

Adding Aluminum Hydroxide to Plant Fibers Using *In Situ* Precipitation to Improve Heat Resistance

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Plant fiber is an environmentally friendly, renewable natural resource. It has several excellent properties such as a low density and high softness. These properties make it an especially good raw material for applications such as paper and construction. However, plant fiber has poor resistance to heat, which limits its application in high temperature conditions. Adding aluminum sulfate solution to plant fiber first, and then adding sodium hydroxide solution enables aluminum hydroxide to be distributed uniformly on the surface and interior of a plant fiber. This modification improves the thermo-stability of the plant fiber. Furthermore, compared with the traditional way of filling, using the fiber added aluminum hydroxide by *in situ* precipitation to make paper, the strength properties of the paper decreased slightly. By combining *in situ* precipitation with filling, more aluminum hydroxide could be added to the paper while still maintaining good paper strength and better heat resistance.

Keywords: Plant fiber; In situ precipitation; Aluminum hydroxide; Heat resistance

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INTRODUCTION

Plant fiber is a natural, renewable resource. It has several excellent properties, including being environmentally friendly, renewable, safe, low cost, and having soft features (Dong *et al.* 2008; Cheng *et al.* 2011). Plant fiber is mainly composed of cellulose, hemicelluloses, and lignin; the properties of these three components determine the properties of plant fiber. In thermal analysis, the pyrolysis of hemicelluloses and cellulose occur quickly, with the loss of hemicelluloses mainly occurring between 220 and 315 °C and that of cellulose occurring from 250 to 400 °C. However, lignin is more difficult to decompose; it degrades in a wide temperature range (160 to 900 °C) (Soares *et al.* 2001; Räisänen *et al.* 2003; Jing and Lu 2007; Yang *et al.* 2007). Thus, plant fiber has poor heat resistance and begins decomposing at 220 °C, which limits its application at high temperatures.

Plant fiber is an important raw material, and it has a great influence on the thermal properties of paper. Some special-purpose papers such as heat-resistant label paper, heat-resistant interleaving paper for sheet metal, heat-resistant release paper, *etc.*, require fiber with high thermal stability (Li *et al.* 1999; Matsumi *et al.* 2006; Melgarejo and Mata 2010). Currently, the raw materials of heat-resistant paper are mineral fiber and high performance fibre such as glass fiber, aluminum silicate fiber, carbon fiber, aramid fiber, polyimide amines, *etc.* Although these fibers have greater thermal stability (Li *et al.* 1999; Matsumi *et al.* 2006), plant fiber has more advantages in the cost of production, environmental protection, safety, renewability, bonding strength, and other aspects.

Aluminum hydroxide is a green inorganic flame retardant (Sauerwein 2002; Larché *et al.* 2014; Hoffendahl *et al.* 2015), that has a wide range of applications in heat-resistant and flame-retardant paper (Xu *et al.* 2016). Aluminum hydroxide is usually added unevenly to this paper, reducing the paper strength sharply with increasing aluminum hydroxide (Shen *et al.* 2010). Thus, the addition amount of aluminum hydroxide and heat resistance of paper were restricted.

Many methods have been proposed to reduce the influence of filler on the strength of paper. Plant fiber has been modified *via in situ* precipitation (Ding *et al.* 2009; Shen *et al.* 2010), such that aluminum hydroxide was synthesized on the surface and inside of the fiber. By using this technique, the aluminum hydroxide was distributed evenly on the surface and inside of the fiber (Qian *et al.* 2010) rather than accumulating on the fiber surface. This significantly reduced the influence of aluminum hydroxide on the strength of paper, allowing more aluminum hydroxide to be added. When paper was exposed to high temperatures, the aluminum hydroxide began to decompose, eliminating water and absorbing heat and radiant energy (Moran 1987), resulting in a cooling effect on the fibers that slowed its heating and degradation rates (Khanna and Pearce 2013) and improved the thermal properties of the fiber and paper.

