

PREPARATION OF FLAME RETARDANT AND SMOKE SUPPRESSION PAPER USING AMMONIUM POLYPHOSPHATE (APP)-DIATOMITE AS FILLER



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Abstract :

In situ polymerization was used to prepare ammonium polyphosphate (APP)-diatomite (DE) composite fillers, and flame retardant paper sheets were prepared by adding the composite fillers to paper stock. Properties of the composite fillers were investigated by XRD, FTIR and TGA, and flame retardance and smoke suppression of the filled paper were studied by cone calorimeter. Results show that composite fillers reduce peak heat release rate (PHRR), total heat release (THR) and mass loss rate (MLR) of paper, and promote its char-forming. The rate of smoke release (RSR) and total smoke release (TSR) of paper loading composite fillers are lower than base paper and paper loading only APP, and production rate of CO is lower than paper loading only APP. Among all samples, paper loading APP-10% DE composite filler has the lowest PHRR, THR and MLR, the longest time to ignition (TTI), thus has the best fire safety and flame retardant effect.

Keywords: Ammonium Polyphosphate-diatomite Composite Filler; Flame Retardant Paper; Cone Calorimeter; Flame Retardance, Smoke Suppression

INTRODUCTION :

Paper is mainly made from plant fibers which are flammable materials, however, flame retardance and smoke suppression are desirable for many paper products, such as auto filter, building materials, and decoration materials. Therefore, plant fiber flame retardant paper is a research hotspot in the field of specialty paper (Rie et al., 2012; Yang et al., 2002; Simkovic et al., 2012; Nassar et al., 1999). Impregnation, surface coating and addition of flame retardants to paper pulp are commonly used to manufacture flame retardant paper. Unfortunately, impregnation usually decreases the paper strength, dimensional stability and

moisture resistance, and coating contains combustible starch and latexes, which limit the efficiency of the flame retardant. Loading inorganic flame retardants (such as aluminium hydroxide and magnesium hydroxide) into paper stock is an easy way to produce flame retardant paper, however, its many disadvantages (e.g. high filler loading requirement, low flame retardant efficiency, adverse impact on the physical properties of paper) have greatly limited its application (Shen et al., 2011; Wang et al., 2012).

Ammonium polyphosphate (APP) is a kind of efficient halogen-free inorganic flame retardant containing phosphorus and nitrogen, which is widely used as

flame retardant in organic matter, coating, wood and fiber materials (Guo et al., 2013; Tian et al., 2013; Fan et al., 2013; Garcia et al., 2009; Zhang et al., 2013). However, APP dissolves easily in water due to its moisture absorption and hydrophilicity, if it is used as paper filler alone, part of the APP will be dissolved in water during papermaking process, thus reduces the filler retention in paper and affects the flame retardant property of paper (Lewin et al., 2005; Zhang and Wang, 2001). Diatomite (DE) is a kind of non-metallic mineral with porous structure, which is characterized by a large specific surface area and strong adsorption, and it is usually used as paper filler for its good adsorption, rich resources and low price

(Liu et al., 2013). To make full use of the advantages of APP and diatomite, and develop a high-efficiency composite flame retardant fillers, in this study, APP-DE composite fillers were prepared via in situ polymerization with diatomite as the carrier and phosphoric acid and urea as the reactants. The composite fillers were characterized by X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR) and thermogravimetry analysis (TGA), and their effects on flame retardance and smoke suppression of the filled paper were investigated by using the cone calorimeter.

EXPERIMENTAL

Materials

Phosphoric acid (85%, analytically pure) and urea (analytically pure) were supplied by Shanghai Lingfeng Chemical Reagent Co. Ltd, and diatomite (DE, chemically pure) was obtained from Chinasun Specialty Products Co. Ltd. Softwood pulp and hardwood pulp were procured from Chile (Arauco) and Brazil (Cenibra), respectively. Cationic polyacrylamide (CPAM) was obtained from NALCO (Shanghai) Trading Co. Ltd and silica sol was supplied by Suzhou Tianma Specialty Chemicals Co. Ltd.

