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Synergistic Effect of Ammonium Polyphosphate and Human Hair Keratin on Thermal and Flame Retardant Properties of Cotton Fabric

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Abstract: Wool keratin has natural flame resistant properties such as higher ignition temperature and limiting oxygen index than other natural fibers. In this study, keratin extracted from human hair was used as a flame retardant onto cotton fabric. Moreover, the keratin was also combined with Ammonium Polyphosphate (AP423) to study the synergistic flame retardant action onto cotton fabric. The extracted human hair keratin and finished cotton fabric were then characterized by FTIR and TGA. The flame retardancy was investigated using UL94 tester according to ASTM D 4804 thin material vertical burning test. Cotton fabric treated with 10% AP423 alone exhibited excellent flame retardancy (VTM 0) whereas with 5% extracted keratin alone did not. However, the addition of only 5% AP 423 and 5% extracted keratin improved flame retardancy from no rating to VTM 1.

Key words: Keratin, ammonium polyphosphate, cotton fabric, TGA, UL94 VTM

INTRODUCTION

One of the major problems in textiles fibers is the flammable behavior of fibers. Natural fibers such as cotton, linen and silk burn vigorously and some synthetic fibers such as polyester and nylon burn slowly but melt and drip hot molten polymers. Wool is more difficult to ignite and burn than cotton and some synthetic fibers. Wool composes of α-keratin which has α-helix structure and found in hair, nail, horn, hooves and epidermis mammals. Wool has natural flame resistant properties such as high ignition temperature (570-600°C), low heat of combustion (20.5 kJ g^{-1}), low flame temperature (680°C) and high Limiting Oxygen Index (LOI) (25-28%) (Tian *et al*., 2003). Therefore, keratin could be applied as a flame retardant onto cotton fabric. Keratin is an insoluble protein and can withstand light, water and weather changes because it has disulfide bonds cross-linking between cystine amino acid in its structures. Applications of keratin are commonly used in cosmetics and biomaterials because of its special properties such as biocompatibility, biodegradability, mechanical durability and availability (Rouse and Van-Dyke, 2010; Hill *et al*., 2010).

Ammonium Polyphosphate (APP) is a phosphorus-based flame retardant which has two modes of action in flame retardancy materials, gas theory and dehydration theory. In gas theory, when APP was heated, non-flammable gas (NH_3) was released to dilute oxygen in pyrolysis. In dehydration theory, APP decomposed to phosphoric acid or polyphosphoric acid and then dehydrated cellulose to form char. Moreover, APP is commonly used as a blowing agent and acid source in the intumescent system (Xia *et al*., 2014; Dittrich *et al*., 2014).

In this study, human hair keratin (from commercial source and from extraction by using Shindai solution) was combined with a commercial Ammonium Polyphosphate (AP423) onto cotton fabric using pad-dry-cure process. The synergistic effect of ammonium polyphosphate and keratin on thermal and flame retardant properties of cotton fabric was focused non-flammable gases of keratin (NH_3 and SO_2) were expected to liberate when AP423 and keratin were heated to form intumescent char (Charuchinda *et al*., 2005; Gaan *et al*., 2008). The functional groups of AP423, keratin and finished cotton fabrics and thermal properties were characterized using Fourier Transform Infrared Spectroscopy (FTIR) and Thermal Gravimetric Analysis (TGA). The flame retardancy was investigated using UL94 tester according to ASTM D 4804 thin material vertical burning test.

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Table 1: Formulations of flame retardant finishing

Formulation	AP423 (wt%)	KC[a] (wt%)	KS[b] (wt%)	Formulation	AP423 (wt%)	KC[a] (wt%)	KS[b] (wt%)
Unfinished fabric	0	0	0	AP5	5	0	0
KC1	0	1	0	AP7	7	0	0
KC3	0	3	0	KC1AP5	5	1	0
KC5	0	5	0	KC3AP5	5	3	0
KS1	0	0	1	KC5AP5	5	5	0
KS3	0	0	3	KS1AP5	5	0	1
KS5	0	0	5	KS3AP5	5	0	3
AP1	1	0	0	KS5AP5	5	0	5
AP3	3	0	0				

