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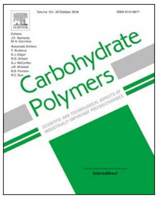

Acid-base synergistic flame retardant wood pulp paper with high thermal stability

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ABSTRACT

Acid-catalytic degradation caused by acid source flame retardants is the main reason for a decline in thermal stability of flame-retarded lignocellulosic materials. In the present research, a guanidine phosphate (GP)/borax (BX) flame retardant system based on acid-base synergistic interaction was designed and used in wood pulp paper (WPP) to solve this problem. Results showed that the treated WPP obtained good flame retardancy with a limiting oxygen index (LOI) value of 35.7%. As a basic flame retardant, borax could chemically combine with the acids released by guanidine phosphate, thus decreasing the acidity of the system in the initial heating stage. In this way, acid-catalytic degradation is greatly retarded on the lignocelluloses to improve thermal stability (the temperature of maximum degradation peak from 286 °C to 314 °C). Meanwhile, borax was also advantageous to form a denser and firmer condensed phase through reinforcement of the acid-base reaction product, borophosphates, allowing it to provide a protective barrier with higher quality.

1. Introduction

Lignocellulosic materials, which consist mainly of hemicellulose, lignin and cellulose, are among the most renewable and biodegradable resources on earth (de Andrade Neto, de Souza Cabral, de Oliveira, Torres, & Morandim-Giannetti, 2016; Parveen, Patra, & Upadhyayula, 2016; Peleteiro, Santos, Garrote, & Parajó, 2016; Pereira, Silveira, Dupree, & Skaf, 2017). Their applications in fields such as paper, film, packaging, coating, tissues, medicines and composite materials have increased in recent years (Fan, Chen, Yao, Sun, & Jin, 2017; Iyer, Zhang, & Torkelson, 2016; Iyer & Torkelson, 2015; Mohtar, Tengku Malim Busu, Md Noor, Shaari, & Mat, 2017; Zhang et al., 2017). Effective utilization of lignocellulosic materials not only reduces dependence on fossil resources but also benefits the protection of ecological environment. However, due to the intrinsic flammability of lignocellulosic materials, they can easily cause fire disasters (Kamali & Khodaparast, 2015; Lowden & Hull,2013). Accordingly, their flame-retardant modification is significant and important for those products with fire-proofing requirements.

In order to endow lignocellulosic materials with flame retardance, it is necessary to use various flame retardants (FRs) to treat them. Generally, acid source FRs have been widely used for lignocellulosic materials (Gaan & Sun, 2007; Mngomezulu, John, Jacobs, & Luyt, 2014; Nguyen, Chang, & Condon, 2014). Taking advantage of the catalytic mechanism of the released acids, the FRs could promote carbonization of lignocelluloses. With formation of the charring layer effectively isolating the heat, oxygen and flammable volatiles, self-extinguishment of the flaming materials occurs to protect inner lignocellulosic matrix.

However, an obvious shortcoming of acid source FRs is their acid-catalytic degradation effects. It is known that the produced acids from FRs have opposite influence on lignocelluloses at different temperature ranges when heated. At lower temperature range (generally 260–345 °C), the catalytic degradation effect is dominant, which can accelerate the decomposition of materials to release more flammable volatiles. It is clear that the catalytic degradation effect is detrimental to thermal stability and flame retardance. However, at higher temperature ranges (over 345 °C), the catalytic charring effect is more dominant, which is helpful to improve flame retardance.

Numerous previous investigations reflected the inherent features of acid source flame retardants. For example, Zhang etc., adopted a novel acid source flame retardant, ammonium salt of ethylene glycol diphosphoric acid (AEGDP) for cotton (Jia, Lu, Zhang, Liang, & Zhang, 2017). The result showed that the flame retardant indicated high efficiency to catalyze the dehydration of cotton to form chars, and the flame retardant cotton fabrics could achieve a limiting oxygen index (LOI) value as high as 41%. However, the acid-catalytic degradation effect made

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the thermal stability of cotton fabrics decreased by near 80 °C compared with the non-flame retardant sample. Similarly, Fang etc. (Fang et al., 2016) coated polyhexamethylene guanidine phosphate and ammonium polyphosphate in cotton fabric. The coated fabric also showed decreased thermal decomposition temperature due to the effect of acid generated by FRs. Obviously, this shortcoming greatly restricts the applications of flame retardant materials in heated environment. Therefore, obtaining excellent flame retardance while retaining good thermal stability is a real challenge for acid source flame retardant lignocellulosic materials.

Except acid source FRs, some alkaline ones, can be also used for lignocellulosic materials. Qu et al. (Qu, Wu, Wu, Xie, & Xu, 2011) impregnated wood with borax and found that borax formed a glassy protective layer that imparted flame retardant properties to the wood. Compared with acid source FRs, alkaline FRs generally have smaller negative influence on the thermal stability of lignocelluloses. However, much lower flame retardant efficiency and a high loading level are obvious shortcomings for this kind of FRs.

Historically, an acid-base system has received little investigation because it is generally recognized that a pair of acid-base FRs is adversarial, as their flame retardance can be counteracted by one another via acid-base neutralization. In fact, our previous investigation concerning magnesium hydroxide (MH)/9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) flame retardant epoxy resin, (Liao, Liu, Jiang, & Li, 2016) confirmed the antagonism effect: alkaline MH could easily react with H_3PO_4, the decomposition product from DOPO, and thus greatly consuming the charring catalyst. Resultantly, both the amount and quality of the chars decreased.