EXPERIMENTAL

Materials

Aluminum sulfate and aluminum hydroxide were supplied by Tianjin Damao Chemical Reagent Factory (Tianjin, China). Sodium hydroxide was supplied by Guangdong Guanghua Science and Technology Company (Guangzhou, China). Bleached softwood pulp was refined in a Mark VI type PFI refiner (Hamjern Maskjn, Hamar, Norway) to a beating degree of 40° SR.

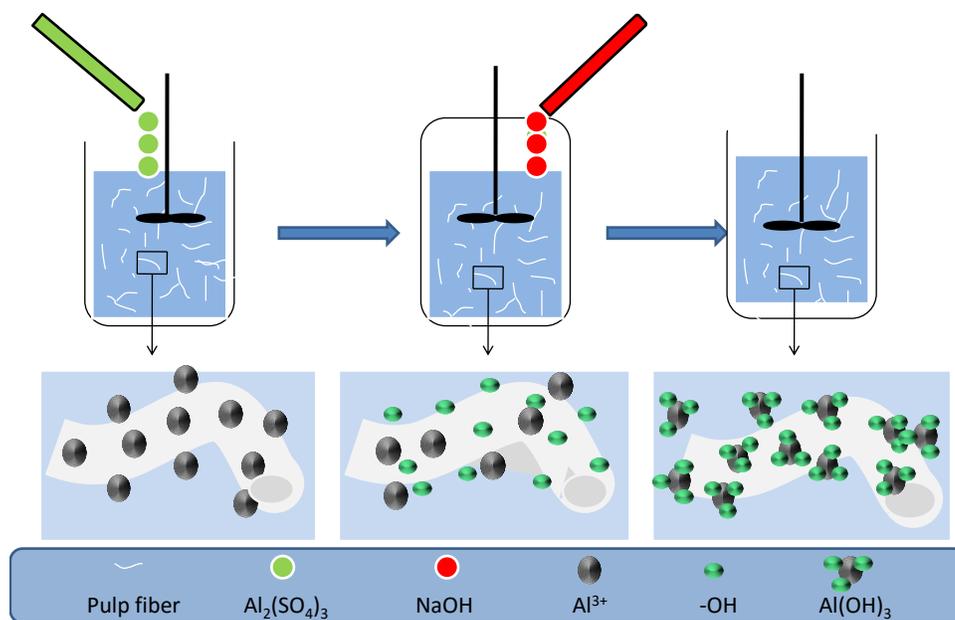


Fig. 1. The reaction process as aluminum hydroxide grows on the surface and inside the fibers *via in situ* precipitation

Fiber Modification

As shown in Fig. 1, 3 g of pulp (oven dry) and 100 mL of $\text{Al}_2(\text{SO}_4)_3$ solution were added into an Erlenmeyer flask, heated at 60 °C, and stirred for 1.5 h. Next, 6 M NaOH solution was added (this dosage is 1.2 times the amount of NaOH required to completely react with the $\text{Al}_2(\text{SO}_4)_3$), and the reaction was heated and stirred for 1.5 h. After the reaction was concluded, the flask was cooled for 0.5 h, and the contents were repeatedly washed with tap water until the last washing liquid became reached neutral pH.

Paper Sheet Preparation and Determination of Paper Properties

Paper sheets with target basis weight of 80 g/m² were prepared by using a model 1600 Econo-Space automatic sheet former system (Réalisations Australes Inc., Canada) according to TAPPI T205 (2002), with the exception that the pressure for wet sheet pressing was kept at 200 kPa. The sheets were dried at 103 °C using a Formax 12 drum dryer (Thwing-Albert Instrument Company, NJ, USA).

The paper sheets were stored in a controlled environment (23 ± 1°C, 50 ± 1% RH) for 24 h before testing. The paper sheet burst index (L&W CE180), tearing strength (L&W 009), and tensile strength (L&W CE062).

