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TERNARY FLAME RETARDANT SYSTEM OF AMMONIUM POLYPHOSPHATE-DIATOMITE-NANO-SiO_2 AND ITS APPLICATION IN FIBROUS MATERIALS

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Ternary composite flame retardantswereprepared via *in-situ*polymerization of ammonium polyphosphate (APP)-diatomite (DE)-nano-$SiO_2$and were used for the improvement of flame retardance and smoke suppression of paper fibrous materials. Thermogravimetric analysis (TGA), limiting oxygen index (LOI), cone calorimeter test (CCT) and scanning electron microscope (SEM)were used to evaluate the thermal stability of the composite flame retardants andthe flame retardance and smoke suppression of paper loading the flame retardants. Results show that the LOI value of paper loading 20% APP-DE-2%nano-SiO_2 reached 26.7%, which was higher than that of paper loading the same dose of the ternary compositefillers. The addition of nano-SiO_2reduced the mass loss of the composite filler at high temperature and promoted the condensed phase flame retardation of the paper loading the composite filler. The existence of nano-SiO_2reduced the heat release rate (HRR) and rate of smoke release (RSR) of paper sample, thereby improving the flame retardance and smoke suppression of fibrous materials.

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*Keywords:*Nano-SiO_2,ammoniumpolyphosphate, Fibrous materials, Heat release rate, Rate of smoke release

1. Introduction

Flame retardant paper fiber materials are widely used as autofilters, home decorative materials anduniforms for firefighting personnel[1-3]. The approaches to improve flame retardance of paper fiber materials include fiber modification, paper surface coating, the addition of flame retardants or additives into papermaking pulp, and so on [4-6]. Among, the addition of flame retardantsin paper is the simplerone.The commonly used flame retardantsinclude metal oxides or hydroxides, boron compounds, halogen-containingflame retardants, nitrogen-containing flameretardants and phosphorus-containing flame retardants. The application of metal oxides or hydroxides has been limited due to their lesseffect and higher dosage. Halogen-containing flame retardants have not been used due to environmental problems and human health hazards.Ammonium polyphosphate (APP)isa kind of flame retardant containing phosphorus (P) and nitrogen (N) which has been favored by people for its small environmental damage, low cost and high flame retardant efficiency. However, it still released many smoke and toxic gases and

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cannot meet the safety requirements against the inhalation of smoke and toxic combustion gases like carbon monoxide (CO). It is said that smoke is the main reason causing casualties in fire, and most of the deaths due to the inhalation of toxic fumes, so people pay more and more attention to smoke release control in the burning process of materials[7]. As a consequence, it must be treated for smoke suppression when APP is used as the main ingredient of flame retardants.In order to achieve good flame retardant and smoke suppression performance, it is necessary to develop a new multicomponent flame retardant system and give play to the synergistic effect of each component.Diatomite (DE) is a non-metallic mineral which is widely used as filler in papermaking industry due to its low cost. The previous studies showed that APP-DE composite flame retardant filler had certain flame retardant and smoke suppression effectfor paper fiber materials due to DE’s high specific surface area and pore volume which can adsorb part of the toxic fumes, that is, the goal of flameretardant and smokesuppression can be achieved by the design of flameretardantsformula[8-9].Metal oxides or hydroxides and silicon-containing compounds, such as titanium dioxide (TiO_2), aluminium hydroxide (ATH) and silicon dioxide (SiO_2), have been proven to have certain synergistic effect with phosphorus-containing flame retardants and are widely used as flame retardant synergist for plastic, rubber, coatings and papermaking industries[10-14].

In this work, a new ternary flame retardant filler was prepared based on the in-situ polymerization of APP-DE-nano-SiO_2 and was used as filler for paper fibrous materials. The optimum flame retardant formula and the flame retardance and smoke suppression mechanism were investigated.

2. Experimental

2.1. Materials

Softwood and hardwood pulp were obtained from Arauco(Chile) and Cenibra(Brazil), respectively. Analytically purephosphoric acid (85%) and ureawere supplied by Shanghai Ling Feng Chemical Reagent Co.Ltd, and chemically purediatomite (abbreviated as DE) was supplied by Chinasun Specialty Products Co., Ltd. Nano-SiO_2 (99.6%, 30±5nmin particle size) was provided by Shanghai Pu ZhenBiotechnology Co., Ltd.Cationicpolyacrylamide (CPAM) was provided by NALCO (Shanghai) Trading Co.Ltd and silica sol was supplied by Suzhou Tian Ma Specialty Chemicals Co.Ltd.

