

Ternary Flame Retardant System Based on the *in-situ* Polymerization of Ammonium Polyphosphate-Diatomite-Aluminium Trihydroxide

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A three-component flame-retardant system was prepared based on *in situ* polymerization of ammonium polyphosphate (APP), diatomite (DE), and aluminium trihydroxide (ATH) to improve the flame retardance and smoke suppression properties of fibrous materials. Compared to the two-component system of APP-DE, the addition of APP-10% DE-4% ATH dosed at a filler load of 20% of the fibrous material reached a limited oxygen index of 27.5%, which was approximately 9.1% higher than the two-component system. The lower mass loss rate and higher residual mass at high temperatures resulted in excellent flame retardance. The synergistic effect on alleviating combustion and reducing heat release was shown by the 16.6%, 22.1%, and 12.5% decreases in the peak heat release rate, total heat release, and average effective heat combustion, respectively. Superior fire resistance was demonstrated by a higher fire performance index and a lower mass loss. A smoke suppression effect was shown by the peak smoke release rate and the total smoke release results that were 28.7% and 15.8% lower than the two-component system, respectively. Based on the porous structure of DE and generated aluminum oxide (Al₂O₃), the outstanding adsorption effect and flame-retardant effect was also demonstrated by the production rate of carbon monoxide (CO) and carbon dioxide (CO₂).

Keywords: Ammonium polyphosphate; Aluminum hydroxide; Diatomite; Flame retardancy; Smoke suppression

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INTRODUCTION

Flame retardant cellulosic materials provide various applications for armed forces, home furnishing and decorations, uniforms for firefighting personnel, auto filters, and more (Mohamed 2005). To meet the safety standards against the inhalation of smoke and toxic combustion gases like carbon monoxide (CO), the requirements for retardant properties are increasingly necessary. There are many approaches to improve flame retardancy, including the use of fillers or additives, surface treatments, and chemical or physical modification. However, the addition of fire-retardant chemicals still initially occurs in the mill (Visakh and Arao 2015).

Among flame retardants, phosphorus-based chemicals are still one of the most widely used additives. One of the most important phosphorus-containing flame retardants, ammonium polyphosphate (APP), has been favored due to its minimal environmental

impact, low cost, and high retardant efficiency (Sha and Chen 2014, 2016). In order to achieve high fire performance levels, it is necessary to develop a flame-retardant system based on a combination of different flame-retardant agents. The concept of synergism is used to optimize flame-retardant formulations and enhance the performance of mixtures of two or more additives. Synergism can be achieved with a mixture of additives (Yen *et al.* 2012), and the synergism between APP and aluminium trihydroxide (ATH) has been shown in previous studies. Metal oxides or hydroxides are the least effective in terms of dosage but are the least expensive of all flame-retardants. They have a certain synergistic effect with phosphorus-containing flame retardants and are widely used as flame retardant synergists for the plastic, rubber, coating, and papermaking industries (Laachachi *et al.* 2006; Gu *et al.* 2007; Lin *et al.* 2011; Friederich *et al.* 2012; Zhou *et al.* 2013). Nonetheless, due to the complexity of chemical additives in cellulosic products, the synergism effect can be weakened due to the lower retention rate. Diatomite (DE) is a non-metallic mineral with a porous structure, strong adsorption capabilities, and a large specific surface area, which is why it is widely used as a filler in cellulosic materials, such as flame-retardant paper (Li *et al.* 2008; Sha and Chen 2014). Previous work has confirmed that APP-DE composite filler can adsorb some smoke and toxic gas (Sha and Chen 2014, 2016). Moreover, the main products of completely burnt cellulosic materials are carbon dioxide (CO₂) and water vapor. However, when paper burns incompletely, it releases CO, which creates smoke, carbon black particles, and other pyrolysis products. The smoke released in the burning process of cellulosic materials can be controlled by reducing the generation and volatilization of the pyrolysis volatiles. Condensed phase char formation can effectively suppress the smoke and toxic gases (Lu and Wilkie 2010; Qian *et al.* 2014). The condensed phase smoke suppression is consistent with the flame-retardant mechanism, and the goal of flame retardance and smoke suppression can be achieved by the design of flame-retardant formulas. To reach a superior flame-retardant effect, better synergism among APP, DE, and ATH should be considered.

