Development of Flame Retardant Property on Sodium Silicate Treated Paper Based Materials

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Abstract. The preparation of cellulose-based flame retardant paper treated with sodium silicate and silicon dioxide (SiO2) colloidal particle by simple immersion process is reported. Cellulose-based paper was preheated at 90°C for surface preparation. The heat treated paper was immersed in solution of sodium silicate-SiO2 at different immersion time ranging from 15 min to 24 hrs. Treated solution diffused into paper coated on the paper fiber and filled the void in the paper microstructure. Treated paper was heated at 90°C to convert an impregnated sodium silicate-SiO2 precursor into silicate framework. The treated paper showed ν_ssym Si-O-Si from siloxane bond at 792 cm⁻¹ which confirmed a presence of SiO2 in paper. Treated paper at 1 hr immersion showed the highest weight percent gain (WPG) of 40% and total combustion time was improved to 14 sec.

1. Introduction
Cellulose-based paper which was made from wood consists of three main compositions including cellulose, hemicellulose, and lignin [1]. The composition varies depending on type of paper and its preparation process such as white paper consists of over 85% of cellulose and 15% of lignin and newspaper contains approximate 50% cellulose, 25% hemicellulose, and 25% lignin [2]. Due to its high flexibility and eco-friendly, papers are widely used for household decoration such as wall papers, paper chair, and other eco-friendly furniture where the flame retardant is required. The burning mechanism of paper originates from a breaking of hydrogen bond of cellulose [1]. At temperature above 250°C, the activation of O–H group causes the cellulose to split to levogluconan. At around 300°C, cellulose starts self-ignition. To prevent paper from burning, sodium silicate-SiO2 colloidal are considered due to its flame retardant properties and green chemicals [1, 3, 4, 5]. These precursors will form silicate network which is covalently bonded to paper. Once paper was treated, silicate network would act as protective layer to protect cellulose structure via mechanism called ceramification [1] while maintaining a paper appearance. Self-ignition of paper will be shifted to higher temperate.
Çiçekler, M et al. [6] studied flame retardant paper by using various chemical flame retardant recipes including borax, boric acid, alpha-x and ammonium polyphosphate. They found that most of flame retardant agent improved flame retardant property of treated paper while ammonium polyphosphate treated paper gave the lowest flame retardant property among all the agents. However, most of flame retardant particles are considered as toxic chemical due to the presence of boron and phosphate.

The development of flame retardant mulberry paper by using a combination of carboxymethyl cellulose (CMC), poly (vinyl alcohol), sodium silicate, and other substances. Thermal degradation property was improved in treated material where a higher temperature is required for burning. However, flexibility of treated paper was decreased due to a coating agent and conflagration rate of fire is higher than expected.

In this work, the development of paper and sodium silicate-SiO\textsubscript{2} composites were investigated. The simple immersion process was used to treat cellulose-based paper with varied immersion time ranging from 15 min up to 24 hrs. The flame retardant property will be evaluated according to total combustion time.

2. Materials and Method

2.1. Preparation of Paper
Cellulose-based filter paper (Whatman no.91, pore size 10 µm) was cut into 1.27 x 12.7 cm\textsuperscript{2} following standard UL94 test for flammability of plastic materials for parts in devices and appliances. All prepared samples were sonicated in diluted acetone for 5 min, rinse with water and dry at 60°C for 8 hrs.

2.2. Preparation of Sodium Silicate Treated Solution
Sodium silicate (AR grade) and silica colloidal (solid content approximate 30% wt, 20 nm, pH 9) in water were purchased from M&P IMPEX (Thailand) and Zhejiang Yuda Chemical Co. Ltd (China). To prepare treated solution, 22 mL of sodium silicate was diluted with 240 mL of RO water to prevent sol-gel formation after adding 120 mL SiO\textsubscript{2} colloidal. Diluted sodium silicate was stirred while adding SiO\textsubscript{2} colloidal. The solution was stirred for 2 hrs to obtain odorless clear treated solution.

2.3. Treating Procedure
Untreated papers were preheated at 90°C in an oven for 8 hrs in order to remove moisture and activate surface. Immersion time was varied from 15 min up to 24 hrs to allow the diffusion of sodium silicate-SiO\textsubscript{2} colloidal into paper. The treated paper was heated at 90°C for 8 hrs to allow water to evaporate and facilitate the formation of silicate framework and cellulose in paper. The initial dried weight before and after treatment were measured. Samples were kept in desiccator at least 12 hrs prior to characterization.

2.4. Characterization
Scanning Electron Microscope (SEM) was used to observe material morphology. Sample were attached with carbon-tape before investigated under SEM. Fourier transform infrared spectroscopy (FTIR) was measured at 500 – 4,000 cm\textsuperscript{-1} to identify ν\textsubscript{sym} Si-O-Si and ν Si-O-C at 792 and 1,100 cm\textsuperscript{-1}. Weight gain after treatment was observed by weight percent gain (WPG). The calculation of dried weight before and after treatment was done following equation 1.

\[ \frac{W_f - W_i}{W_i} \times 100 \]  \hspace{1cm} (1)

where, \( W_i \) is dried weight before treatment. \( W_f \) is dried weight after treatment.

