EFFECT OF OXYGEN PLASMA PRETREATMENT AND TITANIUM DIOXIDE OVERLAY COATING ON FLAME RETARDANT FINISHED COTTON FABRICS

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Flammability properties of plasma pretreated cotton fabrics subjected to flame-retardant treatment were studied. Plasma pretreatment, using an atmospheric pressure plasma jet (APPJ), was applied to cotton fabrics to enhance material properties, while retaining inherent advantages of the substrates. An organic phosphorus compound (flame-retardant agent, FR) together with a melamine resin (crosslinking agent, CL) and phosphoric acid (catalyst, PA) were used. Titanium dioxide (TiO_2) or nano-TiO_2 was used as a co-catalyst for cotton fabrics to improve treatment effectiveness and minimize side effects. Surface morphology of plasma pretreated cotton specimens subjected to flame-retardant treatment showed a roughened and wrinkled fabric surface with high deposition of the finishing agent, caused by an etching effect of plasma and attack of acidic FR. Combustibility of FR-CL-PA-TiO_2 and FR-CL-PA-Nano-TiO_2 treated fabrics was evaluated by a 45° flammability test. FR-CL-PA-treated specimens showed superior flame-retardancy, which was further improved by plasma pretreatment and addition of metal oxide as a co-catalyst. However, in comparison with the control sample, flame-retardant-treated cotton specimens had lower breaking load and tearing strength, resulting from side effects of the crosslinking agent used, while plasma pretreatment might compensate for the reduction in tensile strength caused by flame-retardant agents. In addition, both plasma pretreatment and metal oxide co-catalyst added in the flame-retardant finishing improved the crosslinking process between FR and cotton fabric, minimizing formation of free formaldehyde and allowing the use of FR in industry.

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INTRODUCTION

Textile materials have traditionally been known to be the major causes of spreading of fire because of their inflammability, as well as their ubiquitous presence in our daily lives, in the form of clothing, furnishing materials, household goods, and many other products (Siriviriyanun et al. 2008). Among different textile fibres, cotton, mainly composed of carbon, oxygen, and hydrogen, is used widely but has higher combustibility compared to other fibres. Coating of cotton products with chemicals is an easy and effective approach to reduce inflammability. Therefore, cotton fabric is often treated chemically to prevent ignition of fire by small flames, which often cause degradation of cotton at lower temperatures through the process of dehydration (Siriviriyanun et al.

2008; Wakelyn et al. 2004). Generally speaking, N-methylol dimethylphosphonopropionamide flame retardant agent (FR) is widely used, in combination with a melamine resin crosslinking agent (CL) and a catalyst (phosphoric acid, PA) to impart flame retardant properties to cotton fabrics (Yang et al. 2007). However, due to toxicological and environmental concerns, formaldehyde-based flame retardant agents are currently being phased out and replaced with other coating materials (Yang et al. 2007). It was proved that addition of a TiO_2/nano-TiO_2 co-catalyst could enhance crosslinking of components of the FR-CL-PA flame-retardant formulation (Lam et al. 2010a).

Plasma technologies can help retain inherent advantages of the substrates while enhancing materials properties. Plasma is partially ionised gas, which is overall neutral in nature, containing ions, electrons, and neutral particles produced by the interaction of electromagnetic field with gas under a specified pressure. The active species produced in plasma carry high energy that causes a sputtering or etching effect, which alters the characteristics of fibre surface. The treatment roughens the surface of the materials and is conducive to subsequent use of a large variety of chemically active functional groups (Hwang et al. 2005; Wang et al. 2008; Kaplan 2004; Rajpreet et al. 2004). Among various types of plasma treatments, atmospheric pressure plasma jet (APPJ) is widely used in the textile industry to modify the fabric surface in an environment friendly process that helps reduce use of chemicals and energy (Hwang et al. 2005; Wang et al. 2007; Bourbigot et al. 2007) In this study, detailed information concerning effects of plasma pretreatment on flame-retardant properties of cotton fabric, after FR-CL-PA treatment (with or without using TiO_2 as catalyst), are evaluated. Combustibility of flame-retardant-treated fabrics, evaluated by the 45° flammability test, was also studied, while mechanical strength was analysed by a grab test and the Elmendorf tearing test. Formaldehyde content and surface morphology of treated fabrics were also evaluated.

EXPERIMENTAL

Materials

100% semi-bleached plain weave cotton fabric (58 ends/cm, yarn count 40 tex, in warp; 58 picks/cm, yarn count 38 tex, in weft; fabric weight 175g/m^2), of size 30 cm x 30 cm was used. The flame-retardant agent and cellulose crosslinking agent used were an organic phosphorus compound (Pyrovatex CP New, FR) and a melamine resin (Knittex CHN, CL), both supplied by Huntsman Limited. Analytical reagent grade phosphoric acid (PA) that served as catalyst was supplied by Sigma-Aldrich Co. Co-catalysts used were micro-titanium dioxide (TiO_2, 2 μm diameter) and nano-titanium dioxide (nano-TiO_2, 100 nm diameter) obtained from UniChem Ltd and International Laboratory Ltd., respectively, both having purity of 99.5+%. The alkali was analytical reagent grade sodium carbonate supplied by Sigma-Aldrich Co.

Plasma Pretreatment

Plasma pretreatment of cotton fabric was carried out by an atmospheric pressure plasma jet apparatus, Atomflo 400 Plasma controller integrated with robot, manufactured by Surfx Technologies. The cotton fabric was moved automatically according to the

specified treatment speed. The machine produced a stable discharge at atmospheric pressure with radio frequency of 13.56 MHz. The treatment was carried out using a rectangular nozzle that covered an active area of 50.8 mm x 1mm, and was mounted vertically, above the cotton fabric. Helium and oxygen were used as carrier and reactive gas respectively. The plasma pretreatment of cotton fabric was conducted at different oxygen flow rates as shown in Table 1.

