Digest Journal of Nanomaterials and Biostructures Vol. 12, No. 2, April - June 2017, p. 473 - 481

SYNERGISTIC EFFECT OF NANO-TiO_2, AMMONIUM POLYPHOSPHATE AND DIATOMITE TERNARY SYSTEM ON FLAME RETARDANCY AND SMOKE SUPPRESSION OF FILLED PAPER

H. F. ZHAO[a*], L. Z. SHA[a, b]
[a]*School of Biological and Chemical Engineering/School of Light Industry, Zhejiang University of Science and Technology, Hangzhou, 310023, China*
[b]*Institute of Light Industry and Food, South China University of Technology, Guangzhou, 510641,China*

Ammonium polyphosphate (APP)-diatomite-TiO_2 ternary nanocomposites were prepared via in situ polymerization and subsequently used as fillers for flame retardant paper production. Limiting oxygen index (LOI) and cone calorimeter test (CCT) were used to evaluate the flame retardant and smoke suppression properties of the filled paper, and thermogravimetry (TG) and scanning electron microscope (SEM) were employed to investigate the synergistic flame retardant and smoke suppression mechanism between nano-TiO_2 and APP-diatomite. Results show that APP-10% diatomite-TiO_2 nanocomposites imparts the desired flame retardancy to filled paper when the content of TiO_2 is 4%. Reactions between TiO_2 and APP decomposition products inhibit APP volatilization and reduce the mass loss of composite filler at high temperature. Nano-TiO_2 plays an important role in condensed phase flame retardation and makes the residue more compact and stronger. Synergistic effects between nano-TiO_2 and APP-diatomite impart excellent flame retardancy and smoke suppression to filled paper and reduce its fire risk.

(Received March 10, 2017; Accepted May 22, 2017))

Keywords: Nano-TiO_2, Ammonium polyphosphate, Filled paper, Flame retardancy, Smoke suppression

1. Introduction

With the development of society, paper has been used in more and more fields, e.g., automobile filter materials, building materials and decorative materials where flame retardancy and smoke suppression are required[1-3]. Adding flame retardant fillers into papermaking pulp is a simple and effective way to produce flame retardant paper. Ammonium polyphosphate (APP) is an effective flame retardant containing phosphorus and nitrogen, which has been widely used due to its low impact on environment, low cost and high flame retardant effect. Diatomite is a non-metallic mineral with vesicular structure, large specific surface area, strong adsorption capabilities, and is sometimes used as papermaking filler because of its low cost and wide availability. It has been found that APP-10% diatomite composite filler has a good flame retardant effect on filled paper, however, it still resulted in a lot of smoke and toxic gases[4,5]. Indeed, most fire deaths are due to toxic gases and smoke inhalation instead of burning[6]. So it is necessary to inhibit its smoke release and reduce its smoke toxicity when APP is used as the main flame retardant. It has been reported that many metal oxides, metal hydroxides and silicon-containing compounds, such as TiO_2, aluminum hydroxide (ATH) and SiO_2, had synergy with phosphorus-containing flame retardants, and were usually used as synergists in polymers flame retardant system[7-11]. Some of them act as smoke inhibitors and effectively enhance smoke

---

[*] Corresponding author:zhf9966@163.com

suppression and toxicity reduction effect of the flame retardant system.

In this study, nano-TiO_2 was used as the synergist to improve the smoke suppression properties of flame retardant paper based on APP and diatomite. APP-diatomite-TiO_2 ternary composite fillers were prepared and used to make flame retardant paper. The flame retardant and smoke suppression properties of the filled paper were investigated using LOI and CCT, and the synergistic flame retardant and smoke suppression mechanism between nano-TiO_2 and APP-diatomite was revealed using TG and SEM.

2. Experimental

2.1 Materials

Phosphoric acid (85%) and urea were of analytically pure and were purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd. Diatomite (DE) was supplied by Chinasun Specialty Products Co. Ltd. Commercial nano-TiO_2 (about 6~10 nm) was obtained from Hangzhou Wanjing New Material Co. Ltd. Softwood pulp and hardwood pulp came from Chile and Brazil. Cationic polyacrylamide (CPAM) and silica sol were provided by NALCO (Shanghai) Trading Co. Ltd and Suzhou Tianma Specialty Chemicals Co. Ltd, respectively.