In this work, a novel synergistic retardant system was created based on the *in-situ* polymerization of APP and ATH in the DE possessing porous structure and providing a reaction site for efficient retardancy potential. The optimum formula and mechanism were both explored.

EXPERIMENTAL

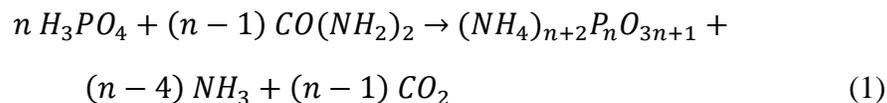
Materials

The softwood pulp and hardwood pulp were obtained from ARAUCO (Santiago, Chile) and CENIBRA (Belo Oriente, Brazil), respectively. Analytically pure phosphoric acid (85%) and urea were supplied by Shanghai Lingfeng Chemical Reagent Co. (Shanghai, China), and chemically pure DE was supplied by Chinasun Specialty Products Co. (Changshu, China). Aluminum hydroxide (Al(OH)₃, 99.6%, 5000 sieve mesh) was provided by Xinxiang Jinsheng New Materials Co. (Xinxiang, China). Cationic polyacrylamide (CPAM) was provided by Nalco (Shanghai, China), and silica sol was supplied by Suzhou Tianma Specialty Chemicals Co. (Suzhou, China).

Preparation of the APP- DE-ATH Composite Fillers

A certain amount of phosphoric acid was poured into a three-necked flask and heated to 70 °C in an oil bath and a certain amount of urea was added into the agitated

flask. The molar ratio of phosphoric acid to urea was controlled at 1:1.8. The reaction is shown in Eq. 1,



The mixture was heated at a rate of 2 °C/min to 3 °C/min. A DE amount equivalent to 10% mass of the generated APP and ATH equivalent to 1%, 2%, 3%, 4%, and 5% mass of the generated APP was added into the flask 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. Then, the solid product was ground to powder and screened to obtain the APP-10% DE-ATH composite fillers with different compositions, which were designated as APP-10% DE-1% ATH, APP-10% DE-2% ATH, APP-10% DE-3% ATH, APP-10% DE-4% ATH, and APP-10% DE-5% ATH. The APP-10% DE composite filler was prepared in the absence of ATH.

Preparation of the Flame Retardant Paper

Flame retardant paper with a basis weight of 100 g/m² was prepared with 25 wt% of softwood pulp and 75 wt% of hardwood pulp as the main fibrous raw materials and 0.2 wt% of cationic polyacrylamide and 0.3 wt% of silica sol were the dual retention aids. The prepared composite fillers at different dosages were used as the flame retardants.

Characterization

The thermogravimetric analysis (TGA) of the composite fillers was performed on a STA 449 F3 TGA thermal analyzer (NETZSCH, Selb, Germany) at a heating rate of 10 °C/min under a nitrogen atmosphere and a flow rate of 50 mL/min. A 10 mg sample was used for the thermal analysis.

The limited oxygen index (LOI) test of the paper samples were performed with a JF-3 digital display limiting oxygen index tester (Glomro, Shanghai, China) according to the ASTM standard D2863-13 (2013). The test samples were 100 mm × 10 mm.

The cone calorimeter tests (CCTs) of the paper sheet were carried out with an FTT 2000 cone calorimeter (Fire Testing Technology, East Grinstead, UK) in accordance with the ASTM standard E1354-16a (2016). The specimens (100 mm × 100 mm × 0.20 mm) were measured horizontally with a standard optional retainer frame and grid at a heat flux of 30 kW/m². The distance between the cone heater and the specimen was 25 mm.

The scanning electronic microscopy (SEM) analysis was performed on the charred residues after the CCTs by using a TM3000 scanning electron microscope (Hitachi, Tokyo, Japan). The resolution of the SEM was 30 nm and its accelerating voltage was 5 kV.

The elemental analysis of the charred residues after the CCTs with and without filler was also determined using an Energy-Dispersive Spectrometer (EDS, JED-2300, JEOL, Tokyo, Japan) on Field-Emission Scanning Electron Microscope (FE-SEM, JSM-7001F, JEOL, Tokyo, Japan).

Tensile strength and bursting strength were tested according to TAPPI standard methods and calculated based on basis weight.