Preparation of APP-DE Composite Fillers and Flame Retardant Paper

A certain amount of phosphoric acid was poured into a three-necked flask and a gas outlet was connected to the flask, it was stirred and heated to 70°C in an oil bath, then a certain amount of urea was added in the flask. The mixture was heated to 130°C at the heating rate of 2~3°C/min, then diatomite which is equivalent to 5%, 10%, 15%, 20% and 25% of the mass of the generated APP was added, respectively. The temperature was kept at 130°C for 15~30 min, then the product was poured into a tray and placed in an oven to solidify at the temperature of 210°C for 2 hr. Finally, the solidified materials were ground to obtain APP-DE composite fillers with different compositions, which were designated as APP-5% DE, APP-

10% DE, APP-15% DE, APP-20% DE and APP-25% DE, respectively. If no DE is added, the pure APP is prepared.

Softwood pulp was beaten to about 40°SR and hardwood pulp was beaten to about 37°SR using a Valley beater. 25% by weight of softwood pulp and 75% by weight of hardwood pulp were mixed and disintegrated in a standard fiber disintegrator to form uniform fiber suspension, then, 0.2% by weight of CPAM and 0.3% by weight of silica sol were added into the fiber suspension as the dual retention aid and stirred well, finally, a certain amount of composite filler was added into the fiber suspension, and paper sheets of 100 g/m² were formed on a standard sheet former, pressed on a presser (LABTECH400-1) at the pressure of 245 kPa for 5 min and dried on a rotary drum dryer.

Characterization

X-ray diffraction (XRD) patterns of the fillers were recorded at room temperature on a Bruker D8 ADVANCE X-ray diffractometer (Bruker, Germany) using Cu Ka radiation ($\lambda_{\text{Cu Ka}}=1.5418 \text{ \AA}$, 40kV, 40mA) and Ni filter in the 2θ range of 5°-60°. The scanning step was 0.02° and the scanning rate was 0.1 s per step. Fourier transform infrared spectra (FTIR) of the fillers were recorded with a FTIR-8400S spectrometer (Shimadzu, Japan) in the range of 400-4000 cm⁻¹. The samples were prepared with KBr pellets. Thermogravimetry analysis (TGA) of the fillers was performed on a STA 449 F3 TGA thermal analyzer (Netzsch, Germany) at a heating rate of 10°C.min⁻¹ under nitrogen atmosphere (at a flow rate of 50 ml.min⁻¹), and the sample mass used in the thermal analysis was 10 mg.

The cone calorimeter tests of the paper samples were carried out with a FTT2000 cone calorimeter (FTT, England) in accordance with the procedures in ASTM international standard method E1354 (ASTM 2004 E 1353-04a). The samples were 100 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 30 kW/m², and the data scans were taken every second. The distance between the bottom surface of the cone heater and the top of the specimen was adjusted to 25 mm as specified in the standard.

Results and Discussion

Characteristics of the APP-DE Composite Fillers

The characteristic diffraction peak of APP-I appears at the 2θ of 14.82°, and the characteristic diffraction peak of diatomite appears at the 2θ of 21.86° (Sun et al., 2004; Manevich et al., 2012; Ma et al., 2014). XRD patterns of the APP-DE composite fillers are shown in Fig.1. The position of the maximum intensity diffraction peak of APP-DE composite fillers is consistent with that of APP-I, indicating that in situ polymerization of APP and diatomite has barely changed the crystal form of APP. However, the diffraction peak intensity is weakened and a small peak occurs at near the 2θ of 21.86°. It can be found that the intensity of the diffraction peak appearing at the 2θ of 21.86° gradually increased and the intensity of the diffraction peak appearing at the 2θ of 14.82° gradually decreased with the increase of the fraction of diatomite in APP-DE composite fillers.