2.2. Preparation of ternary composite fillers and flame retardant paper

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 (the molar ratio of phosphoric acid to urea was controlled at 1:1.8）was added into the agitated flask. The reaction is shown in Eq. 1,

$$\mathrm{n\,H_3PO_4 + (n-1)\,CO(NH_2)_2 \rightarrow (NH_4)_{n+2}P_nO_{3n+1} + (n-4)\,NH_3 + (n-1)CO_2} \qquad (1)$$

The mixture was heated at the rate of 2～3 ℃/min, and a amount of DE equivalent to 10 % mass of the generated APP and nano-SiO_2 equivalent to 1 %, 2 %, 3 %, 4 % and 5 % mass of the generated APPwere added into the flask when the temperature reached 130 ℃. The mixture was stirred rapidly and the temperature was kept at 130 ℃ for 20 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-nano-SiO_2 composite fillers with different compositions, which were designated as APP-10% DE-1% nano-SiO_2, APP-10% DE-2% nano-SiO_2, APP-10% DE-3% nano-SiO_2, APP-10% DE-4% nano-SiO_2, and APP-10% DE-5% nano-SiO_2. The APP-10% DE composite filler was prepared in the absence of nano-SiO_2.

Flame retardant paper with a basis weight of 100 g/m^2 was prepared with 25 wt% of softwood pulp and 75 wt% of hardwood pulp as fibrous raw materials and 0.2 wt% of CPAM and 0.3 wt% of silica sol were used as the dual retention aids. The prepared composite fillers at different dosages were used as the flame retardants.

2.3. Characterization

Thermogravimetryanalysis(TGA) of the composite fillers were performed on a STA 449 F3TGAthermalanalyzer (Netzsch, Germany) ataheatingrateof10℃·min^{-1} under nitrogen atmosphere(at a flow rate of 50ml·min^{-1}), and the sample mass used was 10 mg .

Limiting oxygen index (LOI) tests of paper samples were performed with a JF-3 digital display limiting oxygen index tester (China) according to ASTM standard D2863-13[15]. The sampleused for the test was100 mm ×10mm (length ×width).

Cone calorimeter tests （CCTs）of paper samples were performed on a FTT2000 cone calorimeter (FTT, England) in accordance with the procedures in ASTM E1354-16a[16]. The samplewas100 mm ×100 mm×0.20 mm (length ×width ×thickness) and the tests were conducted using the standard optional retainer frame and grid. Each specimen was wrapped in an aluminium foil and exposed horizontally to a heat flux of 30kW·m^{-2}, and the distance between the bottom surface of the cone heater and the top of the specimen was 25 mm. The data scans were taken every second.

The charred residues after CCTs were observed by using scanningelectronmicroscopy (SEM, TM3000,Hitachi). The resolution of the SEM was 30 nm and its accelerating voltage was 5 kV.

3. Results and discussion

3.1. LOI values of paper

The composite fillers with different amounts of nano-SiO_2 were used to prepareflame-retardant paper. The LOI values for the paper with filler loadingsof 5%, 10%, 15%, 20%, 25%, and 30%are shown in Fig. 1.

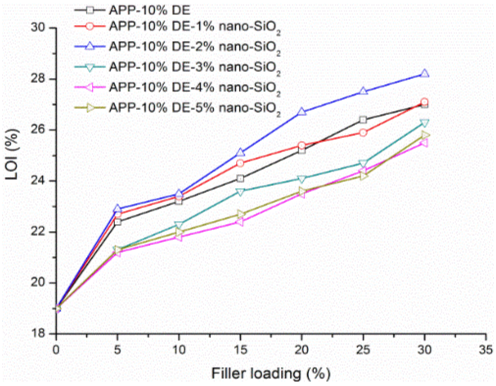


Fig.1. LOI values of paper.

As seen inFig. 1, the LOI values of the paper increased with the increase of filler loading under different formulas. The paper loading APP-10%DE-2% nano-SiO_2 had the highest LOI value and had the best flameretardance, sothe addition of nano-SiO_2at 2% was chosen as the optimum formula. At the same filler loading, a 20% filler loading was required to achieve an LOI value of 26.7%, which met the requirement for fire resistance, so the dosage of APP-10%DE-2%nano-$SiO_2$was set as 20%.