[a]Commercial keratin; [b]Crude keratin

MATERIALS AND METHODS

Experimental: Human hair waste was collected from local hair salon in Bangkok, Thailand. Urea, thiourea, 2-amino-2-hydroxymethylpropane-1,3-diol (Tris), 2-mercaptoethanol and n-hexane were purchased from Sigma-Aldrich. Spectra/Por® dialysis membrane (MWCO 6000-8000 Da) was purchased from Spectrum Laboratories, Inc. Filter Paper (grade 40:8 μm) was purchased from Whatman Ltd. Commercial human hair keratin (98% Hydrolyzed keratin powder) was purchased from Xi'an Aladdin Biological Technology Co., Ltd. Ammonium Polyphosphate (APP) was a micronized APP (phase II) with extremely low water solubility called Exolit® AP423 and was provided by Clariant International Ltd. A plain woven cotton fabric was purchased by Boonchuay Industial Co., Ltd.

Keratin extraction: The crude keratin used in this study was extracted from human hair based on Shindai method by using Shindai's solution containing 25 mM Tris, pH 8.5, 2.6 M thiourea, 5 M urea and 5% 2-mercaptoethanol at 50°C under atmospheric pressure for 72 h (Nakamura *et al*., 2002; Chaliewsak and Charuchinda, 2013). This extraction time was the optimal condition for providing the maximal dry weight yield and protein yield of the crude keratin.

AP423 and keratin solutions preparation: All solutions were prepared by diluting in distilled water and stirred with magnetic stirring bar. The detailed formulations of each solution are given in Table 1.

Cotton fabric finishing: Cotton fabric was finished with the prepared solutions using a padding mangle at 80-90% wet pick up and then cured at 110°C for 3 min.

Characterization: The functional group of AP423, keratin and finished cotton fabric were characterized using Fourier Transform Infrared spectroscopy (FTIR) in transmittance mode (Nicolet 6700, Thermo Scientific, USA). The thermal properties were investigated using Thermal Gravimetric Analysis (TGA) (Mettler-Toledo, USA) under nitrogen condition. The analyses were

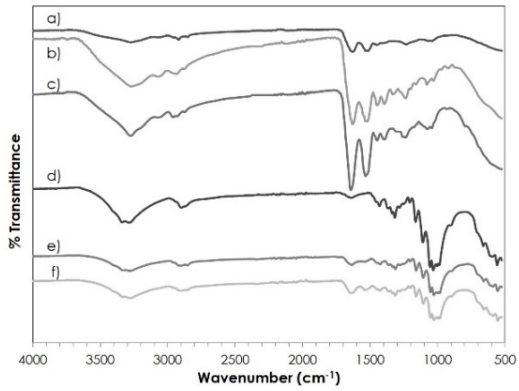

Fig. 1: FTIR spectra of a) human hair, b) commercial keratin, c) crude keratin, d) unfinished cotton fabric, finished cotton fabric e) with 5 wt% of commercial keratin and f) with 5 wt% of crude keratin

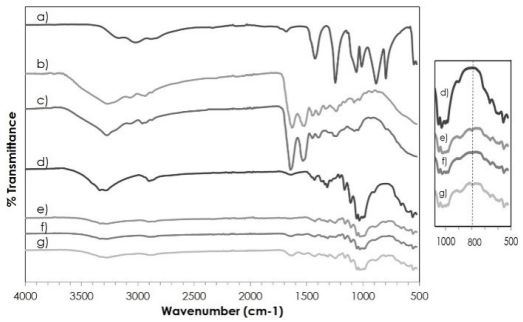

Fig. 2: FTIR spectra of a) AP423, b) commercial keratin, c) crude keratin, d) unfinished cotton fabric, finished cotton fabric e) with 5 wt% of AP423, f) with 5 wt% of AP423 and 5 wt% of commercial keratin and g) with 5 wt% of AP423 and 5 wt% of crude keratin

monitored between 50 and 800°C at a heating rate of 20°C min^{-1} and a gas flow rate of 20 mL min^{-1}. The flame retardancy was tested using UL94 tester (Atlas HVUL2 Horizontal Vertical Flame Chamber, SDL Atlas, Inc, USA) according to ASTM D 4804 thin material vertical burning test. The burning behavior was recorded by digital video camera.