RESULTS AND DISCUSSION

LOI Values

Figure 1 shows LOI values of paper filled with different flame retardant recipes at different filler loadings. As can be seen in Fig. 1, the LOI values of the paper increased with the increased filler loading. The APP-10% DE-4% ATH sample yielded the best LOI value and therefore the best flame-retardance. Although a higher retardant loading resulted in better flame retardance, the LOI value even at filler loading of 20% had achieved 27.5%, which could meet the requirement for fire resistance. Moreover, the addition of ATH at 4% showed the best results and was therefore chosen as the optimum formula.

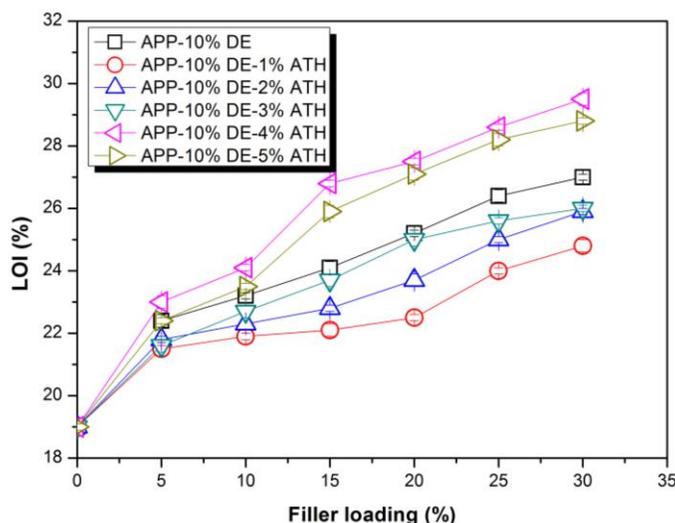


Fig. 1. Changes in the LOI values with different levels of ATH addition as a function of the filler loading

TG Analysis

Figure 2 and Table 1 show the TG and derivative thermogravimetry (DTG) results of different retardants for thermal behavior analysis and contrast. Results in Fig. 2 showed that both the APP-10% DE and APP-10% DE-4% ATH samples exhibited two main mass loss steps within the temperature range of 20 °C to 800 °C. This was because APP was the main component in the two composite fillers. Based on the two-step mechanism for the thermal degradation of APP, the mass loss in the range of 280 °C to 550 °C was mainly due to the release of ammonia (NH₃) and water (H₂O) to form phosphoric acid, which further dehydrated and crosslinked to form ultraphosphate, polyphosphoric acid, and metaphosphoric acid, whose volatilization contributed to the mass loss between 550°C and 787.5 °C (Camino *et al.* 1978, 1985; Camino and Luda 1998). Compared to APP-10% DE, APP-10% DE-4% ATH had a lower initial decomposition temperature, which corresponded to the maximum mass loss rate and higher mass loss in the first mass loss step. Thus, it could be seen that the addition of ATH could decrease the thermal stability of the system at low temperatures and promote the decomposition of APP to release NH₃. Meanwhile, the high amount of hydroxyl groups in ATH will be dehydrated near 300 °C and give rise to mass loss, as shown in Eq. 2.



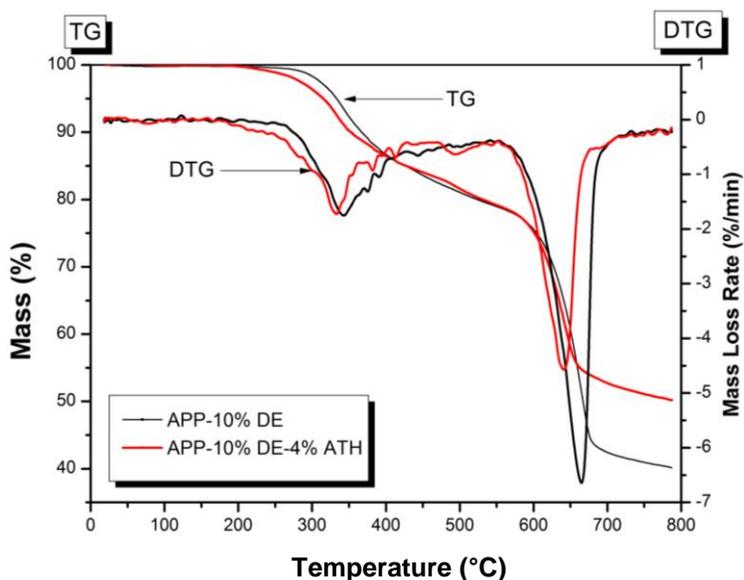


Fig. 2. The TG and DTG curves of the APP-10% DE and APP-10% DE-4% ATH composite fillers