3.2.TGA of composite fillers

The thermalbehavior ofAPP-10% DE and APP-10% DE-2% nano-SiO_2composite fillers are contrasted and theTG and derivative thermogravimetry(DTG) curves areare shown in Fig. 2. Itshows that both the APP-10% DE and APP-10% DE-2% nano-SiO_2composite fillers had two main mass loss steps in the range of 20° C to 800 ° C, because APP was the main component in the two composite fillers. Themass loss in the range of 280 ° C to 550° C was mainlydue to the release of ammonia (NH_3) and water (H_2O) to form phosphoric acid, which further dehydrated and crosslinkedto formultraphosphate, polyphosphoric acid, and metaphosphoric acid [17]. The mass loss in the range of 550 ° C to 787.5° C resulted from the volatilization of phosphoric acid, polyphosphoricacid, and metaphosphoric acid. Compared to the APP-10% DE filler, the APP-10% DE-2% nano-SiO_2fillerhad a lower initial decomposition temperature and a higher mass loss in the first mass loss step, that is, the addition of nano-SiO_2reduced the thermal stability of the system at low temperatures and promote the decomposition of APP to produceNH_3 and H_2O.This is because there were massivehydroxyl groupson the surface ofthe nano-SiO_2 andthese groups will dehydrate by condensation near300° C and give rise to mass loss.At the same time of dehydration, nano-SiO_2 reacted with APP to form fairly stable$[SiO(PO_3)_2]_n$, as shown in Fig.3[12], which restrain the volatilization of thephosphoric acid and the metaphosphoric acid in the second mass loss stepand reduce the mass loss of the system at high temperature. Therefore, the residue of the APP-10% DE-2%nano-SiO_2sample at 787.5° Cwasa little higher than that of APP-10% DE sample.

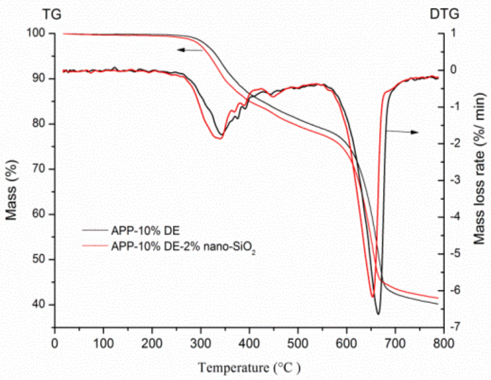


Fig.2.TG and DTG curves of APP-10% DE and APP-10% DE-2% nano-SiO$_2$.

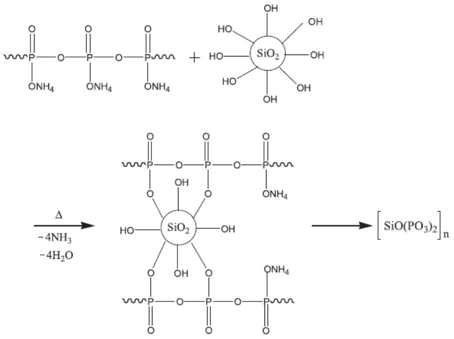


Fig.3.Reaction between nano-SiO$_2$ and APP

3.3. Heat release rate (HRR) of paper

The HRR curves of the paper loading APP-10% DE and APP-10% DE-2% nano-SiO$_2$are shown in Fig.4. It shows that the peak HRR (PHRR) and the total heat release (THR)of the paper loading APP-10% DE-2% nano-SiO$_2$were 34.6kW/m^2 and 1.017 MJ/m^2,which were15.6%and 17.0% lower than that of paper loading APP-10% DE,respectively. In addition, compared to the paper loading APP-10% DE, the time to PHRR (t_{PHRR}) of the paper loading APP-10% DE-2% nano-SiO$_2$was reduced 1 s.Thesedemonstrate thatthe addition of nano-SiO$_2$reducedthe heat release and delayed the combustion of paper.

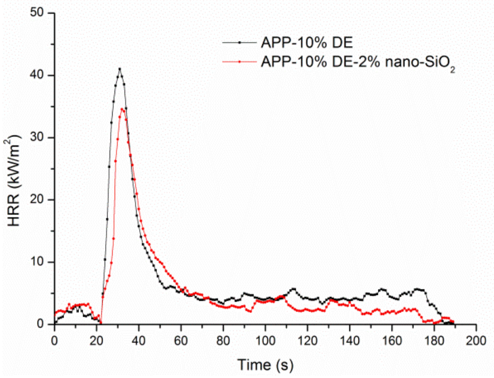


Fig.4. HRR of paper loading APP-10% DE and APP-10% DE-2% nano-SiO$_2$.

