

Effects of Complex Flame Retardant on the Thermal Decomposition of Natural Fiber

Na Xiao, Xue Zheng, Shuping Song, and Junwen Pu *

Natural fiber is a renewable resource characterized by its low cost and environmental friendliness. However, flame retardant properties are one of the biggest limitations for the preparation of composite materials that need to be improved. In this work, a novel complex flame retardant consisting of aluminum hydroxide (ALH) and decabromine diphenyl oxide (PBDE) was proposed to inhibit the thermal decomposition. Flame-retarding paper was made from softwood pulp and complex flame retardant. The thermal properties of the flame retardants were studied using thermogravimetric analysis (TGA). The mechanical properties of paper treated at different temperatures were tested, while the surface characteristics of natural fiber were detected by a scanning electron microscope (SEM) and atomic force microscope (AFM); their specific surface areas were also measured. The optimum value of aluminum hydroxide to decabromine diphenyl oxide was 3 to 1, added at 70% based on dried natural fiber. It also had good flame retardant performance and mechanical properties at 200 °C for 5 min; meanwhile, the tensile index of the handsheet was 82.5 Nm/g, and the specific surface area was 0.414 m²/g.

Keywords: Natural fiber; Aluminum hydroxide (ALH); Decabromine diphenyl oxide (PBDE); Complex flame retardant; Thermal decomposition; Properties

Contact information: College of Material Science and Technology, Beijing Forestry University, Beijing, 100083, PR China; *Corresponding author: jwpu@bjfu.edu.cn

INTRODUCTION

Recently, environmental conservation has become an important research topic. The use of natural fiber in the preparation of composite materials has recently attracted much attention because of its low cost and environmental friendliness (Bhattacharya *et al.* 2008; Ku *et al.* 2011; Liu *et al.* 2006; Xie *et al.* 2010). As a natural polymer, the use of natural fiber offers environmental advantages such as reduced dependence on non-renewable sources (La Mantia and Morreale 2011), degradability, and suitability for combustion as part of a carbon-neutral cycle. Such superior environmental performance is an important factor for the increased future use of natural fiber composites. However, their waterproof, flame retardant, and mechanical properties need to be improved (Jang *et al.* 2000; Jang and Lee 2000; Jeecham *et al.* 2014; Kozłowski *et al.* 1999 ;)

Many papers require stability at high temperatures, *e.g.*, microwave paper, interleaving paper for stainless steel which must overcome high temperature between layers, fireproof paper as components of building materials, and paper friction materials (Hubbe *et al.* 2007; Mwaikambo and Ansell 2002). Under high temperatures, paper fibers will decompose. The decomposition of semi-cellulose and cellulose will cause the

deterioration of the paper strength and cause the physical properties of paper to worsen (George *et al.* 2001; John and Anandjiwala 2008; Rigolo and Woodhams 1992). The most widely used additive-type flame retardants are inorganic compounds, halogenated compounds, and phosphorous compounds (Rigolo and Woodhams 1992; Stark *et al.* 2010; Kozłowski *et al.* 2008; Schartel *et al.* 2003). In addition, boric acid, ammonium phosphates and borates, ammonium sulfate and chlorides, zinc chloride and borate, antimony oxide, sodium borate, and dicyandiamide have also been used as flame retardant additives (Laoutid *et al.* 2013; Sun *et al.* 2012; Chapple *et al.* 2010; Sain *et al.* 2004).

In this work, a novel complex flame retardant consisting of aluminum hydroxide (ALH) and decabromine diphenyl oxide was proposed to inhibit the thermal decay of natural fiber. The flame retarding paper was made from softwood pulp and complex retardant. The thermal properties of flame retardants were studied using thermogravimetric analysis (TGA). The mechanical properties of paper treated at different temperatures were tested and the specific surface areas were measured, while the surface characteristics of natural fibers were detected by a scanning electron microscope (SEM) and an atomic force microscope (AFM).

EXPERIMENTAL

Materials

Pulp

The softwood BSK larch (North America) pulp used in the laboratory trials was kindly supplied by Sichuan Ya'an Pulp Co. Ltd. (Sichuan, China). The initial moisture content was about 10%.

Complex flame retardant

The flame retardant was obtained in solid form. The $\text{Al}(\text{OH})_3$ was a white powder of density 2.42 g/cm^3 , and particle size 800 mesh. PBDE is white powder of $310 \text{ }^\circ\text{C}$ boiling point, $143 \text{ }^\circ\text{C}$ flash point, density 0.9327 g/cm^3 . The flame retardants were purchased from Shandong Sunrise Co., Ltd. (Shandong, China).

