

# Co-application of Sodium Polyphosphate and Chitosan to Improve Flame Retardancy of Cotton Fabric

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An attempt to improve the durability of the flame retardancy to washing of water soluble phosphate-based flame retardant on cotton fabric was studied. In this study, the poorly substantive phosphate treated fabric was further padded with chitosan solution. After drying, the chitosan formed film layer covering the fabric surface, resulting in the improved retention of the water soluble phosphate as evaluated by washing test and then followed by SEM analysis. The flame retardancy was then evaluated by LOI determination and burning behavior including 45-degree flame spread rate were also investigated. In the study, the co-application of chitosan and sodium polyphosphate improved the durability of the flame retardancy in the cotton fabric by decreasing 45-degree flame spread rate about 2.5 times and slightly increasing the LOI values from 17 to 19 when compared to the untreated cotton fabric. Moreover, a carbonaceous char was formed and the afterglow was suppressed.

**Key words:** Cotton fabric, polyphosphate compound, chitosan and flame retardancy

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## การใช้สารประกอบโซเดียมพอลิฟอสเฟตร่วมกับไคโตซาน เพื่อปรับปรุงสมบัติการหน่วงไฟของผ้าฝ้าย

สิริรัตน์ จารุจินดา กาวี ศรีกุลกิจ และ จูติพร โมวัฒน์นะ (2548)

วารสารวิจัยวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย 30(1)

งานวิจัยนี้เป็นการปรับปรุงให้ผ้าฝ้ายที่ตกแต่งหน่วงไฟด้วยสารประกอบโซเดียมพอลิฟอสเฟตร่วมกับไคโตซานมีสมบัติหน่วงไฟที่คงทนต่อการซักล้าง โดยทำการจุ่มอัดผ้าฝ้ายด้วยสารประกอบโซเดียมพอลิฟอสเฟตและอบด้วยความร้อนก่อน จากนั้นจึงนำไปจุ่มอัดอีกครั้งด้วยสารละลายไคโตซาน หลังการอบให้ความร้อนไคโตซานจะเกิดเป็นชั้นฟิล์มเคลือบผิวผ้า และเมื่อนำผ้าฝ้ายไปผ่านการซักล้างและตรวจสอบด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด พบว่าชั้นฟิล์มที่เกิดขึ้นนี้สามารถเก็บกักสารประกอบฟอสเฟตที่ละลายน้ำได้ให้คงอยู่ภายในเส้นใยผ้า ด้วยเหตุผลนี้จึงทำให้การใช้สารประกอบโซเดียมพอลิฟอสเฟตร่วมกับไคโตซานสามารถปรับปรุงผ้าฝ้ายให้มีสมบัติหน่วงไฟที่คงทนต่อการซักล้าง โดยเมื่อนำผ้าฝ้ายที่ผ่านการตกแต่งหน่วงไฟมาทดสอบหาค่า LOI ศึกษาพฤติกรรมการลุกไหม้และหาอัตราเร็วในการลุกลามของเปลวไฟแนว 45 องศา พบว่าผ้าฝ้ายซึ่งตกแต่งหน่วงไฟด้วยสารประกอบโซเดียมพอลิฟอสเฟตร่วมกับไคโตซานที่ผ่านการซักล้างจะยังคงมีอัตราเร็วในการลุกลามของเปลวไฟแนว 45 องศาใกล้เคียงกับที่ไม่ได้ผ่านการซักล้าง โดยมีอัตราเร็วลดลงถึง 2.5 เท่า เมื่อเปรียบเทียบกับผ้าฝ้ายที่ไม่ได้ผ่านการตกแต่งหน่วงไฟ เช่นเดียวกับค่า LOI ที่มีค่าประมาณ 19 ซึ่งสูงกว่าผ้าฝ้ายที่ไม่ได้ผ่านการตกแต่งหน่วงไฟซึ่งมีค่า LOI เพียง 17 ยิ่งกว่านั้นยังพบว่าเกิดถ่านคาร์บอนในปริมาณที่เพิ่มขึ้นในขณะที่การคุ้แดงลดลง

**คำสำคัญ** ผ้าฝ้าย สารประกอบพอลิฟอสเฟต ไคโตซาน สมบัติหน่วงไฟ



## INTRODUCTION

Cotton is the most important textile fiber because of its comfort and worldwide consumption. However, it ignites easily and is frequently implicated in fire. In fires cotton products, such as apparel, curtains, bedclothes, and upholstered furniture, become quickly engulfed and are difficult to extinguish. Since fire accidents cause injuries and fatalities and also devastate property, considerable efforts have been made to develop flame-retardant cotton.

