Influence of Flame Retardants on Flammability of Cellulose-Based Material

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Abstract

This work aims to investigate the application of fire retardant agents in production of fire-proof cellulose-based material. Several agents are used including boron compounds, and ammonium polyphosphate/ diatomite composite filler. The results show that when using a mixture of boric acid and sodium borax at the ratio of 1:1 for impregnation of paper, the combustion speed of paper is reduced significantly. On the other hand, synthesized ammonium polyphosphate/ diatomite filler also provides good flame resistance to the paper when it is used as a filler. The use of composite filler supported by a retention aid like cationic starch seems to be less effective than the impregnation method.

Keywords: Ammonium polyphosphate, Cationic starch, Cellulose, Composite filler, Fire-retardant; Impregnation

1. Introduction

Cellulose is one of the most abundant natural polymers on earth, which possesses a variety of potential properties. Good mechanical properties, biodegradable, hydrophilic are some of outstanding characteristics of cellulose. Cellulose, either as the main component of wood or as cotton fibers in textiles, is flammable causing damage and injury. When ignited, cellulose is thermally decomposed producing volatile compounds speeding up the combustion reaction. Fortunately, cellulose consists of many compositions that can be easily modified and converted into substitutions with fire-retardant property.

Cellulose combustion can be described as two different phenomena, glowing and flaming. These two phenomena represent different hazards and should be approached in different directions. Glowing is a direct oxidation of solid cellulose or its decomposed products. This is basically a slow combustion and is important to some specific products such as carpet, mattress, and insulation. In contrast, flaming is a complex process including both gas and solid phases. In the initial stages of combustion, cellulose is heated initiating endothermic degradation reactions, in which large polymeric molecules are broken into smaller and volatile compounds.

The flaming occurs when pyrolysis products diffuse on the surface and contact with oxygen in the air. This is an exothermal process. Heat released is partly transferred back to the fiber surfaces to maintain the pyrolysis. The pyrolysis reaction is, therefore, going on and on.

Fire-retardants are compounds containing halogen, phosphorous, nitrogen, sulfur, boron, and metals in different combinations. In most cases, fire-retardants can be classified based on one of the following criteria: (1) basic chemistry (organic, inorganic); (2) the presence of one element or a combination of different elements that promote the fire resistance (phosphorous, nitrogen, halogen...); (3) type of chemical (acid, base, ether, ester, oxide, hydroxide, salt); (4) mechanism; (5) ability to maintain their functions (e.g. in washing process, in contacting with light, heat, chemicals...) [1].

In the group of fire-retardants where there is no chemical reaction, inorganic salts are used to reduce decomposition temperature of cellulose and improve the carbonization by catalyzing dehydration and decomposition [2]. Several fire proof derivatives of wood were produced by impregnation of wood using $NH_4H_2PO_4$, $AlCl_3.6H_2O$, $Na_2B_4O_7.10H_2O$, and $KHCO_3$ [3]. Phosphorylated Kraft fibers showed better fire resistance in comparison with the original fibers [4]. When treating filter papers with mixtures of boric acid and borax, the obtained products showed good resistance to heat at temperature up to 700°C [5].

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Chemical modification methods can be carried out using many different chemicals. In principle, even when hydrogen bonds between hydroxyl groups of cellulose are broken, chemicals still can attack in form of esterification or etherification. The esterification occurs in strong acid medium, e.g. nitrogenation, acetylation, phosphorylation, and sulfurylation. These compounds react prior to primary hydroxyl groups (C6). The etherification is conducted in alkaline environment using alkyl halogen agents or sulfate [6].

Among a variety of phosphorous and nitrogen contained compounds, ammonium polyphosphate is a useful fire retardant, which is also a friendly environmentally agent. Different forms of ammonium polyphosphate were synthesized as presented in the work of Watanabe [7]. However, polyphosphoric acid was used earlier as a fire retardant in paper and showed some advantages when the impregnation was conducted at 110°C.

In this work, fire retardants were used in paper in two different ways. Firstly, inorganic compounds including boric acid, sodium borax, and mixtures of these two chemicals were used as impregnation agents. Secondly, ammonium polyphosphate-diatomite filler was synthesized and used as a filler in paper. Flammability of the obtained papers was evaluated based on their combustion test.