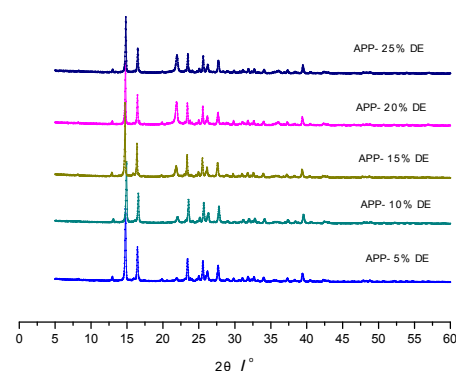


Fig.1. XRD patterns of APP-DE composite fillers

Diatomite has adsorption peaks at 1088 cm⁻¹ and 476 cm⁻¹, which are ascribed to the adsorption of Si-O-Si bond, and APP-I has absorption peaks at 760 cm⁻¹, 680 cm⁻¹ and 600 cm⁻¹, which are

assigned to the stretching vibration of O=P-O groups, -OH groups and O-P-O groups, respectively (Liu et al., 2010; Rangsiwatananon et al., 2008). Fig.2 presents the FTIR spectra of APP-DE composite fillers with different composition. The peaks near 1070 cm⁻¹ and 492 cm⁻¹ are the adsorption peak of Si-O-Si, showing a corresponding displacement compared with that of diatomite. The peaks near 798 cm⁻¹, 681 cm⁻¹ and 600 cm⁻¹ are the adsorption peaks of O=P-O, -OH and O-P-O, respectively. Compared with the characteristic adsorption peaks of APP-I, the existence of diatomite in APP-DE composite fillers resulted in a certain displacements, and these displacements resulted from the adsorption of P-O-Si group formed by combining P-OH on surface of APP with Si-OH on surface of diatomite (Sha and Chen, 2014).

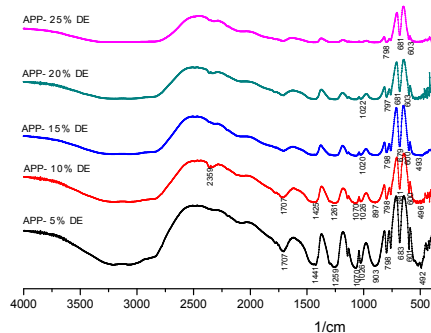


Fig. 2. FTIR spectra of APP-DE composite fillers

TG and DTG curves of APP-DE composite fillers are shown in Fig. 3 and Fig. 4, and the characteristic parameters are shown in Table 1.

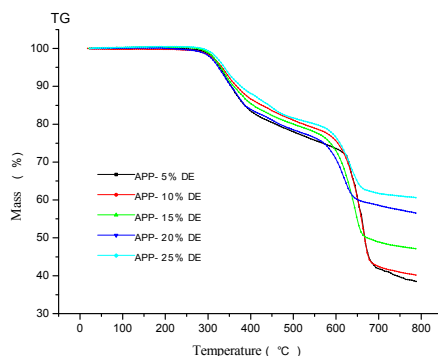


Fig. 3. TG curves of APP-DE composite fillers

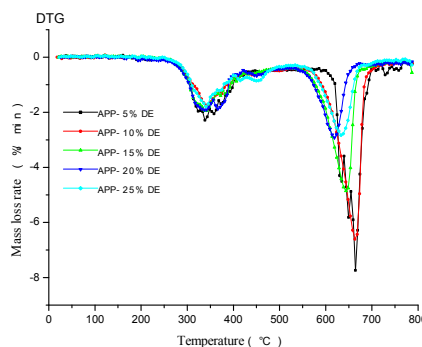


Fig. 4. DTG curves of APP-DE composite fillers

It can be seen from Fig. 3 that APP-DE composite fillers with different fraction of diatomite have similar TG curves,