Table 1 presents the thermal decomposition parameters of APP-10% DE and APP-10% DE-4% ATH. As could be seen, the residual rate of the former filler was 40.1%, while the latter was 50.2%, indicating the successful combination between ATH and the decomposition production from APP. This combination restrained the volatilization of the polyphosphoric acid and the metaphosphoric acid in the second mass loss step, and therefore reduced the mass loss and the mass loss rate of the system at high temperatures (Cinausero *et al.* 2011). Thus, the presence of ATH in the novel flame retardant effectively improved its stability at high temperatures.

Table 1. Thermal Decomposition Parameters of the APP-10% DE and APP-10% DE-4% ATH Composite Filler Samples

Composite Filler	Initial Decomposition Temperature (°C)	Temperature Corresponding to the Maximum Mass Loss Rate (°C)		Maximum Mass Loss Rate (%/min)		Residue Rate at 787.5 °C (%)
		I	II	I	II	
APP-10% DE	312.4	343.0	665.0	1.75	6.64	40.16
APP-10% DE-4% ATH	294.2	333.6	641.7	1.72	4.57	50.19

CCT Results of the Heat Release Rate (HRR)

The HRR curves and CCT results of the paper loading APP-10% DE and APP-10% DE-4% ATH are shown in Fig. 3 and Table 2 respectively. Figure 3 shows that the peak HRR (PHRR) of the paper with APP-10% DE-4% ATH was lower than that of paper with APP-10% DE. As can be seen in Table 2, the PHRR, the total heat release (THR), and the average effective heat combustion (AEHC) of the paper with APP-10% DE-4% ATH were 34.2 kW/m², 0.95 MJ/m², and 9.8 MJ/m², which were 16.6%, 22.1%, and 12.5% lower than those with APP-10% DE respectively. The time to PHRR (t_{PHRR}) and time to ignition (t_{TI}) increased by 1 s and 2 s due to the addition of ATH. All of the above performance demonstrated that the APP-10% DE-4% ATH had superior flame retardance due to the

synergistic effect on alleviating combustion and reducing the heat release of paper from ATH. Namely, the water vapor released from the ATH (shown in Eq. 2) diluted the concentration of the oxygen and combustible gases generated by the paper pyrolysis. Al_2O_3 acted as covering layer to isolate air and block fire, which promoted the function of char forming and reduced the formation of combustible volatiles (Evans 1986).

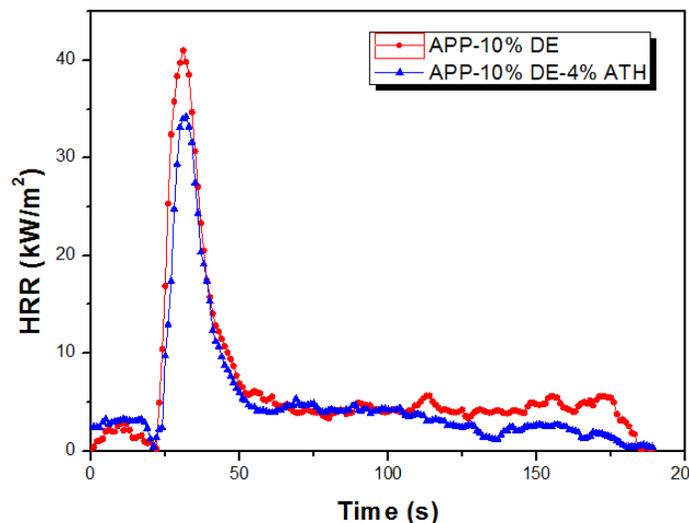


Fig. 3. The HRR of the paper filled with different composite fillers

Table 2. Cone Calorimeter Results of the Different Paper Sheets

Samples	PHRR (kW/m ²)	THR (MJ/m ²)	AEHC (MJ/kg)	t_{PHRR} (s)	t_{T1} (s)	FPI (s.m ² /kW)	ML (%)
APP-10% DE	41.0	1.22	11.2	31	23	0.561	75.1
APP-10% DE -4% ATH	34.2	0.95	9.8	32	25	0.731	71.8

Of the parameters in Table 2, the fire performance index (FPI) designated the ratio of t_{T1} to PHRR and was used to predict whether a material could easily develop drastic combustion after ignition (Ou *et al.* 2001), while the mass loss (ML) designated the flammability of a material (Ye and Qu 2008). Table 2 showed that the paper loading APP-10% DE-4% ATH had higher FPI (0.731) and lower ML (71.8 %) than the paper loading APP-10% DE (0.561 for FPI and 75.1% for ML), reaching a conclusion that the former had better fire resistance.