RESULTS AND DISCUSSION

Functional group of AP423, keratin and finished cotton fabrics: FTIR spectra of AP423, keratin and the finished cotton fabrics are shown in Fig. 1 and 2. Both commercial keratin and crude keratin presented the similar absorption peaks as shown in human hair (3300 cm^{-1} (N-H and O-H), 2900 cm^{-1} (CH_2), 1635 cm^{-1} (amide I), 1525 cm^{-1} (amide II), 1222 cm^{-1} (amide III) and 1300-1000 cm^{-1} (S-S)) which are in agreement with wool keratin in the previous research work by Xu *et al.* (2006). Unfinished cotton fabric presented the absorption peaks at 3300 cm^{-1} (H-bond and O-H), 2800 cm^{-1} (C-H), 1600 cm^{-1} (carboxylate stretch) 1377 and 1270 cm^{-1} (C-H) and 1200-1000 cm^{-1} (C-O) (Chung *et al.*, 2004). The finished cotton fabrics with both commercial keratin and crude keratin presented the new characteristic peaks of keratin (1635 cm^{-1} (amide I) and 1525 cm^{-1} (amide II)) on unfinished cotton fabric. AP423 presented the absorption peaks at 3151, 2997 and 2796 cm^{-1} (ammonium group), 1623 cm^{-1} (P-OH), 1404 cm^{-1} (NH_4^+ bending), 1238 cm^{-1} (P = O), 1050-1000 cm^{-1} (PO_3), 900-800 cm^{-1} (P-O) (Drevelle *et al.*, 2005; Carosio *et al.*, 2012). The finished cotton fabrics with AP423 presented the decrease in intensity of peaks around 3300 and 1200-1000 cm^{-1} with increase in the concentration of AP423 on the fabrics due to the dehydration between P-OH of AP423 and O-H of cotton fabric. In addition, the new absorption peaks at 800 cm^{-1} (P-O) due to the presence of AP423 was also presented. The combination of AP423 and commercial keratin onto cotton fabrics presented the decrease in intensity of peaks around 3300 and 1200-1000 cm^{-1} which was similar to the finished cotton fabric with AP423. In addition, the new absorption peaks at 1635 cm^{-1} (amide I) and 1525 cm^{-1} (amide II) of keratin were also presented on cotton fabric. The combination of AP423 and crude keratin onto cotton fabrics presented the similar peaks to the previous finished fabrics but the different characteristic peak at 800 cm^{-1} (P-O) was found because of the low dispersion of crude keratin and AP423.

Thermal degradation of AP423, keratin and finished cotton fabrics: The thermal degradation of AP423 and the finished cotton fabrics are shown in Fig. 3 AP423 presented two steps of weight loss. The first step started about 175°C to release ammonia gas (NH_3) and water. The second step occurred about 600°C that was the decomposition temperature of AP423 to release volatile of phosphorus pentoxide (P_2O_5) and phosphoric acid or polyphosphoric acid (Charuchinda *et al.*, 2005; Hapuarachchi and Peijs, 2009). Moreover, AP423 presented a large amount of char residue at 39.5%. In case of finished cotton fabrics, all thermal degradation of fabrics finished with AP423 presented two steps that are evaporation step and degradation step. The finished cotton started to degrade about 250°C and char residue increased when amount of AP423 increased due to nonflammable gases (NH_3) released to dilute flammable gases in pyrolysis. It was found that the cotton fabric finished with 7 wt% of AP423 presented the highest amount of char residue (34%).