Scanning Electron Microscopy, Thermogravimetric Analysis, and Differential Scanning Calorimetry

Scanning electron microscopy (SEM) observations of paper samples were carried out using the FEI Quanta-200 environment microscope (Oberkochen, Germany). The paper sample surfaces were coated with gold before observations.

Thermogravimetric analysis (TGA) was performed on a TG 209F3 Tarsus thermogravimetric analyzer (NETZSCH Tarsus, Selb, Germany). The samples were heated from 30 to 600 °C at a heating rate of 10 °C/min and under a nitrogen flow rate of 20 mL/min.

Differential scanning calorimetry (DSC) data were obtained using a TA Q200 differential scanning calorimeter (New Castle, DE, USA). The samples were heated from 30 to 300 °C at a heating rate of 10 °C/min and under a nitrogen flow rate of 20 mL/min.

RESULTS AND DISCUSSION

Distribution of Aluminum Hydroxide

Figure 2 shows the aluminum hydroxide that had been added as dispersed particles by filling accumulated between the fibers and on the fibers surface unevenly; this depleted the strength of the paper. The comparison of the SEM images of the original fiber with the modified fibers (modified with *in situ* precipitation) showed that the aluminum hydroxide was attached to the modified fiber surface uniformly instead of piling on the fiber surface.

As shown in Fig. 3 with the fiber cross-section SEM-EDX analysis, the Al absorption peak appeared in the cell wall of the modified fibers but not in the original fiber. Thus, aluminum hydroxide was successfully added to the fiber cell wall and deposited in the cell cavity. Furthermore, through *in situ* precipitation, Al^{3+} and OH^- ions combined with each other, reacted to form aluminum hydroxide, and deposited not only on the surface of the fibers but also in the interiors of the fibers.