2.2 Preparation of composite fillers and flame retardant paper

A certain amount of phosphoric acid (85%) was poured into a three-necked flask and heated to 70 °C in an oil bath, then the desired amount of urea was added into the flask (the molar ratio of phosphoric acid to urea was controlled at 1:1.8) and the mixture was heated to 130 °C at the heating rate o f 2~3 °C/min. A certain amount of diatomite equivalent to 10% of the generated APP and the desired amount of nano-TiO_2 equivalent to 1 %, 2 %, 3 %, 4 % and 5 % of the generated APP were added, respectively. The temperature was kept at 130 °C for 15~30 min and the product was poured onto a tray and placed in an oven to solidify at 210 °C for 2 hr. The solidified materials were ground to obtain APP-10% DE-TiO_2 composite fillers with different compositions, which were designated as APP-10% DE-1% TiO_2, APP-10% DE-2% TiO_2, APP-10% DE-3% TiO_2, APP-10% DE-4% TiO_2 and APP-10% DE-5% TiO_2, respectively. The product was designated as APP-10% DE in the absence of nano-TiO_2.

Flame retardant paper with a basis weight of $100 g \cdot m^{-2}$ were prepared with 25 *w*% of softwood pulp and 75 *w*% of hardwood pulp as the main fibrous raw materials, 0.2 *w*% of CPAM and 0.3 *w*% of silica sol as the dual retention aids and a certain amount of the prepared composite fillers as the flame retardants.

2.3 Characterization

Thermogravimetry analysis (TGA)

Thermogravimetry analysis of composite fillers were performed using a STA449 F3TGA thermalanalyzer (Netzsch, Germany) at a heating rate of $10\ °C \cdot min^{-1}$ under nitrogen atmosphere (at a flow rate of $50\ ml \cdot min^{-1}$). About 10.0 mg sample was put in an alumina crucible and heated from ambient temperature to 800 °C.

Limiting oxygen index (LOI)

LOI value of paper sample was measured using a JF-3 digital display limiting oxygen index tester (China) according to ASTM D2863-13[12]. The specimens used for the test were 100 mm ×10mm (length ×width).

Cone calorimeter test (CCT)

The cone calorimeter tests of paper samples were carried out with a FTT2000 cone calorimeter (FTT, England) in accordance with the procedures in ASTM E1354-16a[13].The test was conducted using the standard optional retainer frame and grid. Each specimen with dimensions of $100 \times 100 \times 0.20\ mm^3$ was wrapped in an aluminium foil and exposed horizontally to an external heat flux of $30\ kW \cdot m^{-2}$.

Residues analysis

The morphology of the charred residues after cone calorimeter tests was observed by using a digital camera and a scanning electron microscope (SEM, TM3000, Hitachi).

3. Results and discussion

3.1 LOI values of different filled paper

Composite fillers with different amount of TiO_2 were used as fillers to prepare flame retardant paper, and the LOI values of paper loading 5%, 10%, 15%, 20%, 25% and 30% of different composite fillers are shown in Fig. 1.

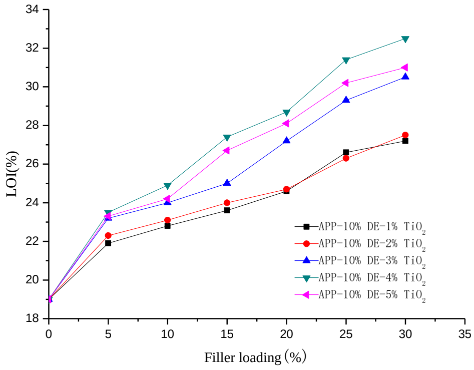

Fig.1.LOI values of different filled paper

Fig.1 showed that the LOI value of base paper (paper with no filler) is about 19%, and the LOI values of filled paper present a rising trend with the increase of filler loading, and tend to rise with the increase of TiO_2 content in composite fillers at the same filler loading until TiO_2 content reaches 4%. For paper loading 20% composite fillers, the LOI values increase from 24.6% to 27.2% as the TiO_2 content in composite fillers changes from 1% to 3%, and paper filled with APP-10% DE-4% TiO_2 has the maximum LOI value of 28.7%. However, when the TiO_2 content further increases to 5%, the LOI value of filled paper falls to 28.1%. It indicates that there is a good synergistic effect between TiO_2 and APP only when they reach a reasonable proportion, and in this experiment, the optimal synergistic flame retardant effect between TiO_2 and APP occurs when the TiO_2 content in composite filler is 4%.