The thermal degradation of the finished cotton fabrics with commercial keratin are shown in Fig. 4 and crude keratin are shown in Fig. 5. Both commercial keratin and crude keratin presented two steps of weight loss. The first step was the evaporation step occurred below 100°C. The second step was the degradation step of keratin from about 200°C up to about 600°C to release nonflammable gases that are ammonia gas (NH_3) and sulfur dioxide gas (SO_2) (Brebu and Spiridon, 2011). Commercial keratin started to degrade at higher temperature (~250°C) than that of crude keratin (~200°C). Moreover, commercial keratin exhibited higher char residue (17.7%) than that of crude keratin (10%). All thermal degradation of finished cotton fabrics were similar to cotton fabric and presented two steps that are evaporation step and degradation step. The finished cotton fabrics started to degrade a similar temperature to cotton fabric at about 350°C and char residue increased when amount of keratin increased. The cotton fabric finished with 5 wt% of crude keratin presented higher amount of char residue (9.8%) than that of 5 wt% of commercial keratin (8.3%). This may be because crude keratin released nonflammable gases at lower temperature than that of commercial keratin which resulted in the interruption of the degradation of fabric.

The thermal degradation of cotton fabrics finished with AP423 and commercial keratin (KC5AP5) and crude keratin (KS5AP5) are shown in Fig. 6 and 7. All thermal degradation of finished cotton fabrics were similar to unfinished cotton fabric and presented two steps that are evaporation step and degradation step. The finished cotton fabrics started to degrade at about 260°C. The cotton fabric finished with 5 wt% of AP423 and 5 wt% of crude keratin (KS5AP5) presented higher amount of char residue (34%) than that of 5 wt% of AP423 and 5 wt% of

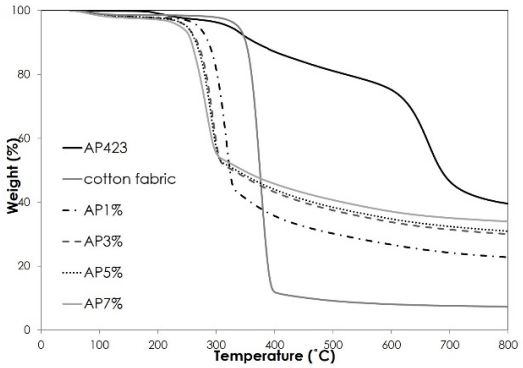

Fig. 3: TGA curve of AP423 and finished cotton fabrics with AP423

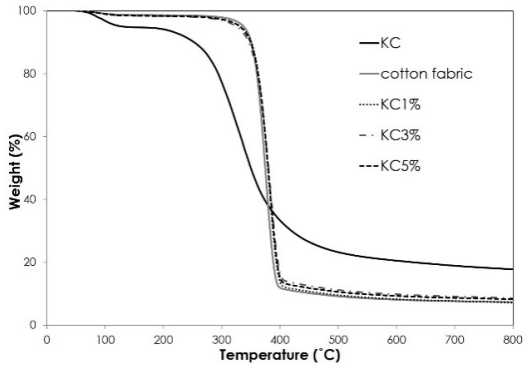

Fig. 4: TGA curve of commercial keratin (KC) and finished cotton fabrics with commercial keratin

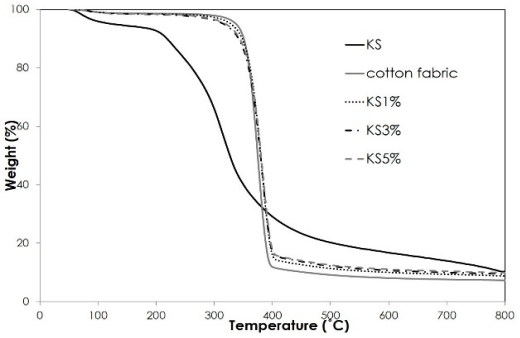

Fig. 5: TGA curve of crude keratin (KS) and finished cotton fabrics with crude keratin

commercial keratin (KC5AP5) (31.5%). This may be due to crude keratin released nonflammable gases at lower temperature than that of commercial keratin to impart synergist activity with AP423 and interrupt the degradation of fabric.