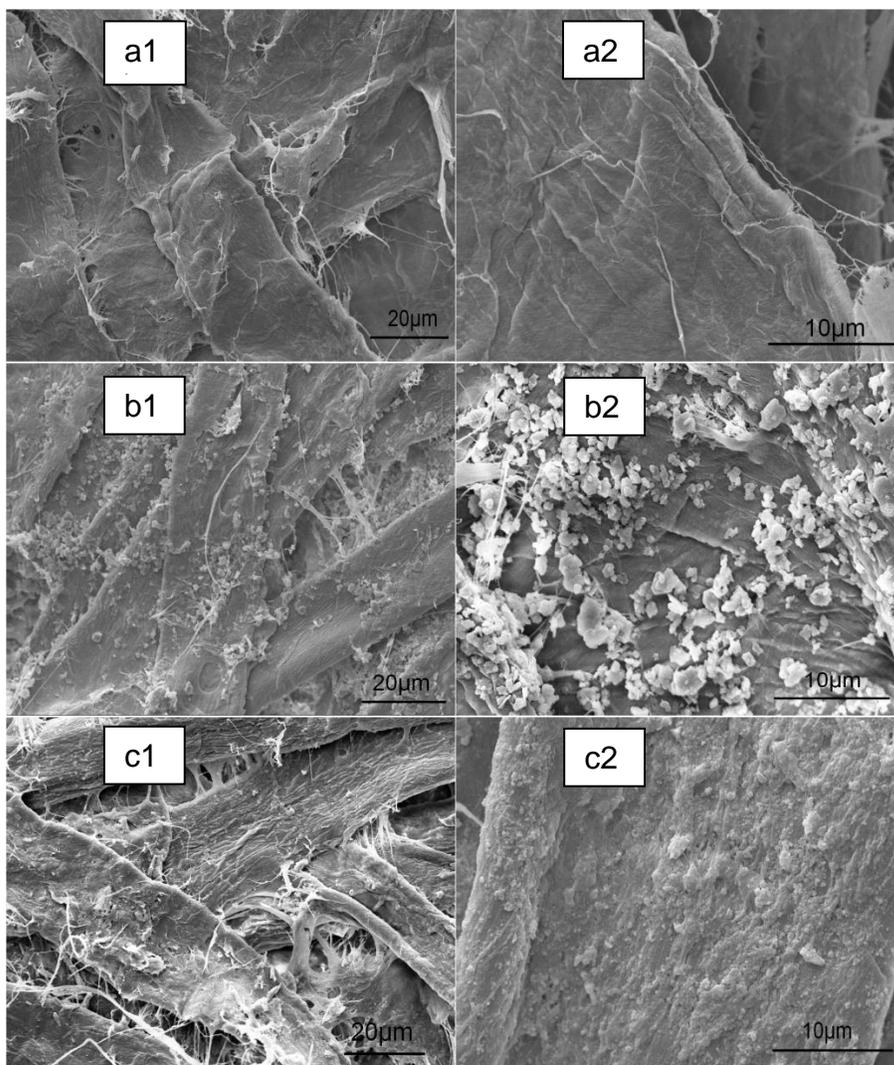


Fig. 2. SEM micrographs of surface of paper (1) and fiber (2). (a1 and a2) no aluminum hydroxide; (b1 and b2) 30% aluminum hydroxide loading by filling (based on the total dry weight of the pulp and filler); (c1 and c2) 30% aluminum hydroxide loading by *in situ* precipitation (based on the total dry weight of the pulp and filler)

Physical and Thermal Stability Properties of Paper

The strength properties of paper deteriorated after the addition of fillers to the paper. However, at the same basis weight and same content of aluminum hydroxide (based on the total dry weight of the pulp and filler), paper with aluminum hydroxide added *via in situ* precipitation had better strength properties than the paper with aluminum hydroxide added *via* filling. Table 1 shows three scenarios: the aluminum hydroxide was not added to the blank paper, the aluminum hydroxide was added to the modified paper *via in situ* precipitation, or the aluminum hydroxide was added to the filled paper *via* filling. The aluminum hydroxide loading level was controlled at 10%, 20%, 30%, and 40% (based on the total dry weight of the pulp and filler). With increasing levels of aluminum hydroxide in the paper, either filled or modified, the strength properties (breaking length, burst index, and tear index) decreased. However, when the degree of strength decline between papers was compared, the paper with aluminum hydroxide added *via in situ* precipitation was stronger than the paper with aluminum hydroxide added *via* filling.