The use of halogen-based flame retardants to reduce the flammability of cotton is one of the most efficient ways of reducing the fire hazard. However, because of their corrosivity, the presence of dioxin, a carcinogen, and suspected smoke toxicity by products such as HBr and HCl, many European countries such as Sweden and Germany have legislated regulations to restrict halogen-based flame-retarded textile products.<sup>(1)</sup> Consequently, public interest concerning environmentally friendly, non-halogen-based flame retardants have been increasing.

Phosphorus-based flame retardants have been a major source of interest to replace halogen compounds because of their environmentally friendly by-products and their low toxicity. Also their low production of smoke in fire furthers their appeal. They are highly effective flame retardants for cellulose and cellulose derivatives. These compounds promote dehydration and char formation.<sup>(2)</sup>

In our previous study,<sup>(3)</sup> cotton fabric treated with 3% of phosphoric acid exhibited good flame retardancy and acceptable tensile strength retention. The flame was self-extinguished after removing the ignition source. However, the durability of the flame retardancy to washing was, unfortunately, poor due to the water solubility of the phosphoric acid. Moreover, it was found that the fabric turned yellow and became tender when the concentration of phosphoric acid increased.

An attempt to improve the durability of the flame retardancy to washing was further investigated. In this study, chitosan, which is a natural biopolymer containing a hydroxyl group and an amino group, was co-applied with sodium polyphosphate onto cotton fabric using pad-dry process in order to overcome the above mentioned deficiency. Due to the ionic-ionic attraction, chitosan could retain the phosphoric acid. Moreover, due to the presence of amino nitrogen, it was expected that the co-application of chitosan would impart a synergistic activity

with the phosphoric acids by enhancing the formation of intumescent chars.<sup>(2,4)</sup> The surface characterization of the treated cotton fabrics was examined to analyze the effect of chitosan/sodium polyphosphate on the fabric surface using SEM analysis. The durability of the flame retardancy to washing of the treated cotton fabrics was then examined by conducting flammability tests such as the 45-degree flame spread rate test and the LOI determination.

## EXPERIMENTAL

### Materials

A bleached plain weave, medium-weight (136 g m<sup>-2</sup>), cotton fabric was purchased from Boonchuay Co., Ltd. The densities of the test fabric in the direction of weft and warp yarns were 59 and 65 yarns in<sup>-2</sup>, respectively.

Sodium polyphosphate, the non-durable flame retardant, was supplied by VPC group (Thailand). Flake grade chitosan with a molecular weight of 800,000 g/mole and 85% degree of deacetylation was purchased from Ebase Co., Ltd (Thailand). Analytical grades of acetic acid and potassium persulphate were bought from BHD Laboratory and M&B Laboratory Chemicals, respectively. The crosslinking agent, ethylenediamine tetramethacrylate, was provided by Modern Dyestuffs and Pigments Co., Ltd (Thailand).

### The application of sodium polyphosphate and chitosan to cotton fabric

Bleached woven cotton fabrics were first treated with 5 wt% sodium polyphosphate solution and subsequently to the chitosan solution using a pad mangle set to a pressure nip at 80 percent wet pick up. Then the polyphosphate treated fabric was further treated with a chitosan solution containing the crosslinking agent followed by drying and curing at 60°C for 5 min. The preparation of the chitosan solution was typically carried out as follows: The weighed chitosan flake was dissolved in 8%(v/v) acetic acid aqueous solution under stirring. The amount of crosslinking agent calculated based on 0.5, 1.0, 1.5, and 2.0% of chitosan was added while continuously stirring to obtain homogenous solution. Finally, the dissolved potassium persulphate was added quickly and then the final solution was applied to the cotton fabric immediately in order to avoid the prepolymerization of the crosslinking agent. The detailed formulations of each recipe are given in Table 1.