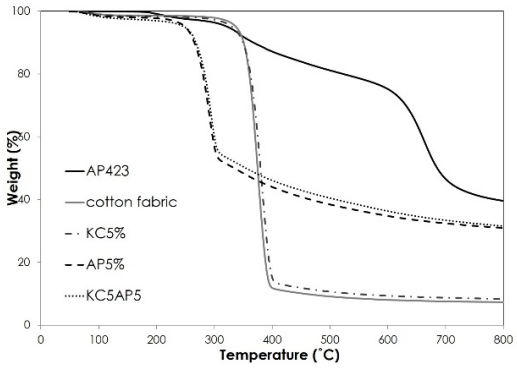

Fig. 6: TGA curve of finished cotton fabrics with AP423 and commercial keratin

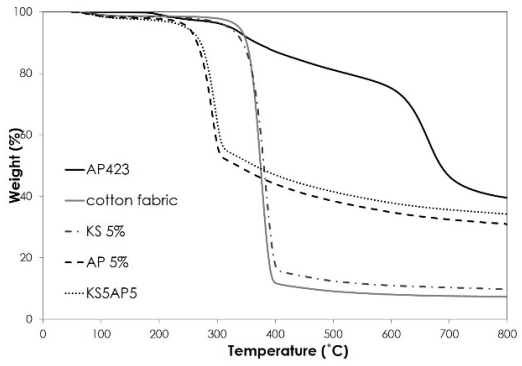

Fig. 7: TGA curve of finished cotton fabrics with AP423 and crude keratin

Flame retardant properties of finished cotton fabrics: Table 2 and 3 shows UL94 classifications of thin material in vertical burning test. The UL94 of unfinished cotton fabric and finished cotton fabrics with AP423 are shown in Table 4. Unfinished cotton fabric was UL94-rated as no rating because the fabric burned out. The afterglow of unfinished cotton fabric was observed for 49.72 sec. The cotton fabrics finished with 5 and 7 wt% of AP423 were UL94-rated as no rating and VTM-1, respectively. Afterglow were not observed. However, when the amount of AP423 increased to 10 wt%, the fabric was rated as VTM-0. The fabric burned after the second flame application <60 sec. Afterglow was not observed. This means that the fabric was classified as flame retardant fabric.

The UL94 of finished cotton fabrics with keratin and combination of AP423 and keratin are shown in Table 4 and 5. Both finished cotton fabrics with commercial keratin and crude keratin were UL94-rated as no rating as well as unfinished cotton fabric. The afterglow of cotton fabrics finished with 5 wt% of commercial keratin and 5

Table 2: Thermal degradation of finished cotton fabrics with AP423, commercial keratin (KC) and crude keratin (KS)

	1st degration (°C)		2nd degration (°C)			1st degration (°C)			2nd degration (°C)		
Variables	On set	End set	On set	End set	Char rersidule (%)	Formulation	On set	End set	On set	End set	Char rersidule (%)
Unfinished fabric	70	105	349	391	7.3	KC5	68	113	348	397	8.3
AP423	176	393	607	711	39.5	KS	65	91	205	386	10.0
AP1	64	106	273	326	22.7	KS1	71	117	351	398	8.8
AP3	63	106	253	305	30.0	KS3	69	118	341	397	9.4
AP5	64	105	255	302	31.0	KS5	70	110	342	398	9.8
AP7	63	108	251	297	34.0	KC3AP5	63	107	257	305	31.8
KC	71	116	247	408	17.7	KC5AP5	63	105	262	304	31.5
KC1	70	111	348	397	7.1	KS3AP5	62	110	256	301	33.2
KC3	68	114	342	399	8.6	KS5AP5	65	110	266	308	34.0

Table 3: Thin material vertical burning test classifications (ASTM D 4804 or ISO 9773)

Conditions	VTM-0	VTM-1	VTM-2
Afterflame time for each individual specimen (t1 or t2)	≤10 sec	≤30 sec	≤30 sec
Total afterflame time for any condition set (t1+t2 for 5 specimens)	≤50 sec	≤250 sec	≤250 sec
Afterflame plus afterglow time for each individual specimen after the second flame application (t2+t3)	≤30 sec	≤60 sec	≤60 sec
Afterflame or afterglow of any specimen up to the 125 mm mark (t1 or t3 (to 125 mm))	No	No	No
Cotton indicator ignited by flaming particles or drops	No	No	Yes