2. Experimental

2.1 Materials

Bleached Kraft hardwood pulp was purchased from An Hoa Paper Corporation (Vietnam) in form of pulp sheets. Some basic properties of the pulp were presented in table 1.

All chemicals used in this work were analytical grades and originated from Vietnam or China.

Table 1. Basic properties of bleached Kraft hardwood pulp purchased from An Hoa Paper Corporation (Vietnam)

Property	Value
Brightness, %ISO	≥ 87
Dirt content, mm^2/kg	≤ 10
Viscosity, mL/kg	≥ 540
Fiber length, mm	≥ 0.6
Ash content, %	≤ 0.3

2.2 Methods

2.2.1 Preparation of boric acid/ borax solutions and their mixtures

The solutions were prepared by dissolving a required amount of boric acid/ sodium borax in distilled water to obtain desired concentrations (i.e. 1, 2, 3, 4, 5 wt%). The procedure was conducted at room temperature or with light heating when needed.

Boric-borax (BO-BA) mixtures were prepared by mixing the two solutions (5 wt% concentration) at different volume ratios as follows: BA/BO = 100/0, 70/30, 50/50, 20/80, 0/100.

2.2.2 Procedure for synthesis of ammonium polyphosphate-diatomite filler

Ammonium polyphosphate-diatomite (APP-D) filler was synthesized following the procedure described by Sha et al. [8].

APP was produced by using phosphoric acid and urea at the ratio of 1:1.8. Concentrated phosphoric acid was poured into a three-neck round bottom flask and heated to 70ºC with continuous stirring. Urea was then added to the flask when the temperature reached 130ºC. The reaction was kept at this temperature for 15 min. The product was transferred into a ceramic tray and placed in an oven at 210ºC for 2 h for solidification. The obtained solid was ground with a mortar, screened and stored in a close container for further applications.

2.2.3 Procedure for impregnation of paper with fire-retardants

Paper test sheet was soaked in an adequate amount of fire retardant solution and kept at room temperature for a required period of time according to experimental design. After half of the time, turn the sheet up side down to ensure the sheet was contacted with the solution equally.

After the impregnation time, excess liquid was removed from the sheet using a felt coating roller. The sample was dried in an oven at 105 ± 2ºC to a constant weight. Adsorbed amount of chemical was then calculated based on the difference in mass before and after the impregnation.

2.2.4 Procedure for pulp preparation and test sheet formation

The pulp sheets were torn into small pieces and soaked in tap water for 24 hours. It was then subjected to beating to obtain a certain refining degree. Before test sheets formation, the pulp was disintegrated for 15 min and water was added to make a suspension of approx. 12.5 g/L. Filler was added to the slurry if necessary. Cationic starch was applied right before the sheet formation as a retention aid when needed. Test sheets were simply produced by using a Buchner filter (ø10 cm) connected with a vacuum pump. The sheets were then dried in an oven at 105 ± 2ºC to constant weight.

2.2.5 Paper combustion test

Test sheets of 5 x 5 cm or ø11 cm were hold vertically about 1 cm above the flame, which is produced by an alcohol burner. After 30 seconds, the paper was collected and dried in an oven at 105 ± 2ºC to a constant weight. Flammability of the sheets were then evaluated based on residue mass of the sheets after the combustion procedure.

2.2.6. Chemical composition analysis

Dry content, α-cellulose, and ash content of the pulp were determined according to TCVN 4407:2010 (ISO 638:2008), TCVN 7071:2002 (TAPPI T 203:1993), and TCVN 10761:2015 (ISO 1762:2001), respectively.

3. Results and discussion

3.1 Chemical compositions of the raw material

Some typical compositions of the bleached Kraft hardwood pulp were presented in table 1.

Table 2. Chemical compositions of bleached Kraft hardwood pulp purchased from An Hoa corporation (Vietnam)

Composition	Value
Dry content, %	85.18 ± 0.13
Ash content, %	0.16 ± 0.02
α-cellulose, %	87.18 ± 0.11

The pulp has high content of α-cellulose with approx. 87 % and relatively low content of ash. This material, therefore, can be considered as a suitable material for the work.