**Table 1. Formulations of flame retardant finishing.**

Formulation	Sodium polyphosphate (wt%)	Chitosan (wt%)	Acetic acid %(v/v)	Crosslinking agent (wt% based on chitosan)	Potassium persulphate (wt% based on chitosan)
UT	0	0	0	0	0
PP	5	0	0	0	0
C	0	2	8	0	0
PPC	5	2	8	0	0
PPCX1	5	2	8	0.5	5
PPCX2	5	2	8	1	5
PPCX3	5	2	8	1.5	5
PPCX4	5	2	8	2	5

**Washing test**

To study the durability of the flame retardancy to washing, the treated cotton fabric was washed according to TIS-121 (3-1975) using non-ionic detergent  $1 \text{ g l}^{-1}$  at  $50^\circ\text{C}$  for 30 min. We then rinsed the fabric with running water for 10 min. The fabric was dried at  $60^\circ\text{C}$  for 5 min and placed in a desiccator for more than 24 hours before conducting the flammability test.

**Surface characterization**

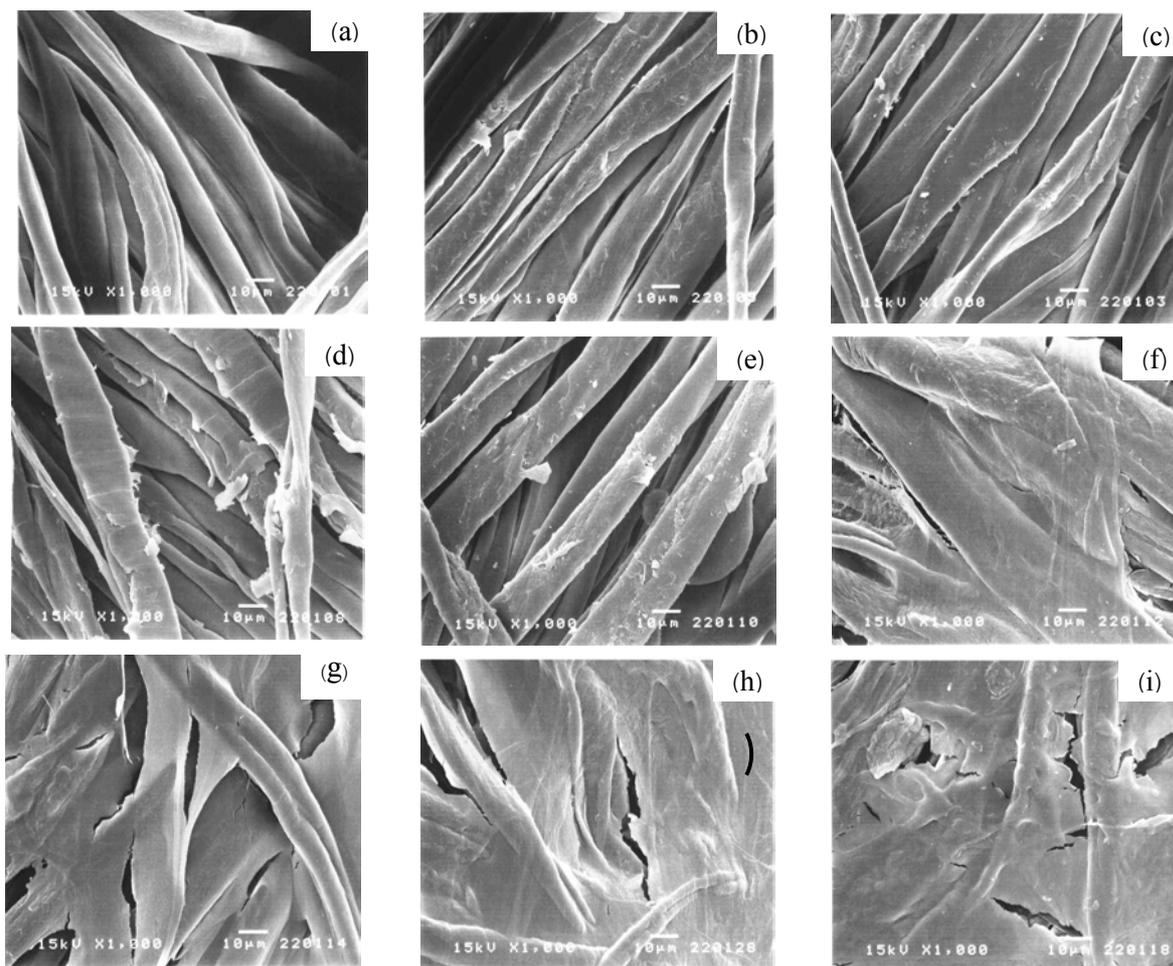
To determine the effect of sodium polyphosphate and chitosan on the durability of the flame retardancy to washing, scanning electron microscope (SEM) examinations of the fabric surfaces were made. Samples were sputter-coated with gold and examinations were done at 15 kV and at a magnification of 1000X.