Table 4: UL94 of unfinished cotton fabric and finished cotton fabrics with AP423, commercial keratin and crude keratin

Conditions	Unfinished fabric	AP5%	AP7%	AP10%	KC5%	KS5%
t_1 or t_2	26.76 sec	14.68 sec	17.08 sec	9.2 sec	19.96 sec	23.46 sec
t_1+t_2 for 5 specimens	133.8 sec	73.4 sec	85.4 sec	46 sec	99.8 sec	117.3 sec
t_2+t_3	49.72 sec	0 sec	0 sec	0 sec	42.34 sec	39.28 sec
t_1 or t_3 (125 mm)	Yes	Yes	No	No	Yes	Yes
Cotton pad ignition	No	No	No	No	No	No
UL94 rating	No rating	No rating	VTM-1	VTM-0	No rating	No rating

Table 5: UL94 of finished cotton fabrics with combination of AP423 and keratin

Conditions	KC1AP5	KC3AP5	KC5AP5	KS1AP5	KS3AP5	KS5AP5
t_1 or t_2	13.8 sec	13.66 sec	14.72 sec	15.42 sec	13.34 sec	15.22sec
t_1+t_2 for 5 specimens	69 sec	68.3 sec	73.6 sec	77.1 sec	66.7 sec	76.1 sec
t_2+t_3	0 sec	0 sec	0 sec	0 sec	0 sec	0 sec
t_1 or t_3 (125 mm)	Yes	No	No	Yes	No	No
Cotton pad ignition	No	No	No	No	No	No
UL94 rating	No rating	VTM-1	VTM-1	No rating	VTM-1	VTM-1

wt% of crude keratin were observed for 42.34 and 39.28s, respectively. The combination of 5 wt% of AP423 and 3 wt% of keratin (KC3AP5 and KS3AP5) and 5 wt% of AP423 and 5 wt% of keratin (KC5AP5 and KS5AP5) onto cotton fabrics were UL94-rated as VTM-1 and afterglow were also not observed. The finished cotton fabric with 5 wt% of AP423 and 3 wt% of crude keratin (KS3AP5) presented the lowest afterflame time (13.34s). This may be due to crude keratin released nonflammable gases at lower temperature than commercial keratin which resulted in the interruption of the degradation of fabric. The synergistic effect of AP423 and keratin can be explained that when keratin was heated, non-flammable gases (NH_3 and SO_2) were released and increased non-flammable gas (NH_3) from AP423 to dilute oxygen in pyrolysis (Charuchinda *et al*., 2005; Gaan *et al*., 2008).

CONCLUSION

Cotton fabric was finished with 1, 3, 5 and 7 wt% of commercial ammonium polyphosphate (AP423), commercial human hair keratin and crude human hair keratin. FTIR spectra affirmed that the performance of AP423 and keratin onto the finished fabric. The thermal degradation rate of finished cotton fabrics decreased when the amount of AP423 and keratin increased. The combination of 5 wt% of AP423 and 3 wt% of crude keratin (KS3AP5) exhibited the lowest thermal degradation rate and the highest amount of char residue. Thus, thermal degradation of finished cotton fabrics depended on amount of AP423 and keratin and non-flammable gases release rate of keratin. UL94 flammability test of the finished cotton fabric with 10 wt% of AP423 was rated as VTM-0. This means that this finished fabric was classified as flame retardant fabric. However, the finished cotton fabric with 5 wt% of AP423 and 3 wt% of crude keratin (KS3AP5) was UL94 rated as VTM-1 and presented the lower afterflame time than that of the finished cotton fabrics with 5 wt% of AP423 alone and also with the same ratios of the combination of AP423 and commercial keratin. This may be due to crude keratin released nonflammable gases at lower temperature than commercial keratin and impart the synergistic effect with AP423. In future study, the intumescent system and char residue

analysis of cotton fabric finished with AP423 and keratin will be studied and used to better understand the synergistic effect of ammonium polyphosphate and keratin onto cotton fabric.

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