containing two obvious mass loss steps at the temperature range from 20°C to 800°C. Before 300°C, the mass loss of APP-DE composite fillers is very little. The first main mass loss phase appears at the temperature range of 280~550°C, and the mass loss is mostly due to the release of NH₃ and H₂O and the cross linking of P-OH to form polyphosphoric acid (Camino et al., 1985). The second phase occurs at the temperature range of 550~750°C, which can be attributed to the release of phosphoric acid, polyphosphoric acid and metaphosphoric acid (Gu et al., 2007). Fig. 4 shows that DTG curves of all the APP-DE composite fillers have two peak values of mass loss rate, occurring at the temperature range of 300~400°C and 600~700°C, respectively. However, it can be found from TG and DTG curves that APP-DE fillers containing different fraction of diatomite have different residual mass at the end of the TGA and different mass loss and peak values of mass loss rate. It can be known from Table 1 that the residual mass of APP-DE composite fillers increase with the increase of diatomite content, and the mass loss, peak values of mass loss rate of APP-DE composite fillers show a descending trend with the increase of diatomite content. It indicates that the thermal stability of APP-DE composite fillers improve with the increase of diatomite content.

Table 1. TGA parameters of different APP-diatomite composite fillers

APP-DE composite fillers	Mass loss in the 1st phase (~550 °C) (%)	Peak values of mass loss rate in the 1st phase (%/min)	Mass loss in the 2nd phase (~750°C) (%)	Peak values of mass loss rate in the 2nd phase (%/min)	Residual mass (~787 °C) (%)
APP-5% DE	24.24	2.26	60.42	7.74	38.52
APP-10% DE	21.05	1.75	59.05	6.64	40.16
APP-15% DE	19.97	1.97	52.27	4.86	47.15
APP-20% DE	21.46	1.92	42.62	2.92	56.56
APP-25% DE	18.36	1.80	38.96	2.84	60.64

Cone calorimeter test of the filled paper

Based on the early limiting oxygen index (LOI) test (Sha and Chen, 2016), the LOI value of paper reached 25.2%, meets the basic requirement of fire resistance, as the loading of APP-10% DE filler was 20 wt %. Therefore, cone calorimeter tests were performed on different paper loading 20% filler to analyze their heat release rate (HRR), peak heat release rate (PHRR), total heat release (THR), time to ignition (TTI), time to PHRR (TTP), mass loss rate (MLR), rate of smoke release (RSR), total smoke release (TSR), smoke toxicity and so on.

Heat release rate (HRR)

HRR, especially PHRR is the most important parameter to evaluate fire safety of materials (Gilman et al., 2006; Gilman, 1999). HRR curves and data of base paper (paper with no filler) and paper with different fillers are shown in Fig. 5 and Table 2.

PHRR of base paper is 73.71 kW/m², and PHRR of paper with APP, APP-5% DE, APP-10% DE, APP-15% DE, APP-20% DE and APP-25% DE fillers are 31.5%, 27.8%, 44.4%, 25.3%, 23.3% and 17.1% lower than that of base paper, respectively. THR of base paper is 2.050 MJ/m², also higher than that of paper with different fillers. These demonstrate that paper loading APP and AP-DE composite fillers can effectively control the heat release of paper in the process of combustion, and make the combustion more gently. Because polyphosphoric acid generated by heating dehydration of APP is a strong dehydrating agent, and it can catalyze paper dehydration to form char through the esterification reaction of cellulose (Guo et al., 2013), on the other hand, it can also cover the surface of paper in the form of a noncombustible liquid membrane to inhibit combustion and reduce heat release. Along with the combustion, polyphosphoric acid further dehydrate to form metaphosphoric acid, which can further promote paper dehydration to

form char. Eventually, metaphosphoric acid can generate phosphorus oxide and cover the surface of paper to prevent it from burning. In addition, NH₃ and H₂O are generated during the process of APP decomposition, and they can dilute the concentration of O₂ and other flammable volatile gases in the combustion system, thereby reduce the peak heat release rate of paper. Among the samples, paper with APP-10% DE has the lowest PHRR and THR, meaning that it has the best flame retardant effect than other paper. Paper with APP is inferior to paper with APP-10% DE due to higher dissolution and loss of APP during papermaking process, and APP retention in paper loading pure APP is lower than in paper loading APP-10% DE, furthermore, there is a synergistic flame retardant effect between APP and diatomite (Chen et al., 2001). However, with the increase of diatomite content in composite fillers, APP content in composite fillers decrease, leading to a lower flame retardant effect, because APP is the effective flame retardant composition.