Smoke Release Rate (RSR) and Total Smoke Release (TSR)

The RSR and the TSR of the paper with different retardants are shown in Figs. 4 and 5. The peak RSR and TSR of the paper with the APP-10% DE-4% ATH composite filler were $0.386 \text{ m}^2/\text{m}^2\text{s}$ and $8.61 \text{ m}^2/\text{m}^2$, respectively, which were 28.7% and 15.8% lower than that of the paper with APP-10% DE. The addition of ATH in the composite filler had an obvious smoke suppression effect, since the Al_2O_3 generated by the ATH decomposition covered the surface of the paper and hindered the generation of smoke (Zhang *et al.* 2008). In addition, Al_2O_3 has a porous structure with a large specific surface area and can absorb the smoke particles released from the combustion of paper.

Although the APP-10% DE composite filler had comparatively strong flame-retardant properties, its smoke release cannot be ignored. The paper with the APP-10% DE composite filler still had a high PHRR and TSR, although the DE in the filler could serve as an adsorbent. The addition of the ATH in the composite filler could effectively solve the contradiction between the flame retardance and smoke suppression of the APP.

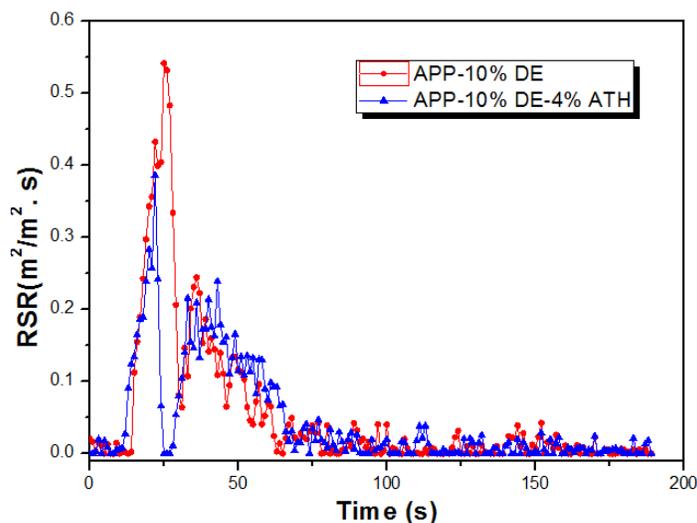


Fig. 4. The RSR of the paper with different composite fillers

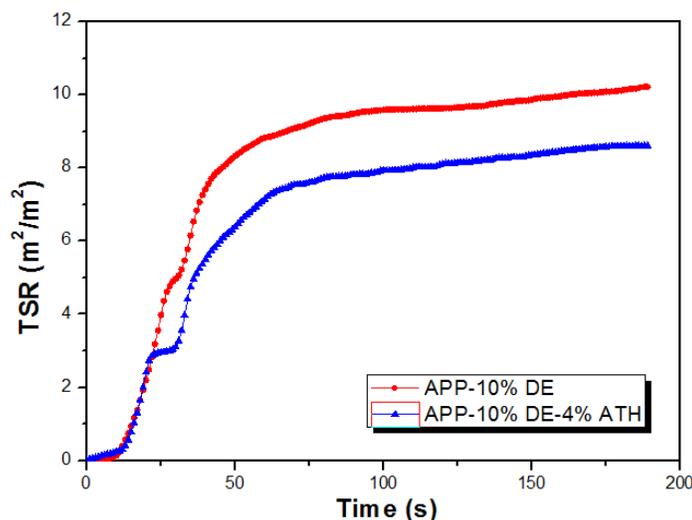


Fig. 5. The TSR of the paper with different composite fillers

Smoke Toxicity

Carbon monoxide (CO) is one of the most common toxic gases in fire, and it is generated by incomplete combustion. While CO₂ itself is nontoxic, it can lower the concentration of the oxygen (O₂) in the air, which is an indirect danger. The production rate of CO (COP) and CO₂ (CO₂P) of the paper loading APP-10% DE and APP-10% DE-4% ATH composite fillers are shown in Figs. 6 and 7.