Table 1. Plasma Pretreatment Conditions

Treatment Symbol	Output power (W)	Substrate speed (mm/s)	Helium flow rate (L/min)	Oxygen flow rate (L/min)	Jet-to-substrate distance (mm)
PT1	120	10	30	0.2	3
PT2	120	10	30	0.4	3

Flame-retardant Two-bath Pad-Dry-Cure Treatment

Plasma pretreated cotton fabric samples were treated with different pad formulations as shown in Table 2. A two-bath method was used for the treatments. In the first bath, the fabrics were dipped and padded with flame-retardant agents (FR-CL or FR-CL-PA) until a wet pick-up of 80% was achieved at 25°C. The fabrics were then dried at 110 °C for 5 minutes. In the second bath, dipping and padding processes (80% wet pick up) were performed, using TiO_2 / nano-TiO_2 solution dispersed in 10% Matexil DN-VL (dispersing agent). Subsequently, padded fabrics were dried at 110 °C for 5 minutes and were then cured at 170 °C for 1 minute. After curing, the treated specimens were then neutralized with 30 g/L sodium carbonate for 0, 15, or 30 minutes at 50 °C. After neutralization, the specimens were rinsed in 50 °C running water. Finally, the fabrics were conditioned at 21±1 °C and 65±5% RH for 24 hours, prior to any further treatment.

Table 2. Flame-retardant Treatment Conditions

Sample Symbol	FR	CL	PA (85%)	TiO₂	Nano-TiO₂
F1	40%	5%			
F2	40%	5%	2.5%		
F4	40%	5%	2.5%	0.2%	
F6	40%	5%	2.5%	0.4%	
F24	40%	5%	2.5%		0.2%
F26	40%	5%	2.5%		0.4%

* Concentration percentage measured based on weight of volume.

Scanning Electron Microscopy (SEM)

The surface morphology of cotton fibres was examined with a JEOL JSM-6490 Scanning Electron Microscope, with an accelerating voltage of 20kV and a current of 10μA at a high magnification power up to 10000X.

45° Flammability Test

In a preliminary study, with some modification to the ASTM D1230-94 standard, it was found that a flame impingement time of 4 seconds was sufficient to cause some of the samples to "fail", thus providing a useful differentiation among samples in terms of their flammability. In addition to determining pass/fail of treated specimens, burning time, char length, and burning speed (char length divided by burning time) were studied based on the modified ASTM D1230-94 standard. In the present study, flammability of all specimens was measured using the 45° flammability tester for apparel textiles (The Govmark Organization, Inc.). The specimens were tested after home laundering for 0, 1, and 5 normal machine cycles at 27±3 °C and tumble dried, according to AATCC 135-2004. The specimens were inserted in a frame and held in the flammability tester at an angle of 45°. A standardized flame, of 16 mm flame length, was applied to the fabric surface near the lower end for 4 seconds.

Strength Tests

Tensile properties were measured in accordance with the ASTM D5034-95 standard using the constant-rate-of-extension (CRE) Instron 4411 tensile testing machine.

Tearing strength was measured with an Elmendorf Tearing Tester manufactured by the Thwing-Albert Instrument Co., according to the ASTM D1424-96 standard.

Determination of Formaldehyde

The amount of free formaldehyde and formaldehyde extracted partly through hydrolysis by means of a water extraction method was measured according to the ISO 14184-1-1999 method.

RESULTS AND DISCUSSION

Morphological Study

Figure 1a shows the morphological structure of the untreated cotton fibre at a magnification of 2000X. From longitudinal view, cotton fibre is flat with a twisted ribbon-like structure caused by spiraling of cellulose fibrils. The SEM images show some integrity in cotton fibres with smooth surface and normal spiral structure. The presence of natural folds running parallel along the cotton fibre axis is also observed.