In this work, a pair of acid-base FRs including guanidine phosphate (GP) and borax (BX), was employed in wood pulp paper (WPP). BX could effectively control the acidity in the initial heating stage of WPP, thus decreasing the negative effect of catalytic degradation of released phosphorous acids on the lignocelluloses and remarkably enhancing thermal stability. However, it is exceptional that such acid-base system showed obvious synergism rather than antagonism generally recognized. It was found that the charring amount and quality was enhanced and better flame retardancy was achieved despite the consumption of the acid catalyst. Our following investigations revealed the corresponding mechanisms. It is believable that our research can provide valuable information for designing and preparing high performances, flame retardant lignocellulosic materials.

2. Experimental work

2.1. Material and regents

Wood pulp paper was supplied by Shengyi Technology Company (Shanxi, China), with a thickness of 0.30 mm and weight of 129 g/m^2; Guanidine phosphate (PubChem CID: 6452957) and borax (PubChem CID: 16211214) was purchased from Shanghai Macklin Biochemical Company (Shanghai, China).

2.2. Preparation of flame retardant WPP

GP/BX solutions with different mass ratios (total concentration of the solution: 7 wt%) were prepared by adding the FRs into deionized water with mechanical stirring. The resulting solutions were used to coat WPP samples with dimensions of 160 mm × 180 mm × 0.30 mm, and every sample had a fixed FR content (15 wt%) by controlling the coating mass of the solution. Finally, the flame retardant WPP samples were dried to a constant weight (9.41 ± 0.02 g) under vacuum for 24 h at 100 ° C.

2.3. Characterization

Vertical burning tests were performed with the HK HVR (HK Detection Equipment Co., Ltd, Zhuhai, China) instrument on samples with dimensions of 70 mm × 210 mm × 0.30 mm according to the TAPPI T461OS-79 testing procedure.

Limiting oxygen index tests were carried out on a digital display oxygen index instrument JF-3 (Nanjing Jiangning Analysis Instrument Co., Ltd, China) on samples with dimensions of 60 mm × 140 mm × 0.30 mm according to ASTM-D2863.

Thermal combustion properties were measured using a microscale combustion calorimeter (MCC; Fire Testing Technology Ltd, UK). The WPP samples (~5 mg) were heated to 700 °C at a heating rate of 1 °C/s under nitrogen. Afterwards, the volatile and anaerobic thermal degradation products were mixed with a gas stream containing 20% oxygen and 80% nitrogen and were placed into a combustion furnace heated to 900 °C.

Thermogravimetric analysis (TGA) tests were conducted on TGA Q50 (TA Instruments Co., Ltd, New Castle, DE, USA). ~8 mg samples were heated to 700 °C at a heating rate of 10 °C/min with a flow rate of 50 ml/min under nitrogen.

The pH tests were performed on a MIK-pH100 (Hangzhou Meacon Automation technology Co., ltd) instrument. WPP samples with the dimension of 50.0 mm × 50.0 mm × 0.3 mm were carbonized at different temperature (150, 200, 250, 300, 350, 400, 450 and 500 °C) for 5 min in a muffle furnace (Xiangtan Huanfeng instrument Co., ltd). The carbonized WPP samples were dipped into 20 ml deionized water and stirred, and the pH values were measured with a pH meter (pH value of deionized water: 6.8).

The surface morphologies of the WPP samples before and after carbonization (500 °C for 5 min) were observed using a scanning electronic microscope (SEM) (JSM 5900LV, JEOL Ltd., Tokyo, Japan). The samples were placed on a sample holder using conducting carbon cement and then coated with a thin layer of gold using a sputter coater.

Attenuated total reflectance-Fourier transform infrared spectra (ATR-FTIR) of the charring layers of WPP were recorded with a Nicolet 20SXB Infrared spectrometer.

X-ray photoelectron spectroscopy (XPS) measurements of char surface were performed on a Shimadzu/Kratos AXIS Ultra DLD multifunctional spectrometer (Manchester, UK). Photoelectrons were excited with monochromated Al Kα radiation. Detection was done with a delay-line detector (DLD) and a concentric hemispherical analyzer (CHA).

3. Results and discussion

3.1. Flammability properties

A vertical burning test and LOI measurement were first used to evaluate the flammability of the flame retardant WPP with different acid-base ratios. Fig. 1 shows the real combustion processes during the vertical flame test. The flame retardant mechanism of BX featured formation of a glassy coating, which held back gas diffusion and decomposition to combination water to lower combustion temperature. Although BX could quickly extinguish the burning WPP by limiting oxygen and heat supply, the BX-WPP sample remained smoldering after 150 s, and the LOI value was only 24.7% (Table 1), resulting in a flame retardant rating of B-2. By contrast, the acid source flame retardant GP showed much better flame retardancy, and it endowed WPP with 35.2% of LOI rating and a flame retardant rating of B-0. However, a great amount of smoke was observed during the burning of GP-WPP, which was in accordance with the results of other acid source flame retardant lignocellulosic materials (Li, Zhao, Zhang, & Zhao, 2016). According to the exhibited flame retardance and smoking phenomena, it could be concluded that the released acid by GP could effectively catalyze the dehydration and charring to effectively retard the flame. However, serious smoking resulted from the following two aspects: firstly, the decomposed products were quickly released due to acid-catalytic degradation effects on the paper; secondly, the formed chars were not dense and firm enough to withstand (Green, 1996), the shock of the