The ratio of TTI to PHRR is designated as fire performance index (FPI), which is often used to predict flashover potential of materials, and the ratio of PHRR to TTP is designated as fire growth index (FGI) (Wang and Zhang, 2013). FPI and FGI reflect the safety rank of samples directly, and materials having higher

FPI value and lower FGI value get higher safety rank (Schartel et al., 2007; Chen et al., 2007). TTI of base paper is 18 s, about 2 to 3 s shorter than that of paper loading APP and APP-DE fillers due to the earlier decomposition of APP. NH₃ and H₂O generated by APP thermal decomposition adsorb the heat and dilute the concentration of flammable gas in the test system, thus prolong the TTI and reduce the flammability of paper. After ignition, HRR of samples increase rapidly, and the TTP of base paper is 28 s, similar to that of paper loading APP and APP-DE composite fillers except paper loading APP-10% DE filler, which is 3 s longer than that of base paper. Among all the samples, paper loading APP-10% DE filler has the longest TTI, TTP and the lowest PHRR value, so it has the highest FPI value (0.561) and lowest FGI value (1.32), indicates that it gets relatively higher safety rank and is the safest one in fire.

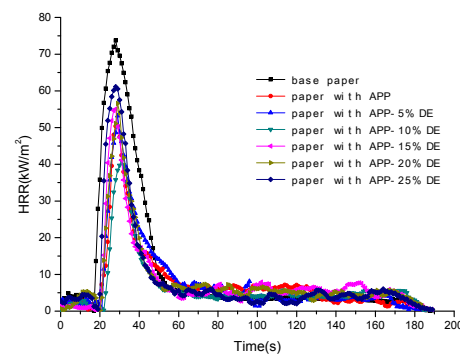


Fig. 5. HRR of base paper and paper with APP and APP-diatomite composite fillers

Table 2. HRR data of base paper and paper with different fillers

Samples	Base paper	APP	APP-5% DE	APP-10% DE	APP-15% DE	APP-20% DE	APP-25% DE
PHRR (kW /m ²)	73.71	50.46	53.23	41.01	55.05	56.56	61.13
Mean HRR (kW /m ²)	12.87	7.75	7.81	6.42	8.04	8.22	8.68
THR (MJ /m ²)	2.050	1.436	1.463	1.223	1.498	1.531	1.564
TTI (s)	18	21	21	23	21	21	20
TTP (s)	28	29	29	31	28	29	28
FPI (s m ² /kW)	0.244	0.416	0.395	0.561	0.381	0.371	0.327
FGI (kW/ m ² ·s)	2.63	1.74	1.80	1.32	1.97	1.95	2.18

Mass loss rate (MLR)

MLR is the thermal decomposition rate of materials under a certain heat radiation intensity and it reflects the pyrolysis, volatilization and burning degree of materials. Table 3 shows MLR and residue data of base paper and paper loading different APP-DE composite fillers.

Table 3. MLR and residue data of base paper and paper with different fillers

Samples	Base paper	APP	APP-5% DE	APP-10% DE	APP-15% DE	APP-20% DE	APP-25% DE
Peak MLR (g/s)	0.40	0.21	0.22	0.17	0.22	0.24	0.26
Mean MLR (mg/s)	5.30	4.39	4.35	3.96	4.43	4.40	4.34
Residue (mg)	3.6	176.7	178.2	249.0	166.2	170.7	179.9
ML (%)	99.6	82.3	82.2	75.1	83.4	82.9	82.0

Peak MLR of and mean MLR of base paper are 0.40 g/s and 5.30 mg/s, and the residue of base paper after combustion is only 3.6 mg, and the mass loss of base paper reaches 99.6%. After loading different fillers, the peak MLR of and mean MLR of paper are decreased obviously, and the residues of paper are increased significantly, so it can be said that loading APP and APP-DE composite fillers can restrain paper burning and improve char forming. Among these samples, the residue of paper with APP-10% DE composite filler reaches 249.0 mg, further higher than that of other samples, and its mass loss is 75.1%, the lowest one of all the samples, that is, APP-10% DE composite filler has the best flame retardant effect on paper.