3.2 Thermal behavior of composite fillers

TGA of APP-10% DE and APP-10% DE-4% TiO_2 composite fillers are performed to analyze the effect of TiO_2 on the thermal decomposition behavior of composite filler, and the thermogravimetry (TG) and differential thermogravimetry (DTG) curves are shown in Fig.2 and Fig.3.

Fig.2 and Fig.3 show that APP-10% DE-4% TiO_2 has two major thermal degradation steps similar to that of APP-10% DE composite filler, because both these two composite filler have large percentage of APP. The mass loss in the range of 280~550 °C is mainly due to the release of NH_3 and H_2O to form phosphoric acid, metaphosphoric acid, and pyrophosphoric acid, while the mass loss in the range of 550~787.5 °C corresponding to the volatilization of phosphoric acid and metaphosphoric acid[14]. There is no obvious difference between APP-10% DE-4% TiO_2 and APP-10% DE at low temperature, however, the maximum mass loss rate of APP-10% DE (6.64 %/min) is apparently higher than that of APP-10% DE-4% TiO_2 (5.11 %/min) at high temperature, and the last residual mass of APP-10% DE -4% TiO_2 (51.12%) is significantly higher than that of APP-10% DE (40.16%). It may be explained that the generated phosphoric acid can react with TiO_2 to produce titanium pyrophosphate (TiP_2O_7) crystals at high temperature according to the following reaction, and the generated TiP_2O_7 densify the residue and cool the system, thereby effectively inhibiting the volatilization of phosphoric acid[7,11].

$$TiO_2+2H_3PO_4 \rightarrow TiP_2O_7+3H_2O$$

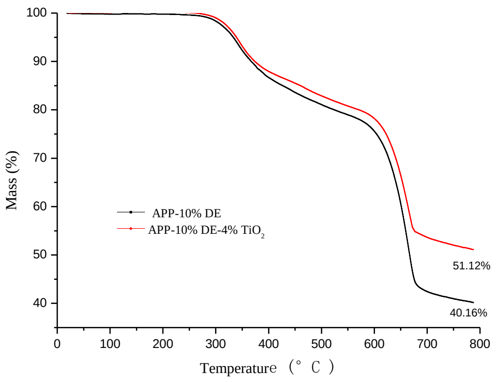

Fig.2. TG curves of composite fillers

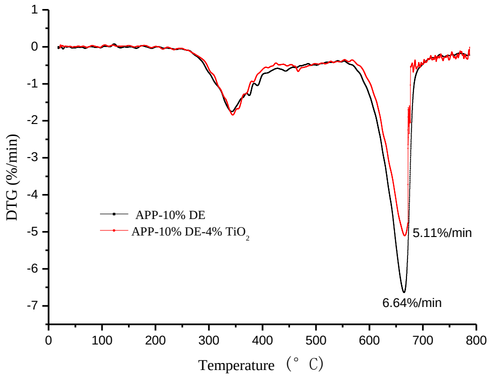

Fig.3. DTG curves of composite fillers

3.3 Cone calorimeter test of filled paper

Cone calorimeter test was performed for paper loading 20% of APP-10% DE-4% TiO_2, and the results were compared with that of base paper and paper loading 20% of APP-10% DE.

Heat release rate (HRR)

The HRR curves of base paper, paper loading APP-10% DE and APP-10% DE-4% TiO_2 are shown in Fig. 4 and the cone calorimeter data are demonstrated in Table 1.