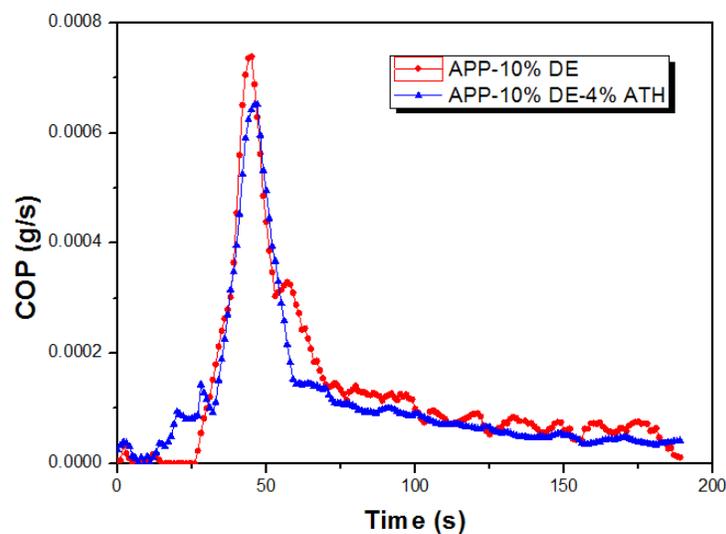


Fig. 6. The COP of the paper with different composite fillers

As shown in Fig. 6, the peak COP of the paper with APP-10% DE-4% ATH was 0.652 mg/s, while APP-10% DE was 0.739 mg/s. The addition of the ATH in the composite filler restrained the COP since the condensed phase of flame retardant that resulted from the synergy of the ATH and APP promoted the carbonization of the paper fiber and decreased the volatilization of the combustible gases. In addition, the Al_2O_3 with a high specific surface area had a good adsorption effect on the smoke. Figure 7 showed that the CO_2P of the paper with APP-10% DE-4% ATH was 0.0347 g/s, while APP-10% DE was 0.0354 g/s. The former composite obviously restrained the complete combustion of the paper sheet and decreased the production of CO_2 , which also contributes to the demonstration of its superior retardancy.

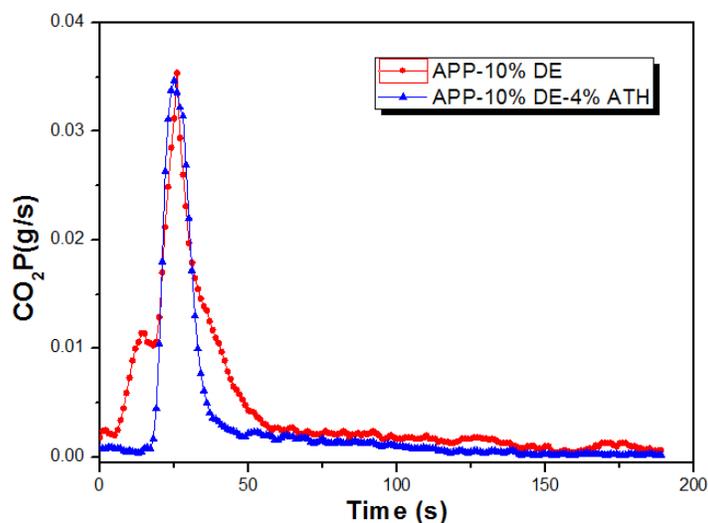


Fig. 7. The CO_2P of the paper with different composite fillers

SEM Images of the Charred Residues

The charred residues of the paper sheets after the CCTs were observed by SEM, as shown in Fig. 8. The APP-10% DE composite filler had a good stabilizing effect on the

fiber skeleton of the paper sheet during the combustion process (Fig. 8a). However, partial paper fibers turned into a flat char layer while being partially ruptured. As shown in Fig. 8b, the charred residue of the paper with APP-10% DE-4% ATH also had a visible fiber texture while comparatively more complete and compact flat char layer without visible fiber breakage or longitudinal cracking. This indicated that the presence of ATH could keep the integrity and stability of the fibers during the carbonization process. Moreover, due to the improvement during carbonization, the original fibrous network structure was protected, and thus the strength of the char layer was enhanced, and the deformation was decreased.