**Flammability test*****Burning behavior and 45-degree flame spread rate***

Burning behavior and 45-degree flame spread rate of untreated and treated cotton fabrics before and after washing were examined using the Atlas 45° Automatic Flammability Tester according to ASTM D1230 (in this study, the ignition time was 5 sec) at  $30^\circ\text{C}$  and  $62 \pm 3\%$  RH. The burning behavior was recorded by digital video camera.

***Limiting oxygen index (LOI) values***

In order to investigate the flammability of untreated and treated cotton fabrics before and after washing, LOI values were determined using the Stanton Redcroft Limiting Oxygen Indexer according to ASTM D 2863-91.



**Figure 1. SEM micrographs of cotton fabrics (1,000 x): (a) untreated (b) treated with sodium polyphosphate (before washing) (c) treated with sodium polyphosphate (after washing) (d) treated with chitosan (before washing) (e) treated with chitosan (after washing) (f) treated with chitosan/sodium polyphosphate (before washing) (g) treated with chitosan/sodium polyphosphate (after washing) (h) treated with chitosan/sodium polyphosphate with the crosslinking agent (before washing) (i) treated with chitosan/sodium polyphosphate with the crosslinking agent (after washing).**

## RESULTS AND DISCUSSION

### **Durability assessment of sodium polyphosphate on treated cotton fabric**

The treated fabrics after washing were examined using scanning electron microscopy (SEM). The results are illustrated in Figures 1(a)-(i). Figures 1(a) and (b) represent the micrographs of untreated fabric and sodium polyphosphate treated fabric, respectively. It can be seen that polyphosphate agglomerates are found scattered on the fiber surface. These precipitates were largely removed after washing (Figure 1(c)),

indicating its poor attraction on the fiber surface. Similarly, the SEM micrographs of the chitosan treated fabric obtained before and after washing (Figures 1(d) and (e)) showed similar results to the polyphosphate treated fabric in terms of the chitosan particle distribution and fastness. In the case of the chitosan/ polyphosphate treated fabric, the formation of a chitosan film covering the fabric surface is clearly observed (Figures 1 (f) and (h)). The test of durability of the chitosan toward washing was performed according to

TIS-121 (3-1975) standard test and the results are revealed (Figures 1(g) and (i)). As can be seen, the chitosan coating endured the standard washing test to some extent indicating the moderate attachment of chitosan on the fabric surface. Therefore, it was expected that the layer of chitosan film could improve the wash fastness of sodium polyphosphate by acting as a barrier to slow its diffusion out of the fabric. In the presence of the crosslinking agent, the interpenetrating polymeric network film of the chitosan (IPN<sub>s</sub>) was produced as a result of the interpenetrating polymerization of the crosslinking agent inside the chitosan matrix.<sup>(5)</sup> It was determined that the IPN film exhibited higher performance for sodium polyphosphate retention due to its network structure compared to the chitosan/polyphosphate system. The SEM results obtained after the washing test (Figure 1 (i)) revealed that the IPN film shows the better resistance to washing, judged by the fact that there is little change in the film morphology such as cracking. The effect of IPN chitosan film on the flame retardancy properties of sodium polyphosphate is discussed in the following section.

### **Flammability test**

#### ***Burning behavior and 45-degree flame spread rate***

The results show that the burning behavior of the untreated cotton fabric included very fast ignition and flame spread. Furthermore, afterglow which is as great a fire hazard as the flaming of the volatile products was observed. The flame spread very quickly at the rate of 0.84 cm s<sup>-1</sup> and burned the entire fabric. In the case of fabric treated with chitosan solution alone, it was found that the treated fabric ignited immediately, but flame spread rate was slightly lower. Some amount of char was formed and afterglow was observed. It can be explained that the primary amino nitrogen of chitosan may decompose to ammonia which is a non-flammable gas which dilutes the flammable gas during heating. Therefore, flame spread rate was slightly lower than that of the untreated cotton fabric.