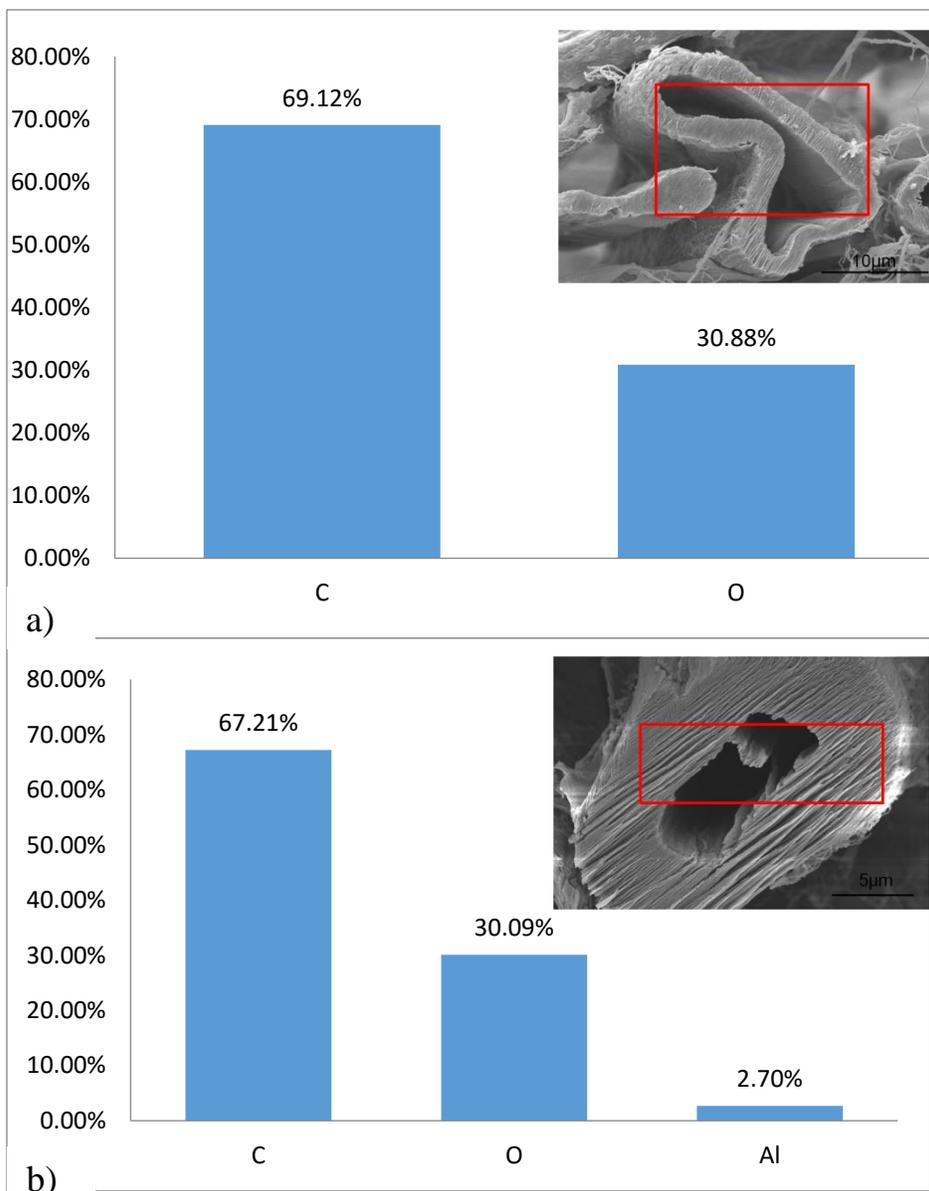


Fig. 3. SEM-EDX analysis of the cross section of fiber, in atomic percent. (a) no aluminum hydroxide; (b) 30% aluminum hydroxide loading by *in situ* precipitation (based on the total dry weight of the pulp and filler)

When the aluminum hydroxide content of the paper was up to 40%, the strength properties of paper with aluminum hydroxide added *via* filling declined significantly, which affected the use of paper seriously, while the strength properties of the paper with aluminum hydroxide added *via in situ* precipitation was well preserved, such that the paper could meet the requirements of use. This was due to the aluminum hydroxide added *via* filling piling on the fiber surface and between the fibers, affecting the formation of hydrogen bonds and bonding between the fibers. This reduced the bonding strength between fibers. Thus, the strength properties of the paper were reduced seriously. Of the aluminum hydroxide added to the paper *via in situ* precipitation, a portion was distributed in the interior of fiber, which did not affect the bonding strength between the fibers; the other portion was uniformly distributed on the surface of fibers, which had less effect on the formation of hydrogen bonds and bonding between the fibers.

Table 1. Paper Strength Properties

Paper	Aluminum hydroxide Content (%) [*]	Breaking Length (km)	Burst Index (kPa.m ² /g)	Tearing Index (mN.m ² /g)
Control	0	6.58	5.30	1.79
Aluminum hydroxide <i>via</i> Filling	10	4.56	4.22	1.73
	20	3.95	2.59	1.45
	30	2.50	1.57	1.08
	40	1.39	0.76	0.69
Aluminum hydroxide <i>via in situ</i> Precipitation	10	5.71	4.06	2.04
	20	5.24	3.86	1.75
	30	5.16	3.48	1.47
	40	4.62	2.89	1.04