Rate of smoke release (RSR)

Smoke performance of flame retardant material during combustion plays an important factor concerning fire safety, heavy smoke can hinder escape and toxic gases act as one killer during the fire hazard (Jiao et al., 2015). RSR

is an important parameter to evaluate smoke releasing property of materials, and the RSR curves and data of paper samples are shown in Fig. 6 and Table 4. It can be found that paper loading only APP has two obvious peaks of RSR and its peak value is 0.785 m²/m²s, while base paper and paper loading APP-10% DE composite filler have a peak value of 0.662 m²/m²s and 0.542 m²/m²s respectively, which are lower than that of paper loading only APP. Peak RSR of the other samples of paper are lower than above three samples and have a slight difference with each other. The change of TSR of samples is consistent with that of RSR. RSR and TSR of paper loading APP are larger than other samples due to the generation of NH₃, water vapor and other non-flammable gases after thermal decomposition of APP, and these gases mix with volatiles formed by paper burning to form the main ingredients of smoke. In addition, non-flammable gases generated by APP decomposition cause incomplete combustion of volatile combustible matter, or make them escape

with the hot air before being fully burned, thus result in a high RSR and a large amount of smoke. Therefore, pure APP is not suitable to be used as flame-retardant filler in paper. RSR and TSR of paper loading APP-DE composite fillers are lower than that of paper loading APP and base paper, and the second peak of their RSR curves become small or disappear due to the existence of diatomite in composite fillers, which is a porous non-metallic mineral with large specific surface area and strong adsorbability. Diatomite in composite fillers can adsorb the smoke released during combustion and reduce the RSR and TSR of samples.

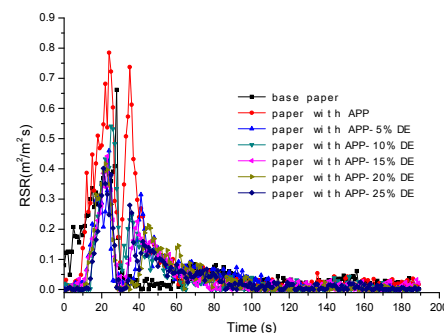


Fig. 6. RSR of base paper and paper with APP and APP-DE composite fillers

Table 4. RSR and TSR of base paper and APP-diatomite composite fillers

Samples	Base paper	APP	APP-5% DE	APP-10% DE	APP-15% DE	APP-20% DE	APP-25% DE
Peak RSR (m ² /m ² s)	0.662	0.785	0.460	0.542	0.442	0.416	0.402
TSR (m ² /m ²)	13.453	18.309	9.533	10.218	9.303	8.929	8.478

Smoke Toxicity

The production rate of toxic gases is also an important factor to evaluate fire risk. CO is the most common toxic gas in fire, and it is generated by the incomplete combustion of materials. CO₂ itself is nontoxic, but it would be injurious to people by lowering the consistency of O₂ in air. The production rate of CO (COP) and CO₂ (CO₂P) are measured by cone calorimeter and are shown in Fig. 7, Fig. 8 and Table 5. It can be seen from Fig. 7 and Table 5 that COP of paper with only APP has the highest COP peak (0.902 mg/s) and has two peaks which are all higher than that of base paper and paper with other fillers, and this indicates that toxic gas generated

by paper with only APP is more than other samples. The main reason is that phosphoric acid generated by APP thermal decomposition dewater paper fiber, and phosphoric acid can further form solid polyphosphoric acid or polymetaphosphate at high temperature, which covers the surface of paper fiber and promotes the carbonization of paper fiber, resulting in incomplete oxidation of pyrolysis products. Meanwhile, NH_3 and water vapor generated by APP decomposition have flame retardant effect in gas phase and inhibit complete combustion of gaseous fiber decomposition products, thereby increasing the production rate of CO. COP of base paper is 0.716 mg/s, 20.6% lower than that of paper with only APP. COP of paper with other fillers are lower than that of paper with only APP due to the existence of diatomite, which can adsorb the released CO.