3.2 Investigation on influences of fire-retardant impregnation on flammability of paper

3.2.1 Influence of boric acid/ sodium borax concentration when used separately for impregnation

As can be seen from Fig. 1, when using boric acid or sodium borax independently as impregnation agents, the papers show improvements in their flammability. Between the two compounds, borax provides the paper with higher fire proof.

In both cases, increasing concentrations result in increasing amount of paper residue after combustion test.

3.2.2. Influence of borax/boric acid ratio when used together

Mixtures between sodium borax and boric acid at different ratios were used for the impregnation test. Changes in mass of residual papers versus these ratios are presented in Fig.2.

According to Fig.2., the paper residues are clearly affected by the BA/BO ratios. As the percentage of borax increases from 0 to 50% (corresponding to the decrease in percentage of boric acid from 100 to 50%), the paper residue has been enhanced (from 25.68% to about 78%). This indicates that the flame retardancy of the paper has been improved.

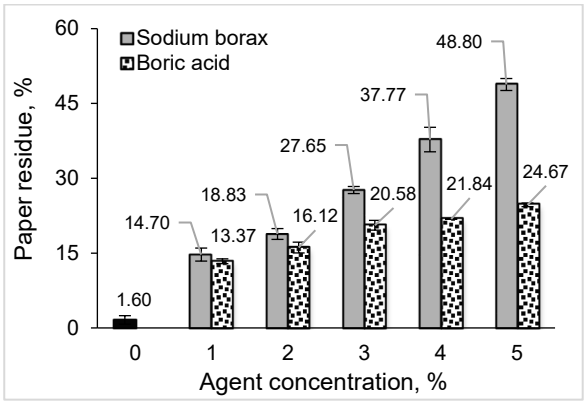

Fig. 1. Influence of borax and boric acid concentration on flammability of paper when used separately; impregnation and burning time were 5 min and 30 s, respectively

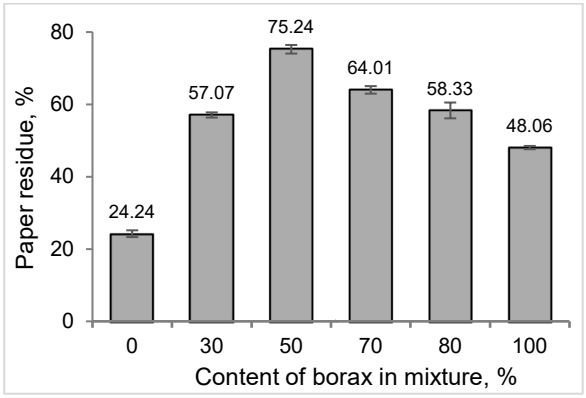

Fig. 2. Influence of borax/ boric acid ratio on flammability of paper when used in mixtures; impregnation and burning time were 5 min and 30 s, respectively

When increasing the percentage of borax from 50 to 100%, the residual amount of paper was decreased from 78% to 52%, indicating that the fire retardancy of paper has been limited. This phenomenon can be explained by the fact that these compounds have low melting points and form layers when heated at high temperature [9]. When borax and boric are used together in a mixture, the two chemicals act in different mechanisms and both have advatages as well as disadvantages. On the one hand, the presence of borax limits surface flame to spread but is also able to contribute to glowing or smoldering. On the other hand, boric acid reduces smoldering and glowing combustion but influences slightly flame spread. Combination of these agents takes advantages of them

and contributes to the fire-retardant ability of the samples.

Based on these results, it can be concluded that the fire-retardant solution containing 50% borax and 50% boric acid provides the best flame retardancy for paper.

3.2.3 Influence of impregnation time

Impregnation time has significantly influenced the paper loss weight after the combustion test. Changes in mass of paper residue dependent upon soaking time of the paper tests in the mixture of borax and boric acid (50/50 w/w) were illustrated in Fig 3. When dipping in the solution for 45 min, the flammability of the paper shows the best effect with approx. 83 % of the paper weight remained. Increasing the impregnation time, the residue mass reduced dramatically. This could be explained by saturation level of the sheet. Once this level is reached, the sheets are no longer able to adsorb any solution.