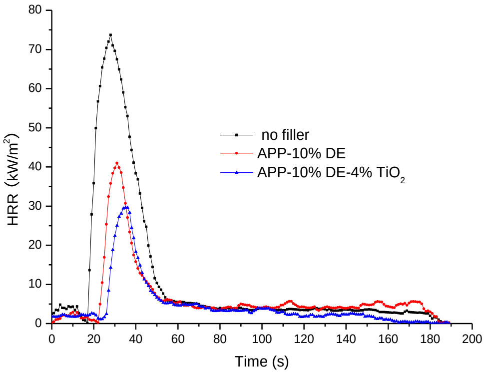

Fig.4. Heat release rate of base paper and paper sheets loading composite fillers

Table 1 Heat release and mass loss of paper sheets

Samples	Base paper	APP-10% DE	APP-10% DE-4% TiO_2
PHRR(kW/m^2)	73.71	41.01	29.64
THR (MJ/m^2)	2.05	1.22	0.83
t_{PHRR}(s)	28	31	35
TTI (s)	18	23	27
FPI (sm^2/kW)	0.24	0.56	0.91
Mass loss (%)	99.64	75.10	68.62

Fig.4 shows that the peak heat release rate (PHRR) of paper loading APP-10% DE-4% TiO_2 is lower than that of base paper and paper loading APP-10% DE, and the time to ignition (TTI) and time to PHRR (t_{PHRR}) of paper loading APP-10% DE are longer than that of base paper, but shorter than that of paper loading APP-10% DE-4% TiO_2.

It can be seen from Table 1 that the PHRR of paper loading APP-10% DE-4% TiO_2 is 29.64 kW/m^2, which is 59.8% and 27.7% lower than that of base paper and paper loading APP-10% DE composite filler, and the total heat release (THR) of paper loading APP-10% DE-4% TiO_2 is 0.83 kW/m^2, 59.5% and 32.0% lower than that of base paper and paper loading APP-10% DE composite filler. In addition, t_{PHRR} of paper loading APP-10% DE-4% TiO_2 is 35 s, which is 7s and 4 s longer than that of base paper and paper loading APP-10% DE, all these data demonstrate that APP-10% DE composite filler can effectively retard the combustion of paper and reduce its heat release. However, APP-10% DE-4% TiO_2 has better flame retardant effect than APP-10% DE composite filler, namely, there exists synergistic flame retardant effect between TiO_2 and APP which further delays and retards the combustion of paper. The flame retardant effect of APP-10% DE-4% TiO_2 occurs through the mechanisms of gas phase and condensed phase flame retardation. NH_3 and H_2O released by APP thermal decomposition dilute the concentration of oxygen and combustible gases, act as the gas phase flame retardants, on the other hand, esterification reaction between phosphoric acid and polyphosphoric generated by APP thermal decomposition and cellulose promotes the dehydration and char forming[15]. As a heat-resistant filler, TiO_2 can precipitate or adhere to the surface of char layer during combustion, cut off the spread of flame and block the conduction of heat, thereby delaying the combustion and reduce the HRR and THR.

TTI of paper loading APP-10% DE-4% TiO_2 is 27 s, which is obviously longer than that of base paper and paper loading APP-10% DE, so the addition of APP-10% DE-4% TiO_2 improve the security of filled paper. Fire performance index (FPI) is defined as the ratio of TTI to PHRR, and is usually used to predict whether a material can easily develop drastic combustion after ignition. The higher the PFI, the better fire resistance[10,16]. The FPI of paper loading APP-10% DE-4% TiO_2 is 0.91 sm^2/kW, which is 3.73 and 1.62 times higher than that of base paper and paper loading APP-10% DE. From the view of FPI, synergistic effect of TiO_2 and APP postpones flashover of filled paper and further decreases its fire risk.

Mass loss (ML) is also an important parameter to express the flammability of a material. Table 1 shows that paper loading APP-10% DE-4% TiO_2 has lower ML (68.62%) than base paper (99.64%) and paper loading APP-10% DE (75.10%), namely, paper loading APP-10% DE-4% TiO_2 has better char forming, and condensed phase char forming is the main flame retardant mechanism.

Rate of smoke release (RSR) and total smoke release (TSR)

RSR and TSR of paper loading APP-10% DE and APP-10% DE-4% TiO_2 are shown in Fig.5 and Fig.6.

Fig.5 show that the peak rate of smoke release of paper loading APP-10% DE-4% TiO_2 composite filler are 0.378 $m^2/m^2 \cdot s$, which is 42.8% and 30.2% lower than that of base paper (0.662

m^2/m^2s) and paper loading APP-10% DE (0.542 m^2/m^2s). And it can be seen from Fig.6 that the total smoke release of paper loading APP-10% DE-4% TiO_2 is 7.93 m^2/m^2, 41.0% and 22.4% lower than that of base paper (13.45 m^2/m^2) and paper loading APP-10% DE (10.22 m^2/m^2).These data indicate that TiO_2 has significant smoke suppression effect. On one hand, TiO_2 can form dense protective layer on the surface of paper, thereby reducing paper combustion and the release of smoke. On the other hand, nano-TiO_2 has high specific surface area, so it can adsorb part of the smoke and toxic gases. Although APP-10% DE composite filler has good flame retardant effect, its smoke release cannot be ignored, the addition of TiO_2 can effectively solve the problem.