Methods

Complex flame retardant preparation

Aluminum hydroxide (ALH) and PBDE were dispersed within the water separately with the mixer H518 supplied from Messemer Company England. They were mixed together to form complex retardants, and added into the pulp. $\text{Al}(\text{OH})_3$ and PBDE were both dispersed to 10% concentration, and the final complex flame retardants with 10% concentration as well.

Preparation and heat treatment of handsheets

Pulp was prepared for 3 min with stirring rates of 1200 revolutions per minute. Test sheets were made from pulp by dewatering on a screen. These sheets were pressed at 0.35 MPa for 5 min and then dried on a plate dryer at $105 \text{ }^\circ\text{C}$ for 10 min. Eight test

sheets were prepared for each treatment. The test sheet grammage (mass per unit area) was 80 g/m², and all handsheets were conditioned according to TAPPI standard conditions before testing (TAPPI Test Method T402 2003). Then, the handsheet samples were treated at temperatures of 200, 250, or 280 °C.

Physical testing

Tensile values were determined according to TAPPI Test Method T 494 (2001). Tensile index strain was performed automatically using a QC 1000 tensile tester from Thwing-Albert Instrument Co. (Philadelphia, PA). An Elmendorf tearing tester, made by Thwing-Albert Instrument Co., was also used. All tests were carried out at 23 ± 1 °C and 50 ± 2% relative humidity (TAPPI Test Method T402 2003).

Thermogravimetric analysis

Data were obtained from 25 to 800 °C using a Netzsch TG209 Jupiter Thermal Analysis System (Germany) in a nitrogen atmosphere with a heating rate of 20 °C/min and a flow rate of 10 mL·min⁻¹.

Nitrogen absorption

The specific surface area of fibers was obtained from a Brunauer-Emmett-Teller (BET) analysis of nitrogen absorption isotherms using a Micromeritics ASAP-2420 (Norcross, GA). The total pore volume was obtained as the volume of absorbed nitrogen at a relative pressure approximating unity. A sample of 2.8 to 3.4 g was weighed, placed into sample tubes, and dried under a vacuum at 100 °C for 4 h. Measurements were made of absorption and desorption in a liquid nitrogen atmosphere and with liquid nitrogen flushing. Pressures of 0.05 < p/p_0 < 0.30 were used to calculate the specific surface area for a monomolecular covering (Sing 1982).

Scanning electron microscopy

Handsheets with and without the complex flame retardant were fixed to an aluminum specimen holder using double-sided tape and coated with gold in a vacuum sputter-coater. The surface morphology was observed using an Hitachi S800 field emission SEM (Japan) operating at an accelerating voltage of 150 kV.

Atomic force microscopy

Atomic force microscopy analysis was conducted to observe the morphology of the natural fiber surfaces using a Veeco Di Multimode SPM instrument (Plainview, NY). Scanning was carried out in air in the contact AFM mode with a tip radius curvature of 10 to 20 nm, a scanning rate of 1.969 Hz, a scan size of 5.000 μm, and a data scale of 1.733 V.

RESULTS AND DISCUSSIONS

Mechanical Properties of Handsheets

The tensile indexes of handsheets with different ratios of ALH and PBDE are shown in Fig. 1.

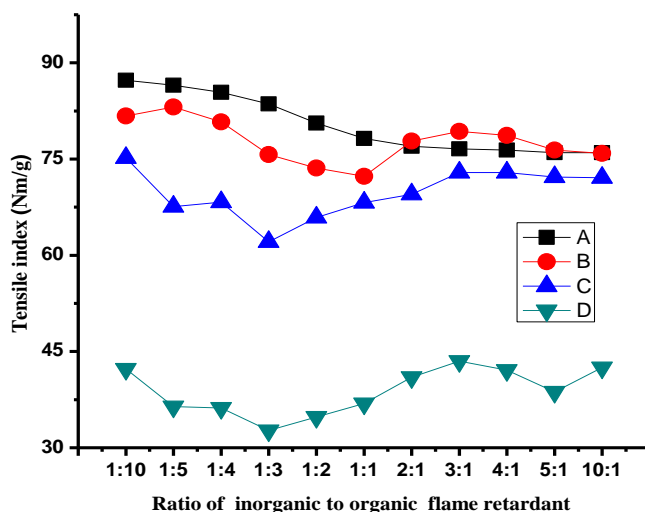


Fig. 1. Tensile index curves of (A) untreated sample, (B) sample treated at 200 °C for 5 min, (C) sample treated at 250 °C for 5 min, (D) sample treated at 280 °C for 5 min