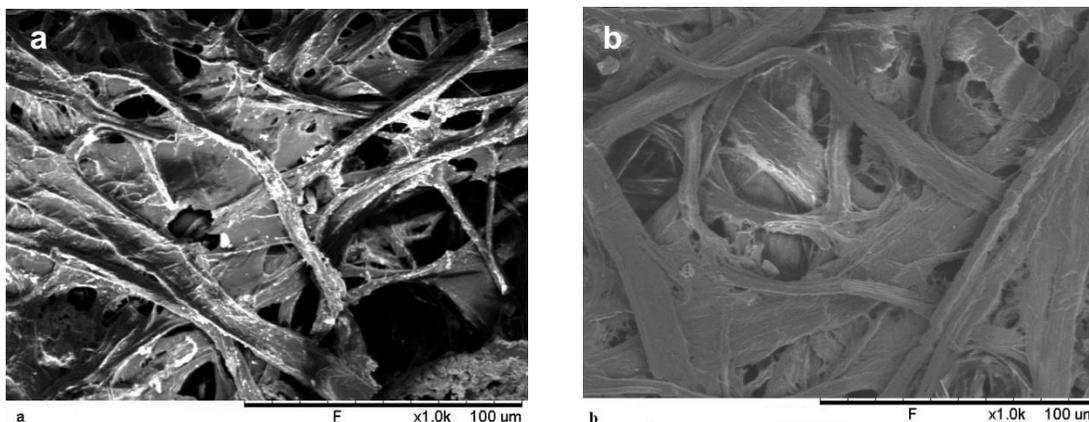


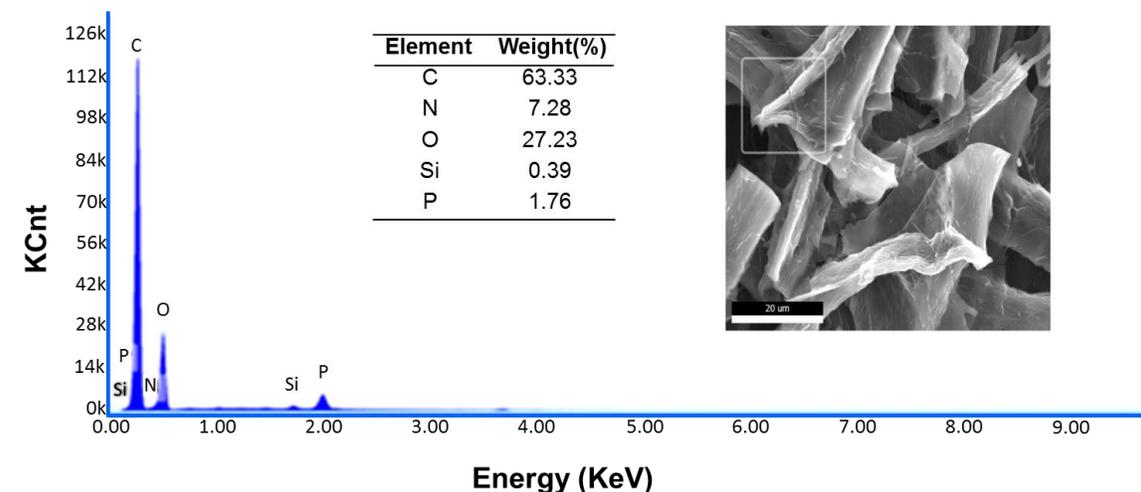
Fig. 8. The SEM images of the charred residues of the paper with (a) APP-10% DE and (b) APP-10% DE-4% ATH