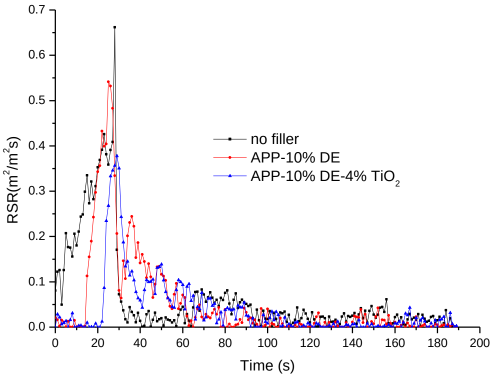

Fig.5. RSR of base paper and paper loading composite fillers

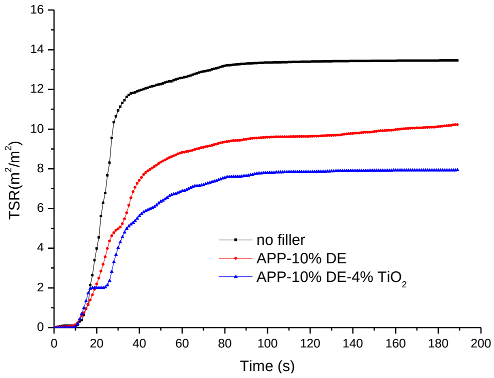

Fig.6. TSR of base paper and paper loading composite fillers

Smoke toxicity

CO is the most common toxic gas in fire, and it is generated by the incomplete combustion of materials. CO_2 itself is nontoxic, but it would be injurious to people by lowering the consistency of O_2 in air. The production rate of CO (COP) and CO_2 (CO_2P) of base paper, paper loading APP-10% DE and APP-10% DE-4% TiO_2 composite fillers are shown in Fig.7 and Fig.8, and the smoke toxicity data are shown in Table 2.

Fig.7 and Table 2 show that the peak COP of paper loading APP-10% DE-4% TiO_2 is lower than that of base paper, however, the CO production of paper loading APP-10% DE-4% TiO_2 is higher than that of base paper. Base paper without flame retardants has fast burning speed and complete burning, so it has higher peak COP and lower CO production. The peak COP and CO production of paper loading APP-10% DE-4% TiO_2 are both lower than that of paper loading

APP-10% DE, that is, the addition of nano-TiO_2 suppresses the production of CO. It because that synergistic effect of nano-TiO_2 and APP leads to good condensed phase flame retardation, which improves the carbonized degree of paper fibers and prevents combustibles from volatilization. Meanwhile, nano-TiO_2 with high specific surface area also has good adsorption for CO.