Figure 1 shows that the tensile strength of the sample without heat treatment decreased with an increase in the inorganic flame retardant ratio; also, the tensile strength of the heat-treated samples decreased and later increased. The figure also shows that the lowest strength for the sample treated at 200 °C was at a ratio of 1:1. For the heat-treated samples, the paper tensile strength increased again when increasing the inorganic content. The lowest points for the samples treated at 250 °C and 280 °C are both at a ratio of 1:3, and when increasing the inorganic content, the paper tensile strength increased again. With increasing temperature, the paper tensile strength decreases, and the sample treated at 280 °C has the lowest tensile strength. This clearly shows that the paper mechanical properties decreased with increasing temperature. When increasing the inorganic content, the paper tensile strength of the sample treated at 280 °C increased again, reaching the highest value at an inorganic to organic ratio of 3:1, after which it started to decrease.

The mechanism is explained as the following: when heated, PBDE degrades to Br, and it reacts to produce BrH. BrH reacts with radicals OH, on one side and it regenerates Br on another side. BrH reduces the density of OH radicals. This reaction leads to the burning reaction prohibited, and it slows down the burning speed, until the burning process is extinguished. The strength of the heat-treated samples first decreased with a reduction in organic flame retardant, due to evaporating water molecules. Fibers decay led to the decomposing of the fibers hydrogen bonds and hydrogen bonds within the water molecules. ALH is decomposed to water and alumina, $\text{Al(OH)}_3 + 2\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$. When Al(OH)_3 is heated to 220 °C, it starts to decompose, and releases the crystal water. During this process, ALH absorbs the energy, and delays the burning polymer, and the released water suppresses the smoke. The complex retardant the inorganic content (ALH) amount increased due to more water evaporated from ALH, which helped form new bonds that in turn strengthened paper. When inorganic content (ALH) amount and organic amount reached the highest point of 3:1, it decreased again because more released water loosened hydrogen bonds of fibers, hence reducing the strength of paper.

Thermogravimetric Analysis

Figures 2a, 2b, and 2c show the thermal properties of organic, inorganic, and complex flame retardants, and the results are summarized in Table 1.