^{*}based on the total dry weight of the pulp and filler

Note: The control paper had no added aluminum hydroxide

The blank paper (with no aluminum hydroxide added), the paper (with aluminum hydroxide added *via* filling), and the test papers (with aluminum hydroxide added *via in situ* precipitation) were tested for thermal stability (30 min at 280 °C), and then the strength properties of these papers were tested (Table 2). The paper with aluminum hydroxide added *via in situ* precipitation and the paper with aluminum hydroxide added *via* filling showed better strength (breaking length, burst index, and tear index) percent retention than the control. The paper with aluminum hydroxide added *via in situ* precipitation showed a little higher strength (breaking length, burst index, and tear index) percent retention than the paper with aluminum hydroxide added *via* filling. In addition, increasing the content of aluminum hydroxide in the paper led to higher strength percent retention, with the percent retention of breaking length and tear index values up to 80%. Thus, the thermal stability of paper was improved with the addition of aluminum hydroxide *via in situ* precipitation.

Table 2. Percent Retention of Paper Strength Properties after 30 min at 280 °C

Paper	Aluminum hydroxide Content (%)	Breaking Length (%)	Burst Index (%)	Tearing Index (%)
Control	0	55	21	57
Aluminum hydroxide <i>via</i> Filling	10	58	23	59
	20	63	28	63
	30	67	35	73
	40	78	47	78
Aluminum hydroxide Added <i>via In Situ</i> Precipitation	10	64	23	63
	20	71	30	69
	30	78	38	73
	40	83	54	80

^{*}based on the total dry weight of the pulp and filler

Note: The percent retention was defined as the strength properties of the paper (heated 30 min under 280 °C) divided by the strength properties of the paper (un-heated).

TG and DSC Analysis of the Papers

As shown in Fig. 4, the paper made with unmodified fibers and the paper made with modified fibers (with aluminum hydroxide added *via in situ* precipitation) had the same weight loss below 220 °C. This part of the loss was caused by the evaporation of water. From 220 to 300 °C, the papers made with modified fibers showed more weight loss. This

is due to the decomposition of aluminum hydroxide. As shown in Fig. 5, comparing the DSC figure of the paper made with original fibers and the papers made by aluminum hydroxide -modified fibers, the paper made with original fibers had one peak at 75 °C; the papers made with modified fibers had two peaks, one at 75 °C and one at 265 °C. The TG and DSC test results indicated that the aluminum hydroxide degraded between 220 and 300 °C. Furthermore, aluminum hydroxide protected the paper through its own decomposition when the paper was used between 220 and 300 °C.