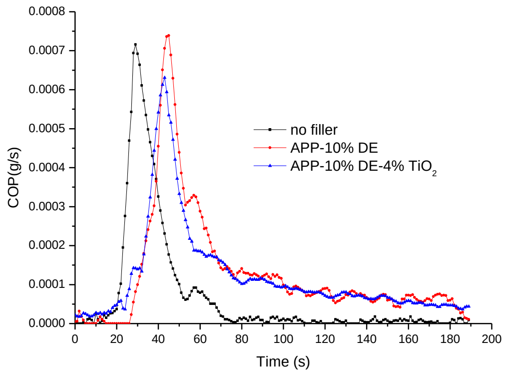

Fig.7. COP of base paper and paper loading composite fillers

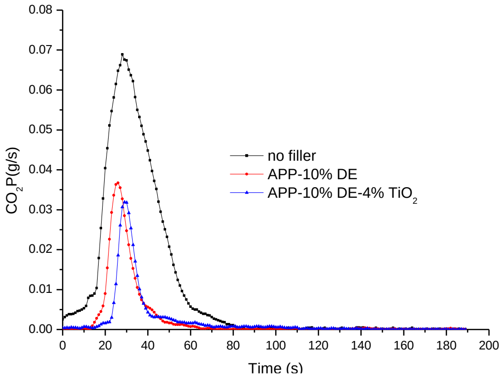

Fig.8. CO_2P of base paper and paper loading composite fillers

Table 2 Smoke toxicity data of base paper and paper loading composite fillers

Samples	Base paper	APP-10% DE	APP-10% DE-4% TiO_2
Peak COP(g/s)	0.000716	0.000739	0.000631
CO production (g)	0.0354	0.0582	0.0477
Peak CO_2P (g/s)	0.0521	0.0367	0.0319
CO_2 production (g)	1.3851	0.6591	0.5352

Fig.8 shows that the curves of CO_2P are similar to that of HRR. Table 2 shows that the CO_2P and total CO_2 production of paper loading APP-10% DE-4% TiO_2 are significantly lower than that of base paper and paper loading APP-10% DE, because the addition of APP-10% DE-4% TiO_2 improves the char forming and flame retardant effect and reduce the volatilization of combustibles and the release of CO_2, moreover, TiO_2 also acts as CO_2 adsorbent.

Morphology of combustion residues

Photos of the residues after cone calorimeter tests were taken by digital camera and are shown in Fig. 9. It shows that little residue is retained after the combustion of base paper and there is hardly shaped char layer, however, paper loading APP-10% DE and APP-10% DE-4% TiO_2 turn into complete char layer after cone calorimeter tests, that is, composite fillers play an important role on condensed phase flame retardation of filler paper.

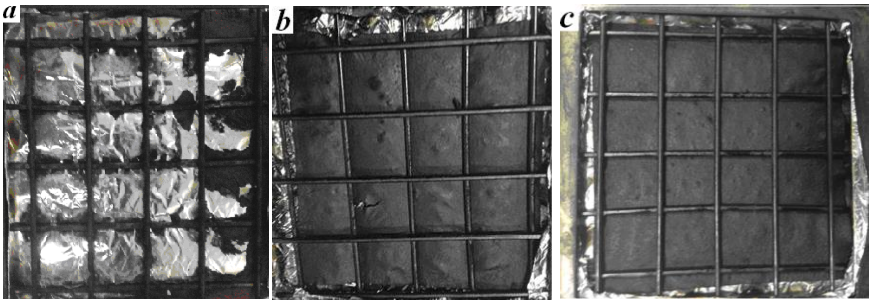

Fig.9. Digital photos of the combustion residues of (a) base paper (b) paper loading APP-10% DE and (c) paper loading APP-10% DE-4% TiO_2

The residual char layer of paper loading APP-10% DE (Fig.9 b) is relatively loose and weak, and has some breakages and bulges on it, while the residual char layer of paper loading APP-10% DE-4% TiO_2 (Fig.9 c) is more compact and has almost no breakage and bulge. The addition of nano-TiO_2 helps filled paper to form more stable and stronger char layer which can effectively withstand gasshock and intumescence during combustion process, and the char layer of this structure is more conducive to improve its heat insulation and oxygen isolation and improve the overall flame retardant and smoke suppression performance of filled paper. This is mainly because that TiO_2 can react with phosphoric acid, metaphosphoric acid and pyphosphoric acid generated by APP thermal decomposition to form TiP_2O_7, which prevent them from volatilization. Nano-TiO_2 has good synergy with APP on char formation, and it can also form a dense protective layer to protect char layer from damage.

SEM images of combustion residues

SEM images of the residues of filled paper after cone calorimeter tests are shown in Fig. 10. The char residue of paper loading APP-10% DE composite filler (Fig.10 a) retains complete fibrous network and has apparent fiber skeleton, but part of the fibers change into flat char layer with some longitudinal fractures. The char residue of paper loading APP-10% DE-4% TiO_2 (Fig. 10b) also has complete fiber texture, however, compared with that of paper loading APP-10% DE, apart from some filler particles on the surface of char layer, there is no apparent fiber breakage and longitudinal crack. That is, the existence of nano-TiO_2 plays a role in maintaining fibers integrity during carbonization process, improves strength and reduces deformation of the char layer, thus improving the char forming and flame retardant effect of filled paper.