Plasma treatment modifies the fabric surface by physical and chemical interactions. Plasma enhances roughness of the fibre surface due to an etching effect, which changes both morphology and roughness of the substrate surface, as presented in Figs. 1b-1c. The results show that there were some continuous micro-cracks and holes parallel to the direction of the fibre axis, and the fibre surface was severely eroded. This shows that plasma treatment increased the roughness of the fibre surface due to the etching effect, which increased with increase in oxygen flow rate, i.e. the etching effect shown in Fig. 1c is greater than Fig. 1b. When oxygen flow rate was increased from 0.2L/min to 0.4L/min, the concentration of active species in the plasma jet was increased, making the etching effect more pronounced.
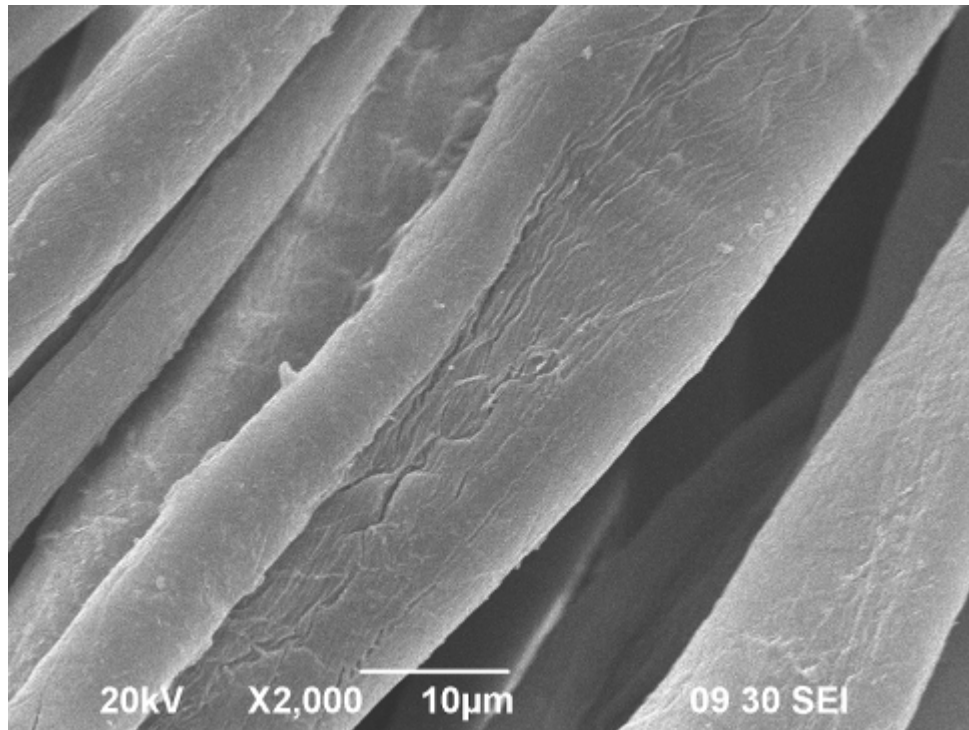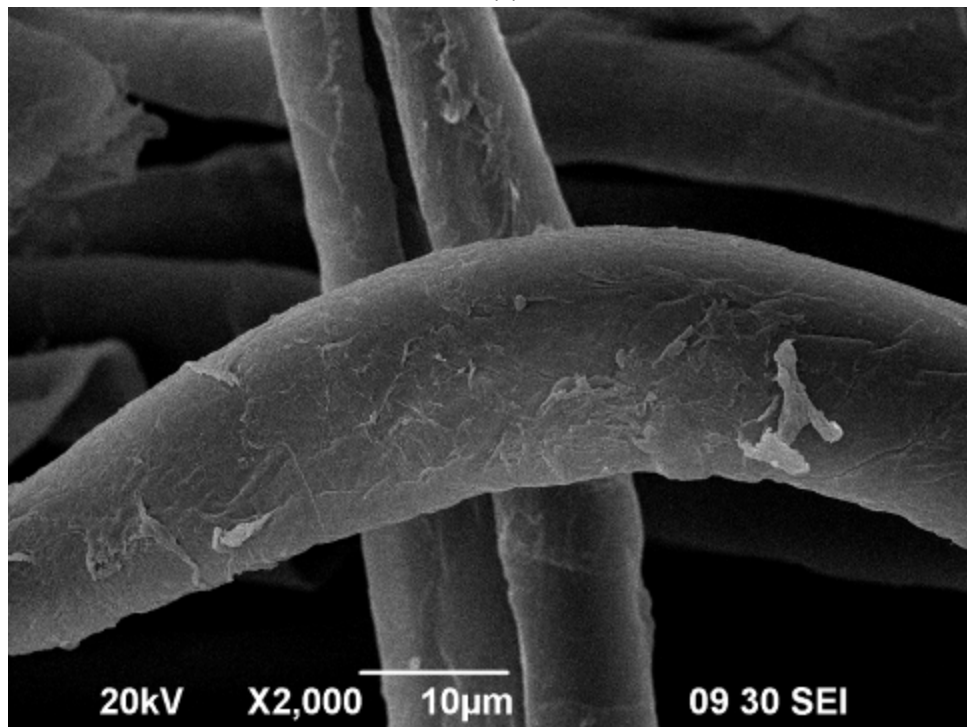
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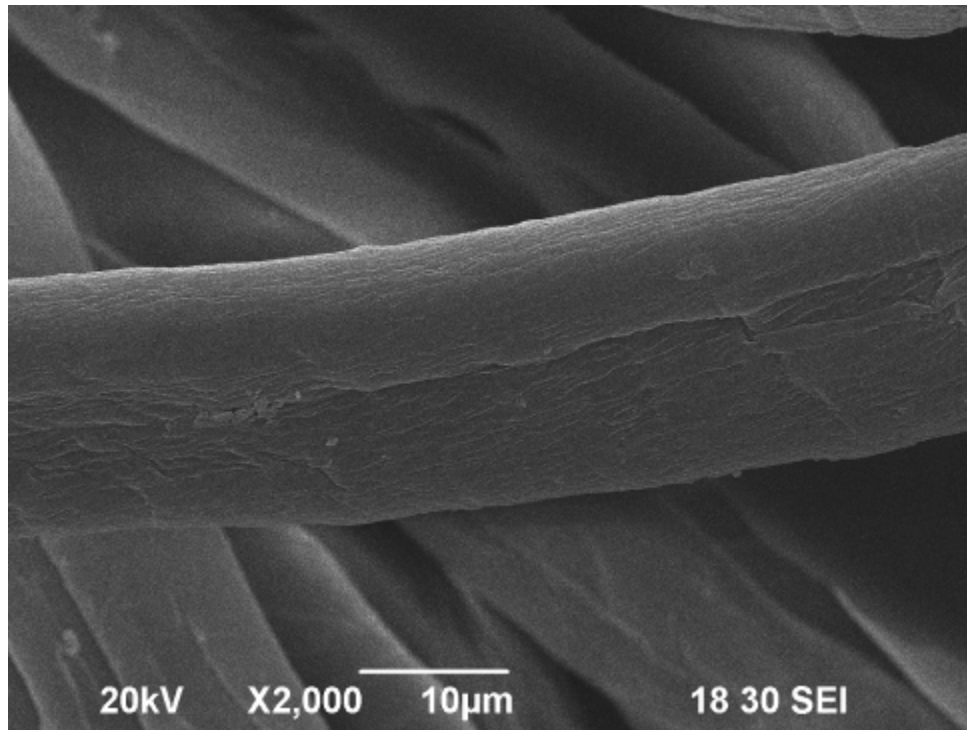
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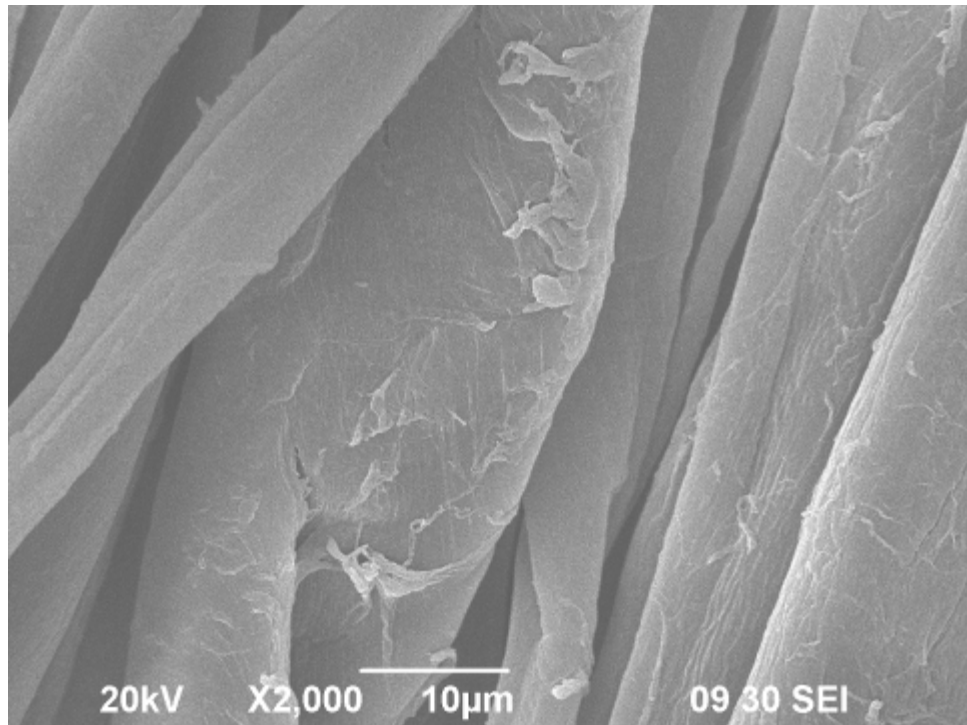
(b)