In the matter of fabric treated with sodium polyphosphate alone, its burning behavior was similar to the untreated one but flame thickness was less. Also, flame spread rate of 0.35 cm s<sup>-1</sup> was much lower than that of the untreated one by about 2.5 times and afterglow was not observed. In addition, when the flame was extinguished, a large amount of char was formed. It can be

explained that when the fabric was heated, sodium polyphosphate decomposed to phosphoric acid or polyphosphoric acid. These generated acids can dehydrate cellulose and transesterify the carboxyl group of cellulose and finally form significant amounts of char. Moreover, these acids can form a molten viscous surface layer. This layer acts as an insulation layer, protecting the fabric from flame, blocking oxygen and preventing further decomposition of the fabric. The water removed can also dilute the flammable gases.<sup>(6)</sup> The polyphosphate used in this study was sodium polyphosphate; its effectiveness as a flame retardant is less than phosphoric acid and ammonium phosphate. In addition, the more highly polymerized the phosphate, the less effective it is as a flame retardant. Its very moderate flame retardancy may be attributed to the volatilization of crystal water at the temperature of ignition. However, it is very effective in suppressing the afterglow. This small amount of phosphorus catalyzes the oxidation of the carbon char to carbon monoxide instead of carbon dioxide during pyrolysis. The lower exothermicity of the former reaction is not sufficient to maintain the continued oxidation of the char.<sup>(7)</sup>

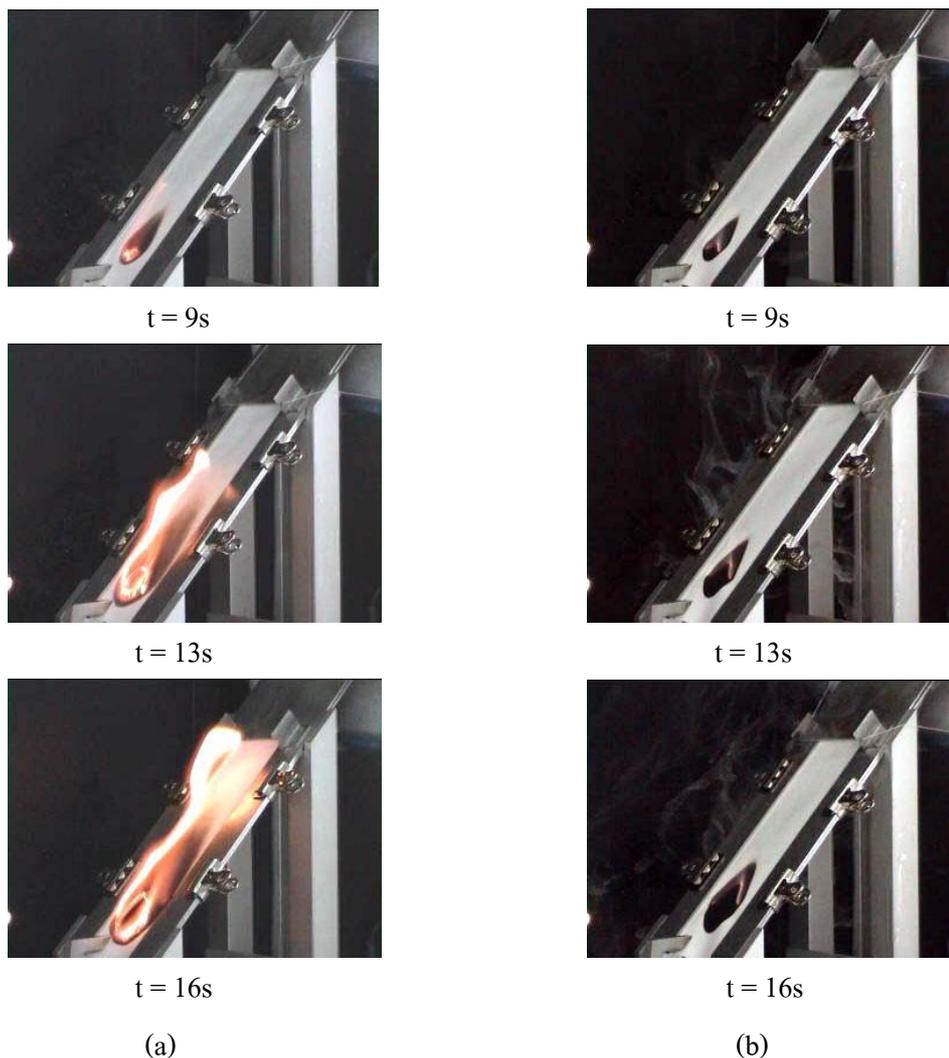
With respect to fabric treated with chitosan/sodium polyphosphate solution with and without crosslinking agents, it was found that its burning behavior and flame spread rate was also similar to the treated one with sodium polyphosphate alone. The flame spread rate ranged from 0.32 to 0.36 cm s<sup>-1</sup> and was lower than that of the untreated one by about 2.5 times and afterglow was not observed. A large amount of char was formed. It can be attributed to the nitrogen component in chitosan which may not impart as a synergist with phosphorus. Figure 2 shows the comparison of the burning behavior of untreated and treated cotton fabrics with chitosan/sodium polyphosphate.