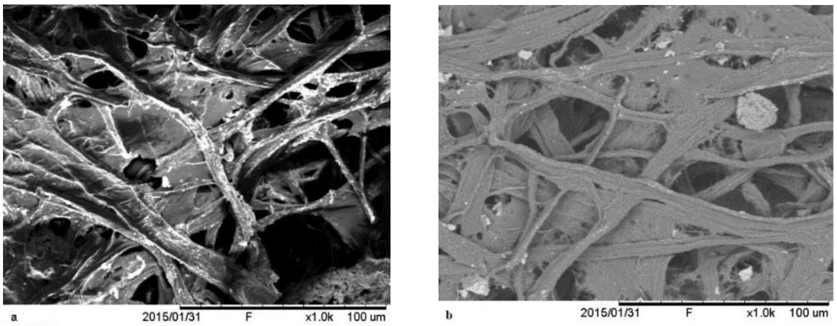

Fig.10. SEM images of the residues of paper after cone calorimeter tests (a)loading APP-10% DE (b) loading APP-10% DE-4% TiO_2

4. Conclusions

APP-10% DE-TiO_2 composite filler has the best flame retardant effect at the same filler loading when the amount of TiO_2 is 4%. TiO_2 reacts with APP decomposition products and restrains their volatilization at the second mass loss step, thereby reducing the mass loss of the composite filler system at high temperature. The addition of nano-TiO_2 in composite filler reduces the heat release rate, smoke release and smoke toxicity of the filled paper, prolongs the time to ignition, and decreases the fire risk of the filled paper. Synergistic effects between TiO_2 and APP in composite filler impart excellent flame retardancy and smoke suppression to the filled paper. APP-10% DE-4% TiO_2 composite filler plays an important role in condensed phase flame retardation and paper loading APP-10% DE-4% TiO_2 composite filler turns into more compact and stronger char layer after cone calorimeter test, without fiber breakage and longitudinal crack.

Acknowledgements

This work was supported by Zhejiang Provincial Key Lab for Chem & Bio Processing Technology of Farm Products and Zhejiang Provincial Collaborative Innovation Center of Agricutural Biological Resources Biochemical Manufacturing (No.2016KF0031).

References

[1]D.H. Rie, S.W. Moon, K.B. Lim, J. Therm. Anal. Calorim. **107**, 535(2012).
[2] H.S. Yang, D.J. Kim, H.J. Kim, J. Fire. Sci. **20**, 505(2002).
[3] I. Simkovic, R. H. White, A. M. Fuller, J. Therm. Anal. Calorim. **107**, 519(2012).
[4]L.Z. Sha, K. F. Chen, Bioresources. **9**, 3104(2014).
[5] L.Z. Sha, K. F. Chen, J. Therm. Anal. Calorim. **123**, 339(2016).
[6]R.G. Gann, V. Babrauskas, R.D. Peacock, J.R. Hall, Fire. Mater. **18**, 193(1994).
[7]B. Friederich, A. Laachachi, M. Ferriol, M. Cochez , R.Sonnier, Polym. Degrad. Stab. **97**, 2154(2012).
[8]N. Cinausero, N.Azema, J.M.Lopez-Cuesta, M.Cochez, M.Ferriol, Polym. Degrad.Stab. **96**,1445(2011).
[9] M.Z. Pan, C.T. Mei, J. Du, G.C. Li, Composites: Part A.**66**,128(2014).
[10]X.L. Chen, Y.F. Jiang, J.B. Liu, C.M. Jiao, Y. Qian, S.X. Li, J. Therm. Anal. Calorim. **120**, 1493(2015)
[11]A. Laachachi, M. Cochez, E. Leroy, P. Gaudon, M. Ferriol, J.M. Lopez-Cuesta, Polym. Adv. Technol. **17**, 327(2006).
[12]ASTM D2863-2013. ASTM International, West Conshohocken, PA (2013).
[13]ASTM E1354-16a. ASTM International, West Conshohocken, PA (2016).
[14] J.W. Gu, G.C. Zhang, S.L. Dong, Q.Y. Zhang, J. Kong, Surf. Coat.Technol. **201**, 7835(2007).
[15] J.B. Guo, M. He, Q.F. Li, J. Yu, S.H. Qin, J. Appl. Polym. Sci. **129**, 2063(2013).
[16] B. Schartel, T.R. Hull, Fire. Mater. **31**, 327(2007).