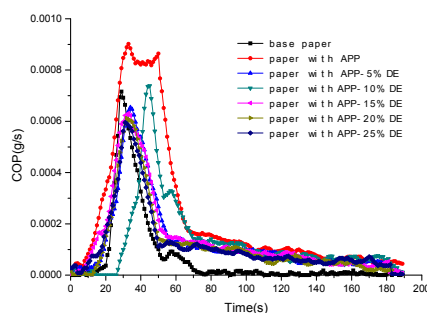


Fig. 7. COP of base paper and paper with APP and APP-diatomite composite fillers

It can also be seen from Fig. 7 that most of CO is produced at the early stage of combustion for base paper, and almost no CO is produced after 80s, that is, the release of CO mainly happens at the stage of flame combustion. However, COP of paper loading APP and APP-DE composite fillers are higher than that of base paper at the late combustion stage, because paper loading flame retardant fillers are carbonized and the late

combustion mainly happens at the char layer, which produces CO as the direct product.

CO_2 P curves in Fig. 8 are similar to HRR curves in Fig. 5. Peak value of CO_2 P of base paper is 0.052 g/s, significantly higher than that of paper with APP and APP-DE composite fillers. A large amount CO_2 is released by base paper due to its full combustion, and APP-DE composite fillers can effectively suppress the production of CO_2 .

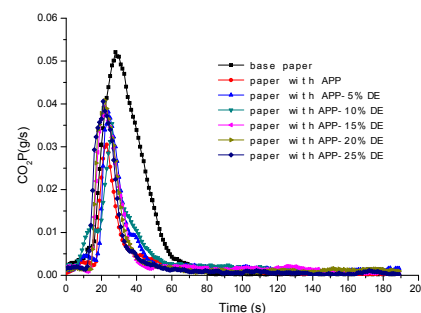


Fig. 8. CO_2 P of base paper and paper with APP and APP-diatomite composite fillers

Table 5. COP and CO_2 P of base paper and APP-diatomite composite fillers

Samples	Base paper	APP	APP-5% DE	APP-10% DE	APP-15% DE	APP-20% DE	APP-25% DE
Peak COP (mg/s)	0.716	0.902	0.654	0.739	0.631	0.612	0.595
Peak CO_2 P (g/s)	0.052	0.031	0.038	0.035	0.039	0.041	0.041

CONCLUSIONS

In situ polymerization of APP and DE changes the X-ray diffraction peak intensity and characteristic IR absorption peak of APP, that is, changes the structure of APP. Thermostability of APP-DE composite fillers increase with the increase of diatomite content.

Paper loading APP and APP-DE composite fillers have lower PHRR, THR and higher residue weight than base paper, that is, APP

and APP-DE composite fillers improve the char forming and flame retardance of paper. Among these fillers, APP-10% DE has the best effect on paper.

The RSR peak value and COP of paper loading APP-DE composite fillers are lower than that of paper loading only APP, and COP decreases with the increase of diatomite content in composite fillers. CO_2 P of base paper is higher than that of paper loading APP and APP-DE composite fillers, and APP-DE

composite filler can effectively suppress the production of CO_2 .

ACKNOWLEDGEMENTS

This work was supported by Key Laboratory of Recycling and Eco-treatment of Waste Biomass of Zhejiang Province (No. 2016REWB33), Zhejiang Provincial Key Lab for Chem & Bio Processing Technology of Farm Products and Zhejiang Provincial Collaborative Innovation Center of Agricultural Biological Resources Biochemical Manufacturing (No.2016KF0031).

REFERENCES

1. Rie, D.H., Moon, S.W., Lim, K.B. J Therm Anal Calorim 107(2): 535-539(2012).
2. Yang, H.S., Kim, D.J., Kim, H.J. J Fire Sci 20(6): 505-517 (2002).
3. Simkovic, I., White, R.H. and Fuller, A. M. J Therm Anal Calorim 107(2): 519-526(2012).
4. Nassar, M.M., Fadali, O.A., Khattab, M. A., et al. Fire Mater 23(3): 125-129 (1999).
5. Shen, J., Song, Z.Q., Qian, X.R., et al. Ind. Eng. Chem. Res 50(2): 661-666(2011).
6. Wang, S.L., Huang, J.L., Chen, F.S. BioResources 7(1): 997-1007(2012).