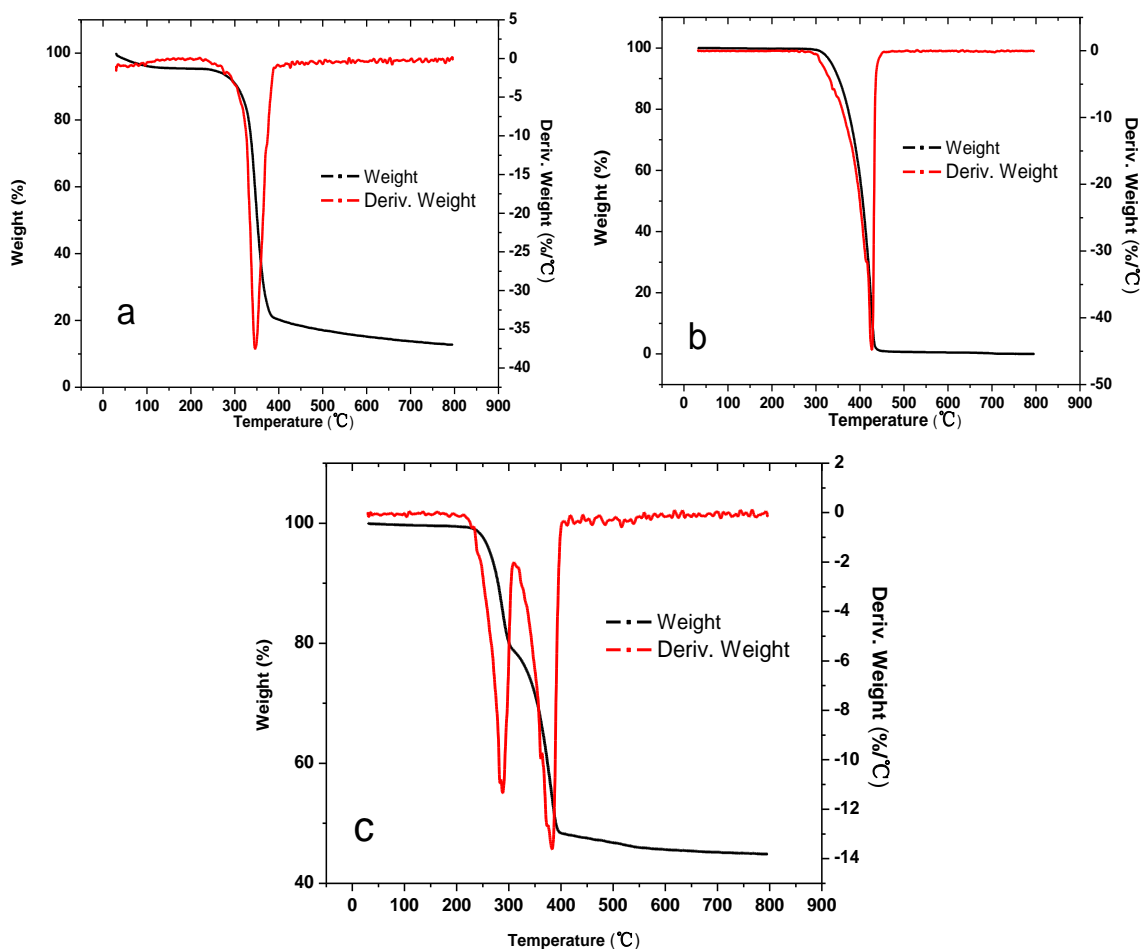


Fig. 2. TGA and DTG curves of ALH (a), PBDE (b), and complex flame retardant (c)

There were three decomposition stages: the first one, between 30 and 150 °C, was attributed to the loss of water, while the second, between 150 and 425 °C, was the main decomposition. The third was between 425 and 800 °C. The major weight losses for ALH, PBDE, and the complex flame retardant were 73.55%, 98.12%, and 50.66%, respectively, when heating from 150 to 425 °C.

The decomposition temperatures for ALH, PBDE, and the complex flame retardant were 345, 425, and 382 °C, respectively. The complex flame retardant papers clearly showed lower degradation mass loss than organic and inorganic flame retardant papers at temperatures from 150 to 420 °C.

Table 1. Thermal Mass Loss of ALH, PBDE, and Complex Flame Retardant

Samples	Thermal Mass-Loss Rate (%)			DTG Peak Temperature (°C)
	30 to150 °C	150 to 425 °C	425 to 800 °C	
ALH	6.95	73.55	6.94	345
PBDE	1.28	98.12	0.43	425
Complex flame retardant	1.35	50.66	2.91	285, 382

Specific Surface Area of Fibers

The specific surface area of fibers with and without complex flame retardant was tested by the method of nitrogen absorption. The added amounts of complex flame retardants were 10%, 40%, 70%, and 100%.

Table 2. Specific Surface Area of Fibers

Parameters	Specific surface area m ² /g
Fibers without flame retardant	0.421
Fibers without flame retardant 200 °C, 5 min	0.390
10% flame retardant paper 200 °C, 5 min	0.395
40% flame retardant paper 200 °C, 5 min	0.410
70% flame retardant paper 200 °C, 5 min	0.414
100% flame retardant paper 200 °C, 5 min	0.418

The above table shows that the specific surface area of natural fiber was decreased by heat treatment and is improved by adding complex flame retardant. This means that adding flame retardant into paper prevents fiber decomposition.

Fiber Morphology Analysis

SEM analysis

The SEM images of the surface of fibers prepared with 70% complex flame retardant based on dried natural fiber are shown in Figs. 3a and 3b.

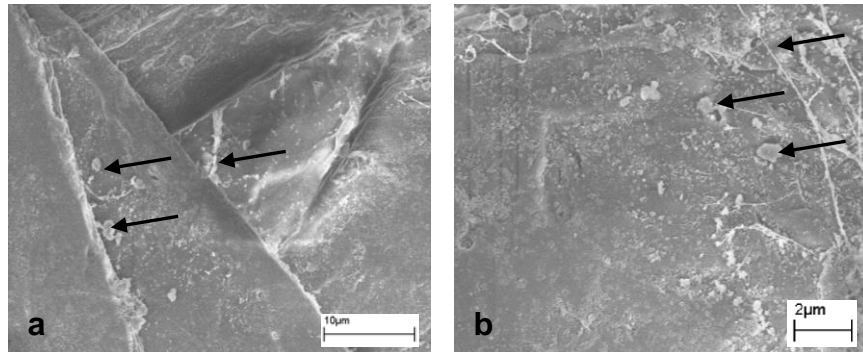


Fig. 3. SEM micrographs of natural fiber, magnified (a) 4000 times and (b) 7500 times