Fig. 1 (a and b). SEM images of (a) control cotton fibres, (b) PT1 specimen, (c) PT2 specimen, (d) PT1-F1 specimen, (e) PT2-F1 specimen, (f) PT1-F2 specimen, (g) PT2-F2 specimen, (h) PT1-F4 specimen, and (i) PT1-F24 specimen

(c)

(d)

Fig. 1 (c and d). SEM images of (a) control cotton fibres, (b) PT1 specimen, (c) PT2 specimen, (d) PT1-F1 specimen, (e) PT2-F1 specimen, (f) PT1-F2 specimen, (g) PT2-F2 specimen, (h) PT1-F4 specimen, and (i) PT1-F24 specimen

(e)

(f)

Fig. 1 (e and f). SEM images of (a) control cotton fibres, (b) PT1 specimen, (c) PT2 specimen, (d) PT1-F1 specimen, (e) PT2-F1 specimen, (f) PT1-F2 specimen, (g) PT2-F2 specimen, (h) PT1-F4 specimen, and (i) PT1-F24 specimen
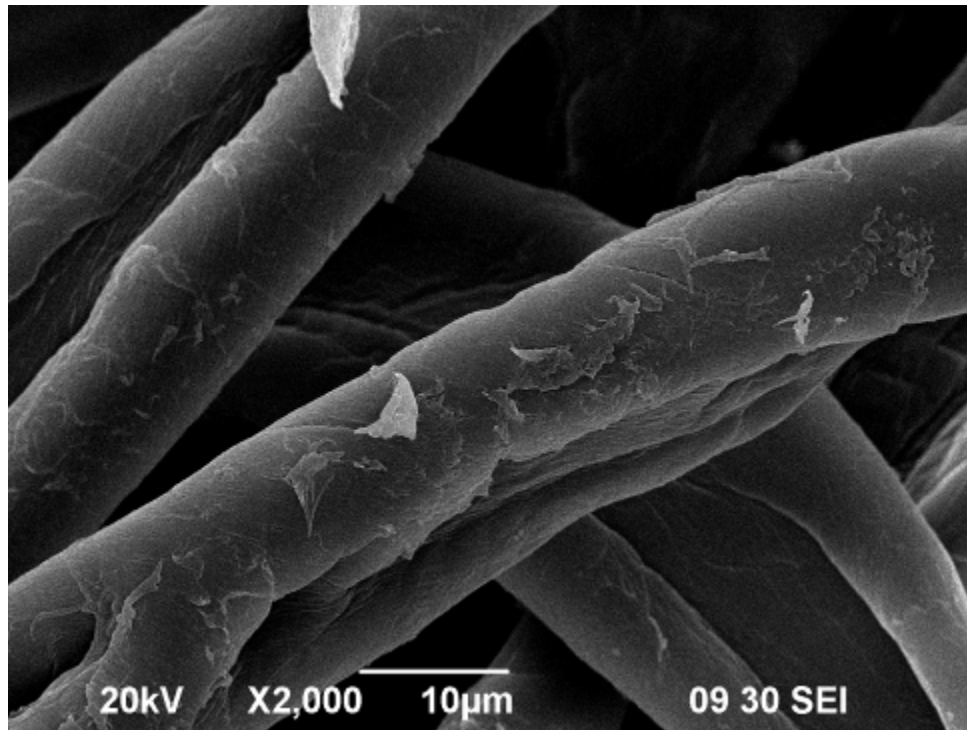
(g)

(h)

Fig. 1 (g and h). SEM images of (a) control cotton fibres, (b) PT1 specimen, (c) PT2 specimen, (d) PT1-F1 specimen, (e) PT2-F1 specimen, (f) PT1-F2 specimen, (g) PT2-F2 specimen, (h) PT1-F4 specimen, and (i) PT1-F24 specimen
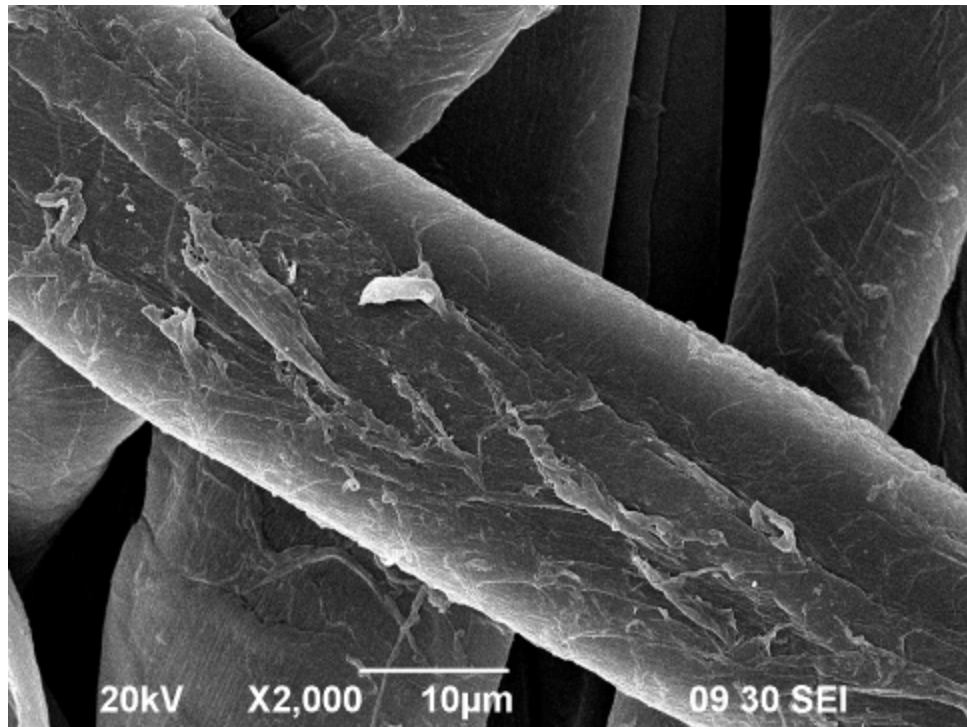
(i)