In the case of durability of flame retardancy to washing, it was found that the burning behavior of fabric treated with chitosan solution alone was unchanged but flame spread rate slightly increased from 0.73 to 0.81 cm s<sup>-1</sup>. The fabric treated with sodium polyphosphate alone lost its flame retardancy. The fabric ignited immediately and burned very strongly with white smoke. Flame spread rate increased from 0.35 to 0.82 cm s<sup>-1</sup> which was nearly the same rate as the untreated sample. Very little char was observed after removing the ignition source. This effect may be caused by the loss of

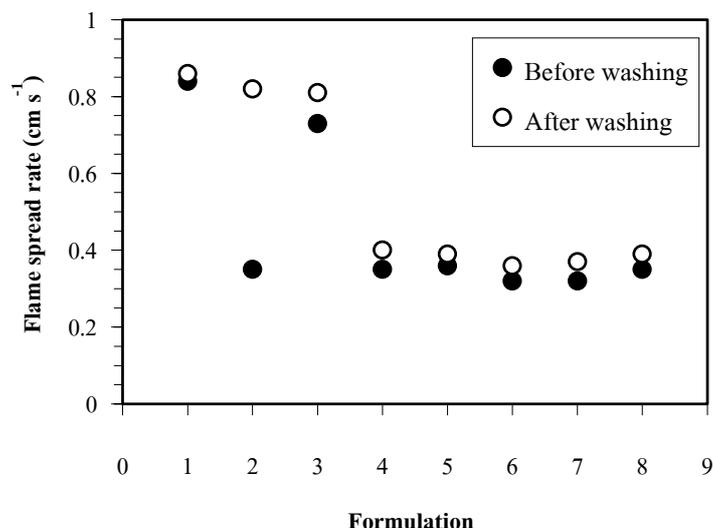
sodium polyphosphate during washing due to its very good solubility in water.

Interestingly, it was found that the fabric treated with chitosan/sodium polyphosphate solution with and without the crosslinking agent enhanced the durability of the flame retardancy to washing. Fabric was ignited within 2 sec and

slightly burned with white smoke. The flame spread rate increased from 0.36 to 0.40 cm s<sup>-1</sup>. A large amount of thick char was observed after removing the ignition source. Figure 3 shows the comparison of 45-degree flame spread rate of untreated and treated cotton fabrics before and after washing.



**Figure 2. Comparison of burning behavior between untreated and treated cotton fabrics at various times (a) untreated cotton fabric (b) treated cotton fabric using chitosan/sodium polyphosphate.**



**Figure 3.** Comparison of 45-degree flame spread rate of untreated and treated cotton fabrics with chitosan/sodium polyphosphate (before and after washing).

Formulation 1 = untreated cotton    Formulation 2 = PP    Formulation 3 = C  
 Formulation 4 = PPC    Formulation 5 = PPCX1    Formulation 6 = PPCX2  
 Formulation 7 = PPCX3    Formulation 8 = PPCX4

**Table 2.** LOI values of untreated and treated cotton fabrics with chitosan/sodium polyphosphate (before and after washing).