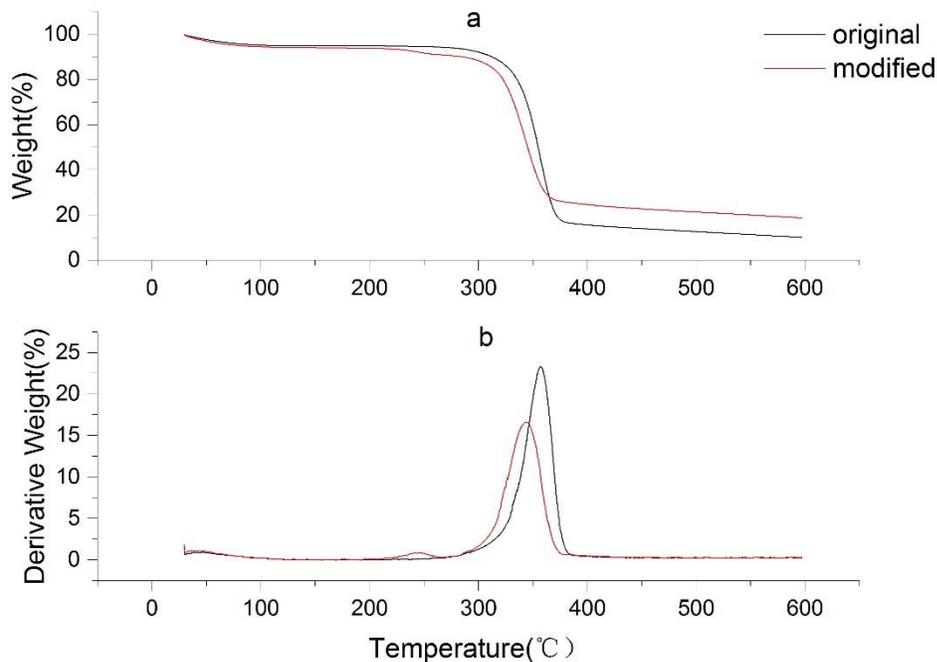


Fig. 4. The TG figure(a) and DTG figure(b) of paper (no aluminum hydroxide added) and modified paper (aluminum hydroxide added *via in situ* precipitation, with 30% content)

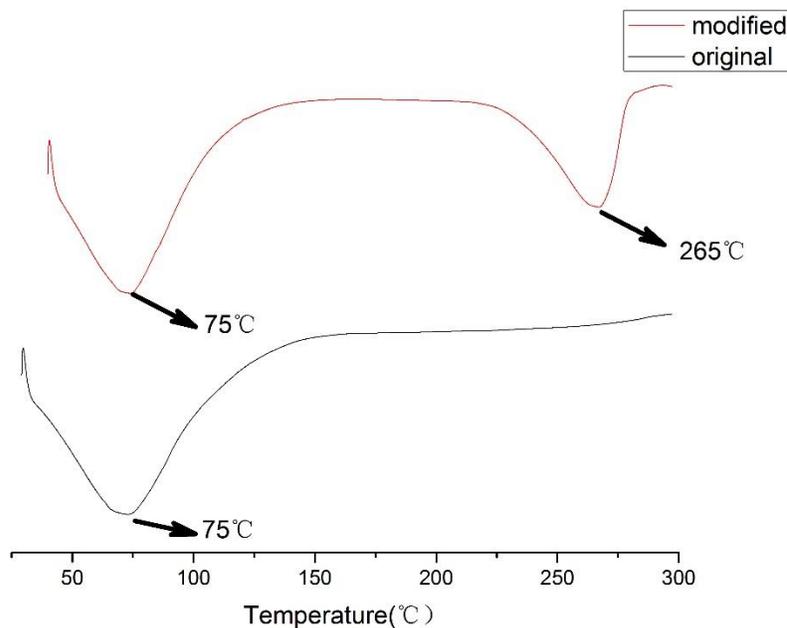


Fig. 5. The DSC figure of paper (no aluminum hydroxide added) and modified paper (aluminum hydroxide added *via in situ* precipitation, with 30% content)

When aluminum hydroxide decomposed, it drew off water and absorbed some of the heat and radiant energy from the paper. Water vapor then acted as a coolant and reduced the surface temperature of the fibers (Moran 1987), which slowed the fiber heating and degradation. Al_2O_3 , as the decomposition product of aluminum hydroxide, covered the surface of fiber and isolated air, and prevented the fiber from burning (Khanna and Pearce 2013). Therefore, aluminum hydroxide improved the flame-resistance and heat resistance of paper.

CONCLUSIONS

1. The aluminum hydroxide added *via in situ* precipitation was distributed evenly on the surface and inside of the fiber and wrapped the fibers tightly. *In situ* precipitation also reduced the impact of aluminum hydroxide on the strength properties of paper. By combining *in situ* precipitation with filling, more aluminum hydroxide could be added to the paper while still maintaining good paper strength, and better heat resistance.
2. When the paper treated with *in situ* precipitation-added aluminum hydroxide were exposed to high temperatures, the aluminum hydroxide would decompose, reducing the impact of temperature on paper. Because the aluminum hydroxide wrapped each fiber, it could protect every fiber at the same time and greatly improve the heat resistance of the paper.

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