Fig. 1 (i). SEM images of (a) control cotton fibres, (b) PT1 specimen, (c) PT2 specimen, (d) PT1-F1 specimen, (e) PT2-F1 specimen, (f) PT1-F2 specimen, (g) PT2-F2 specimen, (h) PT1-F4 specimen, and (i) PT1-F24 specimen
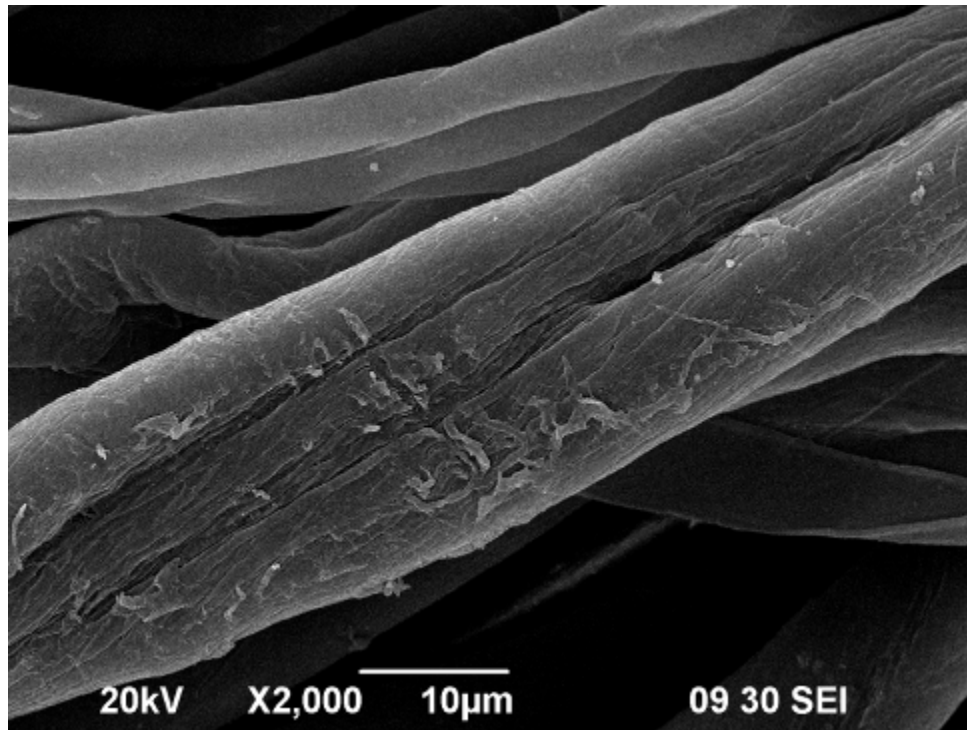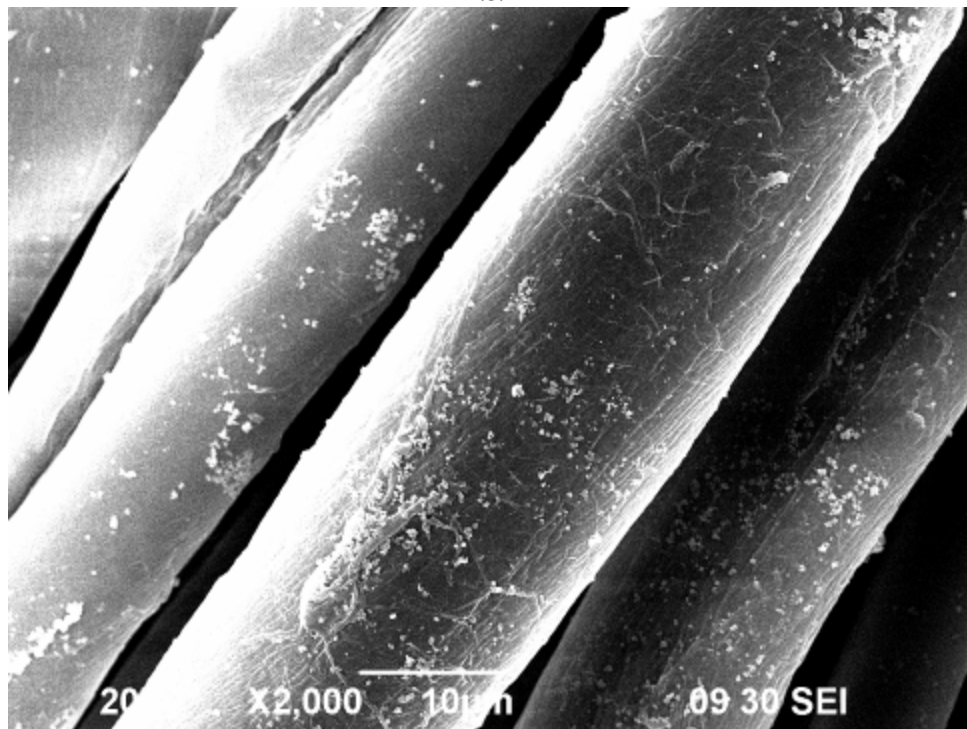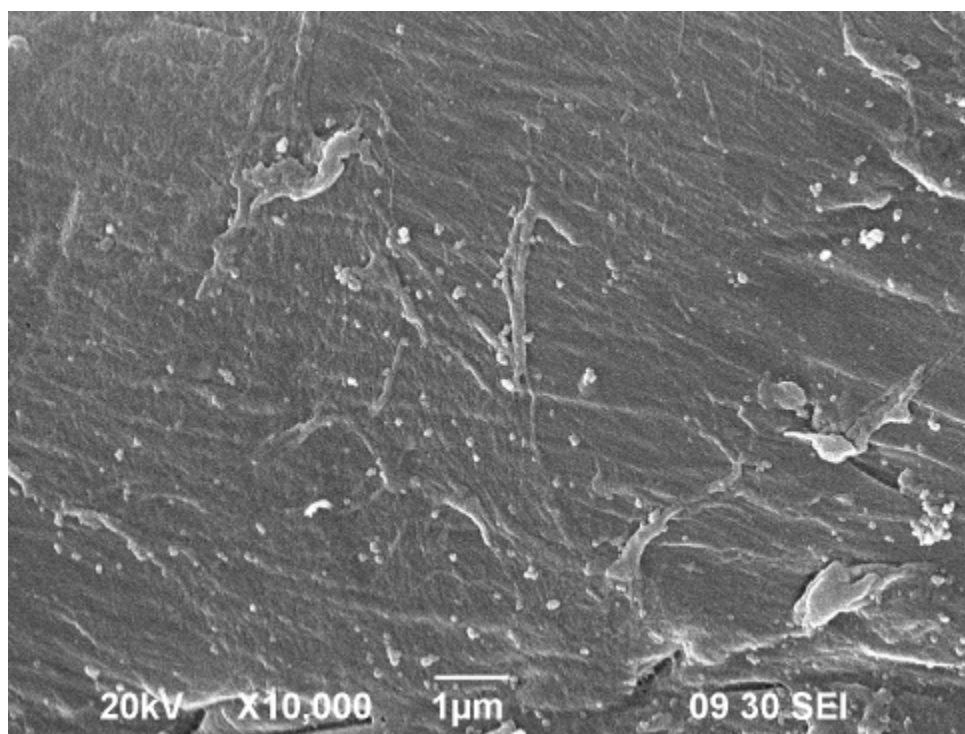
Figures 1d to 1g show SEM images of plasma pretreated (PT1 and PT2) cotton samples subjected to 40% FR and 5% CL with and without 2.5% PA, at a magnification of 2000X. In a previous study (Lam et al. 2010a), SEM images showed that the surface roughness of flame-retardant-treated fabric samples is higher than untreated fabric. High deposition of finishing agents, resulting from application of FR with slight acidity, could be observed on the thickened and wrinkled fibre surface (F1 specimen). The remarkable wrinkling of fibre surface (F2 specimen) was due to the addition of PA, which significantly lowered the pH value of the finishing bath. Compared to specimens treated for FR without plasma pretreatment (Lam et al. 2010a), specimens pre-