Flame retardant performance was carried out according to flammability of plastic materials for parts in devices and appliances (UL94). However, samples cannot classify flame retardant class via this
standard because the samples were not plastic materials. Therefore, sample will be reported for their flame retardant properties by total combustion time.

3. Result and Discussion

3.1. Morphology

![SEM images of untreated and treated cellulose-based paper using sodium silicate](image)

**Figure 1.** SEM images of untreated and treated cellulose-based paper using sodium silicate of untreated and treated paper at 15 minutes, 1 hour, and 24 hours immersion for resolution of 500x, 1000x and 1500x.

The morphology of untreated and treated cellulose-based paper were shown in figure 1. Individual fiber can be seen clearly in untreated sample. Treated sample showed a deposition of flame retardant material on the fiber surface and the void between the fiber (yellow circle and arrow). This indicated that sodium silicate cooperated with SiO$_2$ already impregnated into sample.

3.2. Infrared Fourier Transform Infrared Spectroscopy (FTIR)

The functional group of chemical composition in cellulose-based paper with and without treatment was shown in figure 2. Polysaccharide peaks were observed at 1,020 and 1,080 cm$^{-1}$ for v CH–OH and v CH–OH which represent the unit of cellulose and hydroxyl group [7]. Treated cellulose-based papers were identified v$_{\text{sym}}$ Si–O–Si peak at 792 cm$^{-1}$ which suggests a formation of silicate network. However, v Si–O–C at 1,000 – 1,100 cm$^{-1}$ was not clearly identified. It might cause by the overlapping of v polysaccharide of cellulose [7-8]. Moreover, intensity of v O–H of treated sample was decreased according to weaker signal at 3,333 – 3,365 cm$^{-1}$. This can be assumed that hydroxyl group on surface of sample were functionalized and formed silicate framework as same as stronger signal of v$_{\text{sym}}$ Si–O–Si at 792 cm$^{-1}$ and stronger signal of v C–O at 1233 cm$^{-1}$ were detected.
Figure 2. FTIR spectra of untreated and treated cellulose-based paper at 0, 15 minutes, 1 hour, 4, and 24 hours (left), an increased $\nu$ C-O signal (A) and $\nu_{\text{sym}}$ Si-O-Si (B). $\nu =$ stretching vibration and $\nu_{\text{sym}} =$ symmetric stretching vibration.

3.3. Weight Percent Gain (WPG)

Figure 3. Development of weight percent gain (WPG) of cellulose-based paper treated with sodium silicate for various immersion time.
Figure 3 showed the effect of immersion time to weight percent gain (WPG) as a function of immersion time. With increasing of immersion time, WPG was developed into two different periods. Firstly, after immersed sample for 15 – 30 min, WPG was increasing up to 25% which refer to the existent of flame retardant particles inside sample. Secondly, the highest WPG of 40% was obtained at 1 hr immersion which diffusion reached a saturation according to very thin sample. A slightly decreasing of WPG was affected by leaching of lignin in paper since it can dissolve in basic condition (pH 11.5) [9].

3.4. Flame Retardant Performance

Figure 4 showed the appearance of untreated and treated paper with different immersion time before and after flame test. Untreated paper took 8 sec of total combustion for completely burning. Whereas all treated papers, the total combustion time were increased to 10 sec for sample immersed for 30 min, 12 sec for sample immersed for 2, 4, 16 and 24 hrs, and 14 sec for sample immersed for 15 min and 1 hr with remain residue char. According to longer combustion time, it is indicated that higher flame retardant property of treated paper and immersion for 15 min were found to be sufficient to improve flame retardant property of cellulose-based paper. It should be noted that the unburnt area is a stainless forceps pinning area.

4. Conclusion

Sodium silicate-SiO$_2$ showed an improving flame retardant property of cellulose-based papers after treatment. SEM confirmed the existence of sodium silicate incorporate with SiO$_2$ inside sample. FTIR spectra suggested a formation of silicate network between paper and silicate-SiO$_2$, as evidenced by $\nu_{sym}$ Si-O-Si at 792 cm$^{-1}$. The weight percent gain (WPG) was increased with increasing immersion time from 15 min to 1 hr then slightly decreased as caused by leaching of lignin in strong basic condition. The total combustion time of treated papers were significantly increased to 14 sec in cases of immersed sample for 15 min and 1 hr and partially increased to 10 – 12 sec for other treatments. In conclusion, the 15 min to 1 hr of immersion time were sufficient to improve flame retardant property of paper without changing appearance.
Acknowledgement
I would like to thank for all the advised and supports from my advisor and laboratory’s colleagues and financial support from scholarship for young scientists which responding by faculty of Science, Mahidol university.

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