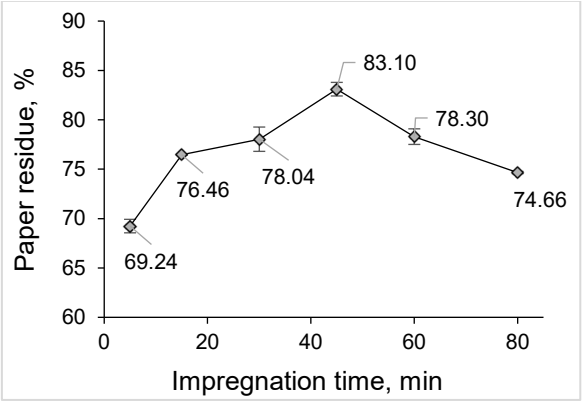

Fig. 3. Influence of impregnation time on flammability of paper when using 50/50 ratio of borax/boric acid for impregnation, burning time 30 s

According to the obtained results, best conditions for treatment of paper were summarized as follows:

- Impregnation solution includes of sodium borax and boric acid of 5 % wt. concentration at the BA/BO ratio of 50/50 (v/v).

- Impregnation time: 45 min.

- The procedure was conducted at room temperature.

3.4 Application of APP-Diatomite filler in paper

APP-Diatomite (APP-D) filler synthesized according to the procedure described in section 2.2.2. was added into pulp suspension of approx. 12.5 g/L and mixed well for about 15 min before sheet formation. Cationic starch was used as a retention aid. The role of cationic starch in papermaking has been widely known as this agent can help retain fines and fillers when it is used in thin stock.

Cationic starch dosage has shown its effect on the chemical retention and therefore influenced the flammability of the paper. As illustrated in Fig 4, the APP-D filler improves dramatically the residual mass of paper after burning in comparison to the blank sample, which was made purely with cellulose fibers.

The role of cationic starch as a retention aid is exhibited as it significantly increases the paper residue of the test sheets from 10.4 % to approx. 17% when the starch dosage is increased from 0 to 3%. However, this improvement seems to slow down when the cationic starch dosages are higher than 2%. This is quite obvious since cationic starch is used in thin stock as a retention aid. Electrostatic forces between cationic charges of the starch and anionic charges on cellulose fibers as well as fillers has led to the retention of the chemicals. However, the addition of cationic starch cannot be unlimited due to saturation level as well as economical issues. Furthermore, redundant cationic starch used can cause a reduction in paper strength, which is not concerned in this research but is still an important issue in papermaking.

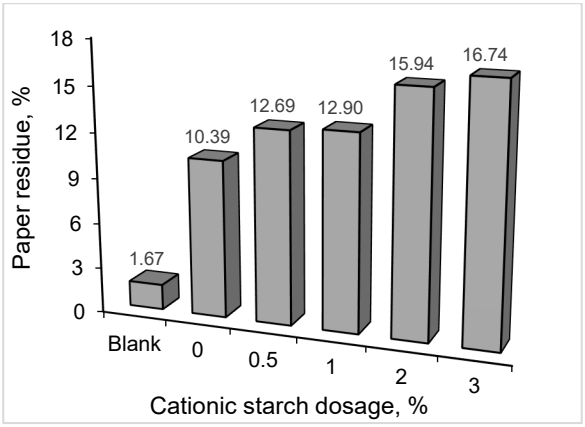

Fig. 4. Influence of cationic starch dosage on chemical retention and flammability of paper

To conclude, the dosage of cationic starch when using APP-D filler should be 2% based on the dry weight of the pulp.

4. Conclusions

Among the two methods studied in this research, the impregnation method shows better effect on improvement of fire-proof property of paper. The conditions for treating paper are as follows: mixture of 5% sodium borax and 5% boric acid solutions at the ratio of 50/50 (v/v); impregnation time: 45 min, and the procedure was conducted at room temperature. The use of composite fillers, such as ammonium polyphosphate/ diatomite supported by cationic starch

can be effective but it needs further investigation including optimal conditions for the synthesis as well as other influencing factors. Effects of impregnation procedure or using fillers on some mechanical properties of paper should also be of interest.

Acknowledgments

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