treated with plasma and then subjected to FR-CL or FR-CL-PA treatment showed significantly higher erosion and etching on surface, as shown in Figs. 1d through 1g.

Figures 1h and 1i show SEM images of plasma pretreated cotton specimens subjected to FR-CL-PA-0.2% TiO_2 and FR-CL-PA-0.2% nano-TiO_2, respectively. The images prove that the irregular shape metal oxide particles are attached on cotton fabric by the padding process. Figure 1h, at magnification of 2000X, shows that the clustered TiO_2 particles were unevenly distributed on the fibre surface, and the size of these particles varied greatly (diameters in the range of 0.3 to 3.3μm). Moreover, Fig. 1i (magnification of 10000X) clearly shows that nano-TiO_2 particles were agglomerated together with particles of diameters in the range of 0.05 to 0.3 μm. The fabric surface was somewhat rough and uneven with a certain degree of agglomeration of particles, which could possibly be attributed to the surface having attracted nano-particles.

Flammability

Combustible textiles are defined as textiles that will ignite and burn or will give off vapors that ignite and burn when exposed to external sources of ignition, while flame retardant systems are intended to impede or stop the polymer combustion process. Flame retardant systems can act either physically or chemically and can interfere with various processes involved in polymer combustion (Laoutid et al. 2009). Phosphorus-based flame retardant agents can be used as additives to the polymer and are known to be active in the condensed and/or vapor phase. The present study measures two critical factors; ease of ignition and flame spread speed. The ease of ignition and the relative ability to sustain combustion measure the flammability characteristics of a material. According to the ASTM D1230-94 standard, progressive burning of a fabric at a distance of 127 mm from a flame is deemed to be "failure" of resistance to burning. Flame spread speed is the time taken by a flame on a burning material (away from the source of ignition) to travel a specified distance under specified conditions. Table 3 presents burning characteristics of plasma pretreated cotton specimens measured by flammability tests. On the other hand, Table 4 shows burning characteristics as determined by flammability tests of plasma pretreated cotton specimens subjected to flame-resistant treatment.

Table 3. Flammability of Plasma-treated Cotton Specimens (unwashed)

Sample	Burning Time (s)	Char Length (cm)	Burning Speed (m/hr)	Pass / Fail
Control	17.86	15.00	30.24	Fail
PT1-treated only	18.15	15.00	29.75	Fail
PT2-treated only	18.82	15.00	28.69	Fail

Previous research has considered flammability of cotton fabrics treated with FR-CL-PA-TiO_2 and FR-CL-PA-Nano-TiO_2 (Lam et al. 2010a). This study evaluated flammability when these treatments were performed after pretreatment with plasma. The results show that the control fabric (without plasma and FR treatment) burned to ashes quickly at a speed of 30.24 m/hr, while the burning speed was slightly decreased after plasma treatment with 0.2 or 0.4 L/min reactive oxygen gas. In general, flame spread on a microscopically raised fabric surface is usually more rapid than on a smooth fabric surface. Hence, plasma-treated fabrics showing slower burning speed can probably be attributed to the fact that plasma treatment removes fabric surface fibrils. High oxygen flow rate implies high concentration of active species in the plasma jet, producing a severe etching effect that alters the material's surface characteristics. Hence, PT2-treated specimens have lower burning speed.

In case of plasma pretreated cotton fabrics subjected to flame-retardant treatment (not neutralized, not washed), the flame extinguished right after removal of the ignition source, with no flame spreading, as shown in Table 4. The fabrics were left with only a spot of char formation and, therefore, the specimens were classified as flame-resistant fabrics. Generally speaking, when fabrics are subjected to thermal decomposition, flame retardants promote formation of solid char, leading to catalytic dehydration, as shown below (Siriviriyanun et al. 2008; Mostashari et al. 2005; Mostashari et al. 2004):

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Table 4. Flammability of Plasma Pretreated Cotton Specimens Subjected to Flame-resistant Treatment (unwashed and washed)