3.4. Rate of smoke release (RSR) of paper

The RSR of the paper loading AP-10% DE and APP-10% DE-2% nano-SiO_2 are shown in Fig.5. The peak RSR and total smoke release (TSR) of the paper loadinthe APP-10% DE-2% nano-SiO_2were 0.41m^2/m^{2}s and 9.64 m^2/m^2, respectively, which were 24.1% and 5.7% lower than that of the paper loading APP-10% DE. This means that the addition of nano-SiO_2in the composite filler had an obvious smoke suppression effect. For one thing, Reticular nano-SiO_2product in the char layerimproved the strength and thickness of the carbide, prevented heat transfer into the material and gas emissions, thereby retarding the thermal oxidation degradation of the inner material and reducing the escape of combustible particles and the generation of flue gas.On the other hand, nano-SiO_2had a strong adsorption effect on the smoke released in the combustion process of paper sample and decreased the RSR of sample due to its large specific surface area and strong adsorptivity.

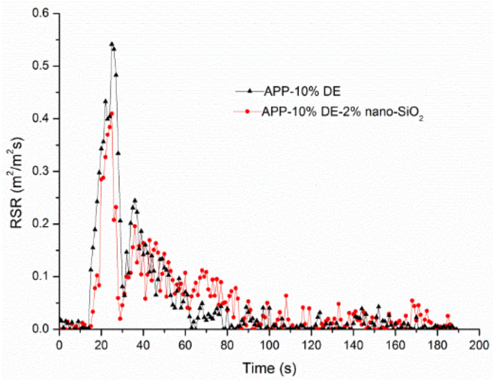
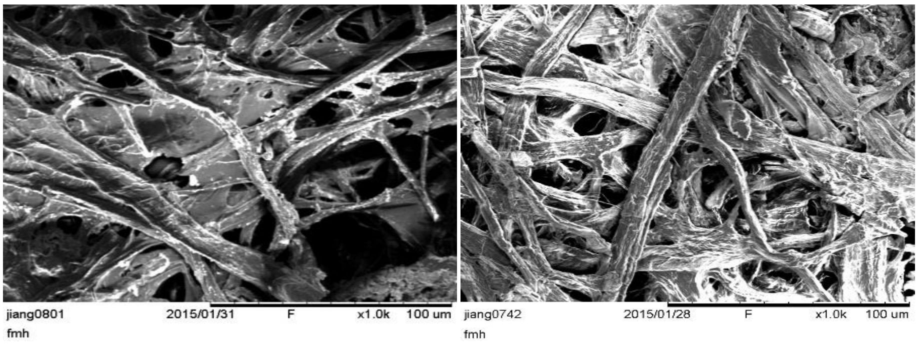


Fig.5.RSR of paper loading APP-10% DE and APP-10% DE-2% nano-SiO_2.

3.5. SEM images of the residues

The residues of the paper samplesafter the CCTs were observed by SEM, as shown in Fig. 6. The char layer of paper sample after CCTs basically maintained the network structure of the paper fiber, indicating that composite flame-retardant fillerplayed a good role in protecting the framework stability of paper sample. For paper loading APP-10% DE, the carbonized fiber presented serious flattening and sticking phenomenon, as shown in Fig.6 (a). However, for the charred residueof paper loading APP-10% DE-2% nano-SiO_2, as shown in Fig.6(b), there was no obvious fiber fracture and longitudinal cracking, and the flattening and sticking phenomenon was slightly. This indicates that the addition of nano-SiO_2played a very important role in keeping the integrityandcompactness of the carbonized fiber. This also means that there existed remarkable synergistic flame retardation between nano-SiO_2 and APP, and they exerted the synergisticcondensed state flame retardanteffect andhad a positive impact on the flame retardance and charring of paper sample.



(a) *(b)*

Fig.6. SEM images of the residues of paper after CCTs: (a) Paper loading APP-10%DE (b) Paper loading APP-10%DE-2% nano-SiO_2.

4. Conclusions

Optimal addition of nano-SiO_2 into APP-10% DE composite filler can improve the flame retardant of paper loading the filler at the same filler loading, paper loading APP-10% DE -2% nano-SiO_2 ternary composite filler had the highest LOI values and the best flame retardant effect.The addition of nano-SiO_2 reduced the thermal stability and promoted the decomposition of the APP-10% DE composite filler at low temperature, however, the reaction product of nano-SiO_2 and APP restrained the mass loss of APP at high temperature and decreased the total mass loss of the system. The addition of nano-SiO_2 reduced the PHRR, RSR of the paper loading the composite filler, promoted the carbonization and improved the flame retardance and smoke suppression of the paper.

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