Formulation	Before washing		After washing	
	% add-on	LOI	% add-on	LOI
UT	0	17.1	0	17.1
PP	4.45	22.1	1.46	17.2
C	2.91	17.2	1.09	17.2
PPC	7.32	20.1	3.31	18.7
PPCX1	7.49	20.3	3.96	19.0
PPCX2	7.68	20.7	4.48	19.3
PPCX3	7.62	20.6	4.45	19.1
PPCX4	7.45	20.4	3.54	18.9

**LOI values**

LOI, which is a measure of flammability of the samples, is the minimum amount of oxygen in an oxygen/nitrogen gas stream mixture that supports combustion. Fibers having LOI values of 21 or below ignite easily and burn rapidly in air (containing 20.8% oxygen). Those with LOI values above 21 ignite and burn more slowly and generally when LOI values increase above approximately 26-28%, fibers may be considered

to be flame retardant. The effect of chitosan/sodium polyphosphate on flame retardancy can be assessed by considering the LOI values. In this study, the LOI values, measured at 29°C and 46% relative humidity, are given in Table 2 and the results were in agreement with the burning behavior. It is seen that the LOI values of 17 (before and after washing) of cotton fabrics treated with chitosan

solution alone were equal to the LOI value of untreated ones. This can be attributed to the fact that the primary amino nitrogen of chitosan has no significant contribution to the flame retardancy of cotton fabric.

In the matter of cotton fabrics treated with sodium polyphosphate alone, it was found that the LOI values were 22 and 17 before and after washing, respectively. One reason for this may be the fact that sodium polyphosphate acts as a char-forming flame retardant; however, LOI values increased to only 22 due to the lower effectiveness of sodium polyphosphate as a flame retardant than phosphoric acid and ammonium phosphate.<sup>(7)</sup> Nevertheless, cotton fabric treated with sodium polyphosphate alone lost its flame retardancy after washing as indicated by the LOI value of 17 which was the same value as the untreated cotton. This may be attributed to the loss of sodium polyphosphate from the fabric during washing due to its very good solubility in water.

In the matter of cotton fabrics treated with the co-application of chitosan/sodium polyphosphate with and without the crosslinking agent, it was found that their LOI values before and after washing were not significantly different. The LOI values before washing were approximately 20.5 which were higher than that of the untreated fabric. Interestingly, the LOI values after washing slightly decreased to approximately 19 but were still higher than that of the untreated one. It is indicated that the co-application of chitosan/sodium polyphosphate with and without a crosslinking agent could improve the durability of flame retardancy to washing. This can be explained in that the moderate attachment of chitosan film on fabric treated with chitosan/polyphosphate without a crosslinking agent observed by SEM (Figure 1(g)) could improve the wash fastness of sodium polyphosphate by acting as the barrier slowing the diffusion out of fabric. Accordingly, the expected IPN film of chitosan produced as a result of interpenetrating polymerization of crosslinking agent inside the chitosan matrix film on the fabric treated with chitosan/polyphosphate with a crosslinking agent also exhibited better resistance to washing as observed by SEM (Figure 1(i)). This was judged by the fact that there is little change in the film morphology such as cracking. Although the crosslinking agent contributed to better resistance to washing, flame retardancy performance, such as the LOI value, burning behavior and flame spread rate were not

significantly different. Therefore, it is inferred that the crosslinking agent may be not necessary in the co-application of chitosan/sodium polyphosphate to cotton fabric to improve the durability of the flame retardancy to washing. It has to be noted that the co-application of chitosan/sodium polyphosphate treated fabric exhibited only a moderate degree of flame retardancy performance since it is generally accepted that materials with an LOI value of greater than 26 are considered to be flame retarded.<sup>(8)</sup>

## CONCLUSIONS

This study shows that the co-application of chitosan/sodium polyphosphate onto cotton fabric could improve the durability of sodium polyphosphate to washing as a result of the formation of the chitosan film layer covering the fabric surface, whereas, the application of chitosan alone could not exhibit such film layer (observed by SEM). The film layer was capable of retaining the water soluble phosphate compound inside the cotton fiber. Furthermore, a crosslinking agent may be not necessary in the co-application of chitosan/sodium polyphosphate treated cotton fabric to improve the durability of the flame retardancy to washing. The system improved the durability of flame retardancy of cotton fabric to washing by decreasing 45-degree flame spread rate ( $0.36 - 0.40 \text{ cm s}^{-1}$ ) about 2.5 times and slightly increasing LOI values from 17 to 19 when compared to the untreated fabric. Moreover, a carbonaceous char was formed and the afterglow was suppressed. However, it has to be noted that the co-application of chitosan/sodium polyphosphate treated fabric exhibited only a moderate degree of flame retardancy performance.

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