Sample Symbol	Neutrali-zation (mins)	Launder-ing (cycle)	PT1-treated				PT2-treated			
			Burning Time (s)	Char Length (cm)	Burning Speed (m/hr)	Pass / Fail	Burning Time (s)	Char Length (cm)	Burning Speed (m/hr)	Pass / Fail
F1	0	0	DNI	0.74	-	Pass	DNI	0.68	-	Pass
F2	0	0	DNI	0.80	-	Pass	DNI	0.81	-	Pass
F4	0	0	DNI	1.14	-	Pass	DNI	0.79	-	Pass
F6	0	0	DNI	1.16	-	Pass	DNI	1.00	-	Pass
F24	0	0	DNI	0.84	-	Pass	DNI	0.88	-	Pass
F26	0	0	DNI	0.79	-	Pass	DNI	0.83	-	Pass
F1	0	1	51.19	13.00	9.14	Fail	56.38	13.00	8.30	Fail
F2	0	1	12.33	2.78	8.12	Pass	13.88	2.88	7.47	Pass
F4	0	1	14.78	2.40	5.85	Pass	22.34	4.08	6.57	Pass
F6	0	1	7.82	1.74	8.00	Pass	20.15	3.06	5.47	Pass
F24	0	1	59.39	11.10	6.73	Pass	12.55	2.19	6.27	Pass
F26	0	1	49.56	10.03	7.28	Pass	DNI	1.71	-	Pass
F1	0	5	58.87	13.00	7.95	Fail	60.33	13.00	7.76	Fail
F2	0	5	18.55	3.91	7.59	Pass	14.36	2.93	7.35	Pass
F4	0	5	DNI	0.73	-	Pass	23.32	3.90	6.02	Pass
F6	0	5	14.71	2.54	6.21	Pass	13.02	2.19	6.05	Pass
F24	0	5	41.74	8.61	7.43	Pass	22.13	4.28	6.95	Pass
F26	0	5	41.79	7.69	6.62	Pass	24.59	4.79	7.01	Pass
F1	15	0	61.30	13.00	7.63	Fail	64.07	13.00	7.30	Fail
F2	15	0	16.88	4.36	9.30	Pass	15.33	3.88	9.11	Pass
F4	15	0	26.82	5.59	7.50	Pass	DNI	0.94	-	Pass
F6	15	0	DNI	1.49	-	Pass	24.40	4.46	6.58	Pass
F24	15	0	18.06	3.89	7.75	Pass	31.34	6.26	7.19	Pass
F26	15	0	DNI	0.89	-	Pass	14.34	3.16	7.94	Pass
F1	15	1	59.12	13.00	7.92	Fail	60.93	13.00	7.68	Fail
F2	15	1	15.54	3.76	8.71	Pass	16.38	3.88	8.53	Pass

F4	15	1	20.77	4.26	7.39	Pass	DNI	2.00	-	Pass
F6	15	1	14.77	2.39	5.82	Pass	32.37	6.50	7.23	Pass
F24	15	1	21.41	3.80	6.39	Pass	15.58	2.53	5.84	Pass
F26	15	1	27.26	5.03	6.64	Pass	39.37	8.16	7.46	Pass
F1	15	5	61.29	13.00	7.64	Fail	58.88	13.00	7.95	Fail
F2	15	5	14.38	2.98	7.46	Pass	19.51	3.85	7.10	Pass
F4	15	5	12.05	2.29	6.84	Pass	23.21	4.79	7.43	Pass
F6	15	5	20.30	3.89	6.89	Pass	17.93	3.21	6.45	Pass
F24	15	5	39.21	7.58	6.96	Pass	30.13	5.93	7.08	Pass
F26	15	5	11.72	1.93	5.91	Pass	29.83	5.58	6.73	Pass
F1	30	0	61.46	13.00	7.61	Fail	65.31	13.00	7.17	Fail
F2	30	0	28.56	6.32	7.97	Pass	18.56	3.84	7.45	Pass
F4	30	0	DNI	1.28	-	Pass	DNI	0.99	-	Pass
F6	30	0	17.88	2.94	5.92	Pass	DNI	1.89	-	Pass
F24	30	0	21.84	4.00	6.59	Pass	DNI	1.19	-	Pass
F26	30	0	24.52	5.01	7.36	Pass	DNI	2.41	-	Pass
F1	30	1	60.13	13.00	7.78	Fail	61.21	13.00	7.65	Fail
F2	30	1	22.12	4.78	7.78	Pass	34.56	7.03	7.32	Pass
F4	30	1	17.25	2.80	5.84	Pass	54.65	10.84	7.14	Pass
F6	30	1	18.08	3.70	7.37	Pass	14.19	2.84	7.20	Pass
F24	30	1	14.05	2.04	5.22	Pass	20.95	3.80	6.53	Pass
F26	30	1	36.92	7.23	7.04	Pass	45.41	8.25	6.54	Pass
F1	30	5	60.33	13.00	7.76	Fail	61.08	13.00	7.66	Fail
F2	30	5	32.56	6.94	7.67	Pass	22.58	4.78	7.62	Pass
F4	30	5	12.64	2.41	6.87	Pass	11.34	2.18	6.91	Pass
F6	30	5	16.17	2.93	6.51	Pass	DNI	0.75	-	Pass
F24	30	5	14.75	2.75	6.71	Pass	16.15	3.43	7.64	Pass
F26	30	5	12.60	1.41	4.04	Pass	DNI	1.76	-	Pass

* DNI stands for "Did Not Ignite

$$(C_6H_{10}O_5)_x \rightarrow 6xC + 5xH_2O \tag{1}$$

According to the above reaction, the black carbonaceous residue (char) that remained on the treated fabric, after the combustion process, can be mainly attributed to the fact that water is removed from the material. This carbonized layer isolates and protects the polymer from the flames and insulates the polymer underneath from the heat. Moreover, it also limits volatility of fuel, preventing formation of new free-radicals, and limits oxygen diffusion, which reduces combustion (Siriviriyanun et al. 2008; Laoutid et al. 2009). Hence, the outstanding improvement in flame retardancy of treated cotton fabric can be explained by the presence of an insulating layer of char residual that develops on the fabric surface during the burning process.