7. Guo, J.B., He, M., Li, Q.F., et al. *J Appl Polym Sci* 129(4): 2063-2069 (2013).
8. Tian, N.N., Wen, X., Jiang, Z.W., et al. *Ind Eng Chem Res* 52(32): 10905-10915(2013).
9. Fan, F.Q., Xia, Z.B., Li, Q.Y., et al. *Prog Organ Coatings* 76(5): 844-851(2013).
10. García, M., Hidalgo, J., Garmendia, I., et al. *Composite: Part A* 40(11): 1772-1776(2009).
11. Zhang, T., Yan, H.Q., Wang, L.L., et al. *Ind Eng Chem Res* 52(18): 6138-6146(2013).
12. Lewin, M. *Polym Degrad Stabil* 88(1): 13-19(2005).
13. Zhang, Z. M.; Wang, S. F. *Fire. Sc. Technol.* 2001(4): 42-43(2001).
14. Liu, J., Wang, H.L., Lü, C.X., et al. *Chem Res Chinese Univ* 29(3): 445-448(2013).
15. "Heat and visible smoke release rates for materials and products using an oxygen consumption calorimeter" ASTM Standard 2004.E1353-04a.
16. Sun, C.Y., Luo, J.Y., Su, X.L. *J. Northeast. Forestry. Univ.* 32(1):94-95(2004).
17. Manevich, V. E.; Subbotin, R. K.; Nikiforov, E. A.; Senik, N. A.; Meshkov, A. V. *Glass Ceram.* 69(5-6), 168-172(2012).
18. Ma, H. N., Wang, B. M., Zhao, L., Yuna, Dawei. *J. Wuhan. Univ. Technol-Mater. Sci. Ed.* 29(5): 877-884(2014).
19. Liu, G. S., Liu, X. C., Yu, J. G. *Ind. Eng. Chem. Res.* 49(12): 5523-5529(2010).
20. Rangsiwatananon, K., Chaisena, A., Thongkasam, C. J. *Porous. Mater.* 15(5): 499-505(2008).
21. Sha, L. Z., Chen, K. F. *BioResources.* 9(2): 3104-3116(2014).
22. Camino, G., Costa, L., Trossarelli, L. *Polym. Degrad. Stabil.* 12(3): 203-211(1985).
23. Gu, J. W., Zhang, G. C., Dong, S. L., et al. *Surf. Coat. Tech.* 201(18):7835-7841(2007).
24. Sha, L. Z., Chen, K. F. *J. Therm. Anal. Calorim.* 123(1): 339-347(2016).
25. Gilman, J.W., Jakson, C.L., Morgan, A.B., et al. *Chem. Mater.* 12(7):1866-1873 (2000).
26. Gilman, J. W. *Appl. Clay. Sci.* 15(1): 31-49(1999).
27. Guo, J. B.; He, M.; Li, Q. F.; Yu, J.; Qin, S.H. *J. Appl. Polym. Sci.* 129(4):2063-2069(2013).
28. Chen, G. C.; He, H.; Lu, Z. M.; et al. *China Plast Ind.* 39(4): 99-102(2011)
29. Wang, Y.; Zhang, J. J. *Hazard. Mater.* 246-247: 103-109(2013).
30. Schartel, B.; Hull, T. R. *Fire. Mater.* 31(5): 327-354(2007).
31. Chen, X. L.; Hu, Y.; Jiao, C. M.; Song, L. *Polym. Degrad. Stab.* 92(6): 1141-1150(2007).
32. Jiao, C. M.; Zhao, X. L.; Song, W. K.; Chen, X. L. *J. Therm. Anal. Calorim.* 120(2): 1173-1181(2015).