Elemental Analysis

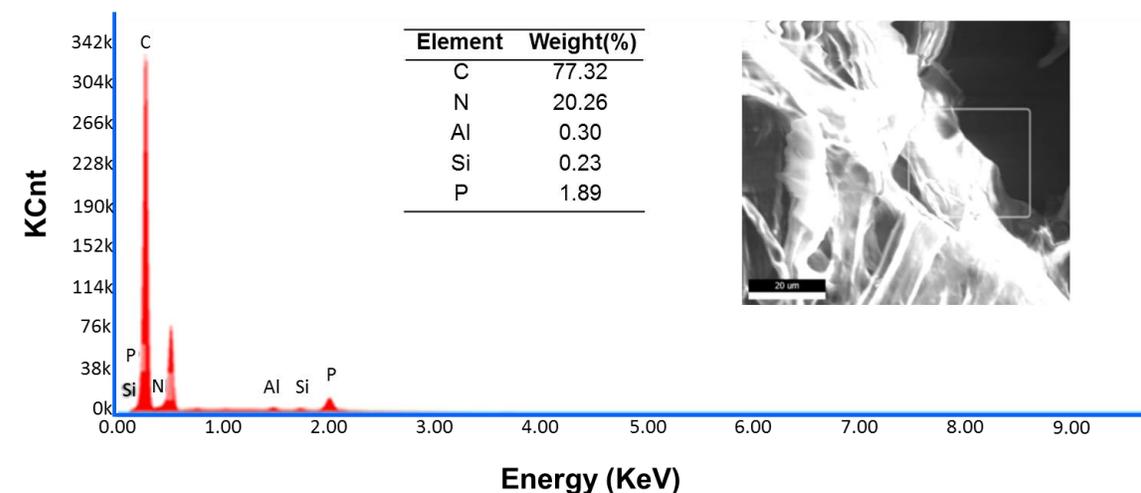
With the residues remaining after CCT, an elemental identification and quantitative analysis by energy dispersive spectroscopy were carried out, and results are shown in Fig. 9. Compared with APP-10% DE, the element aluminum clearly was present in the paper filled with APP-10% DE-4% ATH, which is consistent with the successful polymerization of the involved flame retardant. Moreover, during heating process, ATH could decompose to Al_2O_3 and H_2O . The former will react with H_3PO_4 pyrolysis from APP to produce AlPO_4 . Not only is this reaction endothermic, so that it will bring into lower surface temperature and hinder the burning process, but also the AlPO_4 will form a cover layer, resulting in air isolation, blocking the fire, decreasing the flammable condition, and preventing spreading of the fire. The water decomposed from ATH could also dilute the flammable gas and oxygen to stop the burning.

Mechanical Properties

Mechanical properties including burst index and tensile index of paper without and with different fillers are shown in Table 3. As presented, the burst and tensile index of paper without filler were comparatively higher, since the addition of fillers could hinder the formation of hydrogen bonds, which are the main contribution for strength properties. Compared among the papers filled with different retardants, similar performance was observed, which implied that APP-10% DE-4% ATH hold the optimum fire resistance while the necessary strength properties.



(a)



(b)

Fig. 9. EDS-SEM spectra of paper residues filled with (a) APP-10% DE and (b) APP-10% DE-4% ATH after CCT

Table 3. Mechanical Properties of the Treated Fibrous Materials

	Basis weight (g/m ²)	Burst Index (kPa·m ² /g)	Tensile Index (N·m/g)
Without filler	92.0	6.4±0.2	74.6±0.3
Diatomite	92.9	4.5±0.1	52.6±0.1
ATH	91.2	4.7±0.2	51.9±0.1
APP-10% DE-4% ATH	90.9	4.4±0.2	52.3±0.2

Note: The addition amount of different fillers was controlled at 20% based on the oven-dried fiber.

CONCLUSIONS

1. A flame-retardant system based on the *in-situ* polymerization of the combination of ammonium polyphosphate (APP), diatomite (DE) and aluminum trihydroxide (ATH), here called APP-DE-ATH, was successfully prepared. The formula of APP-10% DE-4% ATH showed the best results.
2. The ATH showed a distinctive synergistic flame retardant and smoke suppression effect when combined with the APP and DE. The addition of the ATH reduced the thermal stability of the composite filler at low temperatures and promoted the decomposition of the APP. The reaction products from the ATH and APP restrained the volatilization of the decomposition products of APP at the second mass loss step and reduced the mass loss of the system at high temperatures.
3. The addition of the ATH reduced the heat release rate, the smoke release, and the smoke toxicity of the filled paper. The ATH also prolonged the time to ignition and decreased the fire risk of the filled paper. By retarding fire in the condensed phase, the addition of ATH can assist the cellulosic materials in presenting a complete and compact char layer with an apparent fiber texture after the cone calorimeter test.

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