong bonds between diatomite and APP in composite filler 2 and less APP was dissolved during the papermaking process.

### Physical Properties of Papers

The tensile index, burst index, and equilibrium moisture regain of paper without filler and paper containing only diatomite, only aluminium hydroxide and composite fillers are shown in Table 2.

**Table 2.** Physical Properties of Paper with Different Fillers

	Basis weight (g/m <sup>2</sup> )	Burst index (kPa·m <sup>2</sup> /g)	Tensile index (N·m/g)	Equilibrium moisture regain (%)
Without filler	92.0	6.4	74.6	5.12
Diatomite (25%)	93.1	4.1	48.3	4.13
Composite filler 1 (25%)	92.5	4.2	49.2	4.18
Composite filler 2 (25%)	90.6	4.6	52.4	4.20
Al(OH) <sub>3</sub> (50%)	89.8	2.4	28.7	4.16

It can be seen from Table 2 that the burst index and tensile index of paper without filler were higher than that of paper with fillers, and they decreased with the increase of fillers, because the addition of fillers hindered the formation of hydrogen bonds between fibers. For the paper specimens containing the same amount of fillers, they had similar physical strength. The tensile index and burst index of paper with 50 wt% aluminium hydroxide were far below paper with 25 wt% composite fillers. Equilibrium moisture regain of paper without filler was higher than paper containing fillers due to the higher hydrophilic of plant fibers than inorganic fillers. When the filler content reached a certain point, the equilibrium moisture regain of paper changed very little.

## CONCLUSIONS

1. The synthesized APP had minimal water solubility when the molar ratio of phosphoric acid to urea was 1:1.8. The synthesized APP belonged to APP-I, and its DP was 91.21.
2. Composite flame-retardant fillers composed of APP and diatomite were prepared by mixing and *in situ* polymerization. APP was adsorbed on the surface of the diatomite. The prepared composite flame-retardant fillers had the same characteristic absorption peaks as APP. Composite flame-retardant fillers made by mixing and *in situ* polymerization had similar TG curves. During thermal degradation, they all had two weight loss steps, which were the same as those of APP.
3. The ash content obtained by paper combustion revealed that the retention of the APP composite flame-retardant filler formed by *in situ* polymerization was very good due to the strong interaction between APP, diatomite, and paper. However, the retention of APP composite flame-retardant filler formed by the mixing method was not as good. Paper with this filler had high weight loss in the combustion test and, after burning, left incomplete residue. The flame retardation performance of composite flame-retardant filler formed by *in situ* polymerization was superior to that of composite flame-retardant filler formed by the mixing method.

## ACKNOWLEDGMENTS

The authors are grateful for the support of the Pulp and Papermaking Engineering Key Discipline of Zhejiang Province.

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Article submitted: December 30, 2013; Peer review completed: March 3, 2014; Revised version received and accepted: March 25, 2014; Published: April 10, 2014.