The figures show the structure of handsheets, revealing a network of fibers that give structural support. The particles observed in the figures are the flame retardant, which adsorbs on the fiber or spreads between the fiber. The arrows indicate the flame retardant particles, and pictures show the distribution and adhesion effects of flame retardants with fibers

Atomic force microscopy (AFM) fiber morphology analysis

AFM images of the surface of natural fibers prepared with 0%, 10%, 70%, and 100% complex flame retardant based on dried natural fiber treated at 200 °C for 5 min are shown in Fig. 4.

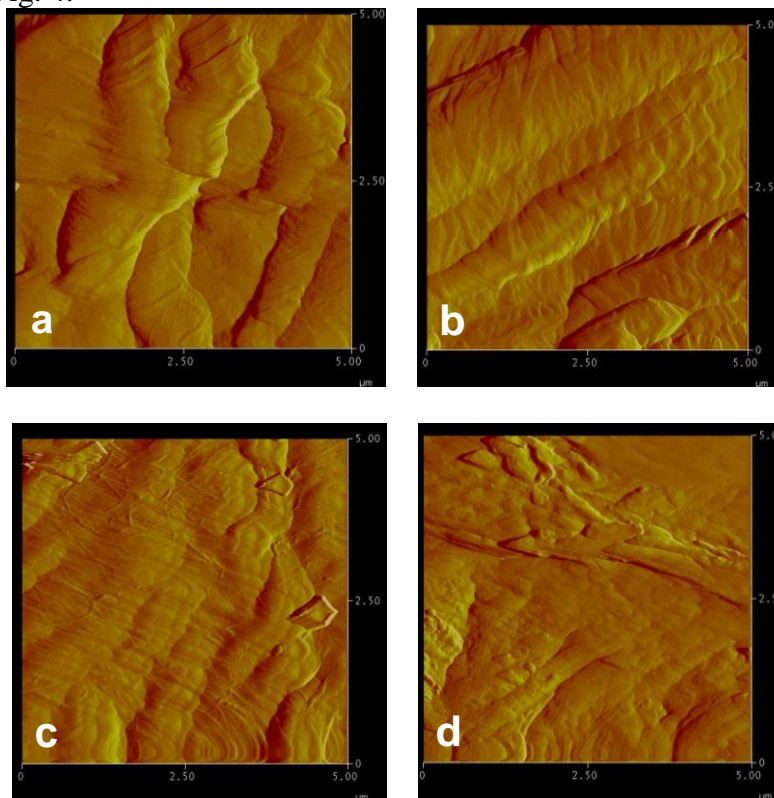


Fig. 4. AFM micrographs of heat-treated fiber with complex flame retardant at (a) 0%, (b) 10 %, (c) 70%, and (d) 100%

The fiber surface without the complex flame retardant was relatively rough, as shown in Fig. 4a, with more pronounced peaks and valleys. This was due to the degradation of the natural fiber. In contrast, the samples with complex flame retardant became much smoother with increasing amounts of complex flame retardant, as shown in Figs. 4b, 4c, and 4d. These changes in morphology probably resulted from the effects of the complex flame retardant on the natural fiber, which limit the degradation. Before the heat treatment, the AFM Rq (root mean square, to indicate roughness of samples) was 25.92 nm; after heat treatment, it started to have the creping skin fiber surface and Rq rose to 37.34 nm, compared to flame retardant paper samples which Rq only slightly increased to 29.86 nm.

CONCLUSIONS

1. In this work, a novel complex flame retardant consisting of aluminum hydroxide (ALH) and decabromine diphenyl oxide (PBDE) was used to inhibit the thermal decomposition of softwood kraft fiber, in paper form.
2. With increasing ratio of inorganic to organic flame retardant, tensile strength first decreased and then increased, but it decreased again after reaching the optimal ratio. The optimum value of ALH to PBDE was 3 to 1 with an added amount of 70% based on the dried natural fiber. The tensile index of handsheet was 82.5 Nm/g, and the specific surface area was 0.414 m²/g.
3. SEM analysis showed that the flame retardant particles were adsorbed on fibers or spread between the fibers. The AFM analysis showed that the fiber surface became smoother with increasing amounts of complex flame retardant after heat treatment, which means that flame retardant particles absorbed more energy to prevent the fiber decay.

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