Table 4 shows that all plasma pretreated F1 specimens subjected to neutralization and/or home laundering failed the flammability test. The results revealed that the crosslinking agent, without complete esterification of cotton, is not effective in reducing flammability of cotton specimens. The use of PA in the system can catalyze the dehydration reaction of terminal alcohols leading to formation of carbocations and carbon–carbon double bonds (Chen et al. 2010), which increases the percent fixation of FR retained on the fabric after multiple laundering cycles or neutralization. The superior performance of PA as catalyst to form stable crosslinked polymeric network maintains the durability of flame-retardant properties of treated fabric. Hence, with addition of PA in the finishing formulation, all plasma pretreated F2 specimens passed the flammability test even after being subjected to neutralization and/or home laundering. The results further confirmed that FR is able to react directly with cellulose through its N-methylol group to form a crosslinked polymeric network when CL-PA is used in the flame-retardant formulation as the bonding is highly resistant to hydrolysis during multiple home launderings (Wu et al. 2006; Yang et al. 2005).

When compared to F2 specimen without plasma pretreatment (Lam et al. 2010a), the burning speed of PT1-F2 specimens and PT2-F2 specimens decreased by 5.18% to 18.38% and 7.09% to 20.96%, respectively. This phenomenon can be explained by the etching effect on the fabric surface caused by plasma pretreatment. The plasma removes organic contamination from fibre surface and thus can avoid interference of bonding between fibre and FR-CL-PA-linkages (Kaplan 2004; Lam et al. 2010b). The etching effect of plasma can also reduce weak boundary layers and increase the surface area to allow more chemicals to be attached, in order to increase fabric's flame-retardant performance (Kaplan 2004; Lam et al. 2010b). In addition, the increase in wettability of cotton fibres may also enhance performance of the flame-retardant treatment. A high concentration of active species in the plasma jet alters the material's surface characteristics greatly and hence the decrease in burning speed of the PT2-F2 specimen.

It has been shown in previous studies that TiO_2/nano-TiO_2 results in a significant reduction in flame spread rate that may be corresponding to the catalytic effects in crosslinking and dehydration reactions (Lam et al. 2010a). Table 4 shows that FR-CL-PA-TiO_2 and FR-CL-PA-nano-TiO_2 treated specimens demonstrated superior results when the fabric was pretreated with plasma. It has been suggested that the polymer degradation kinetics are affected positively and enhanced the thermal stability due to the inclusion of TiO_2/nano-TiO_2 particles (Mosurkal et al. 2008). These catalysts are

effective in many reactions and polymerizations, where they play a vital role in catalyzing the protective thick char formation (isolates and protects the polymer from the flames and insulates the polymer underneath from the heat) (Mosurkal et al. 2008). The findings imply that the metal oxide chemically enhances flame-retardant performance of FR-CL-PA-treated cotton specimens, while plasma treatment further enhances the specimen's flame-retardant performance physically.
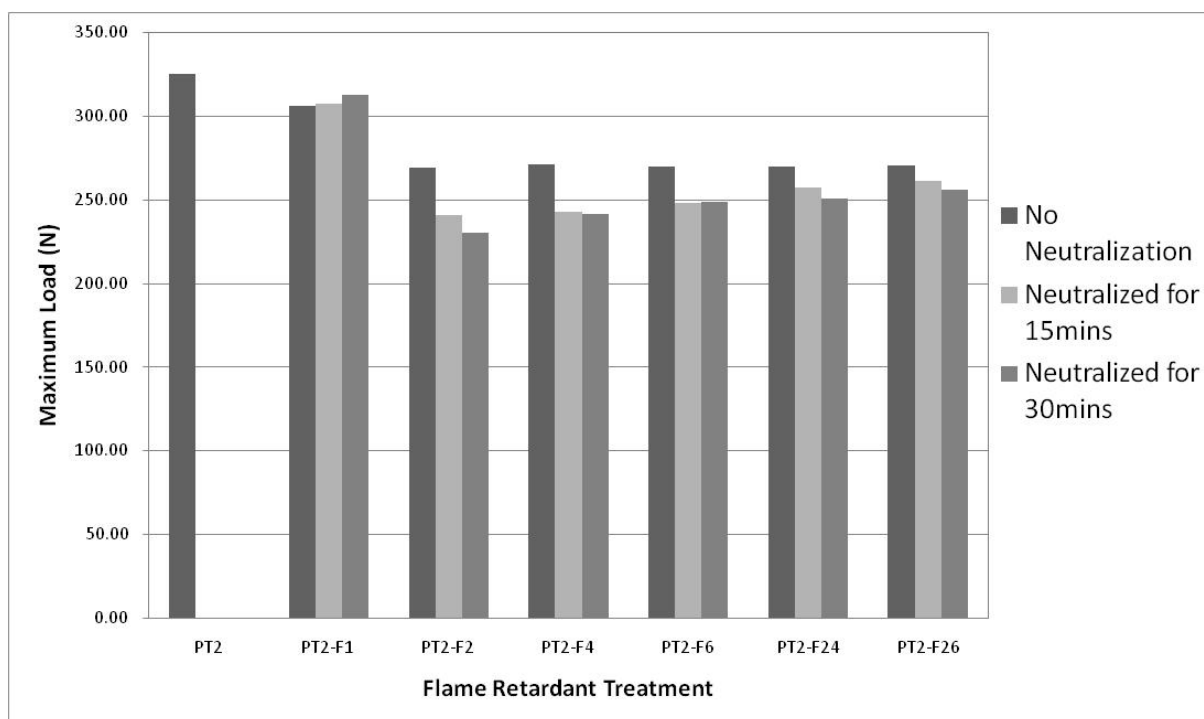
Tensile Strength

Figures 2a and 2b show the tensile strength of cotton fabrics plasma pretreated with 0.2 L/min oxygen and 0.4 L/min oxygen (subjected to different flame-retardant formulations in accordance with Table 2), respectively. As per the previous study, the control sample (without plasma pretreatment and flame-retardant treatment) had 315.01 N maximum load, and the flame-retardant-treated cotton specimens demonstrated even lower breaking load, which could have resulted from the side effects of the crosslinking agent used (Lam et al. 2010a).

Compared to the control specimen, tensile strength of plasma pretreated cotton specimens (PT1 and PT2 specimens as shown in Figs. 2a-2b) was 3.12% to 4.29% higher. In general, tensile strength of fabric highly depends on several factors such as fabric structure, yarn twist, and yarn count. However, plasma treatment is a surface modification treatment that does not affect the fabric's bulk structure. The roughening effect (of plasma treatment) creates more contact points in the fibres (microscopically), resulting in increased inter-yarn and inter-fibre friction (Kan et al. 2006). Therefore, the enhancement in tensile strength may be due to the roughening effect on fibre surfaces, where a larger cohesive force is developed during the application of tensile stress.
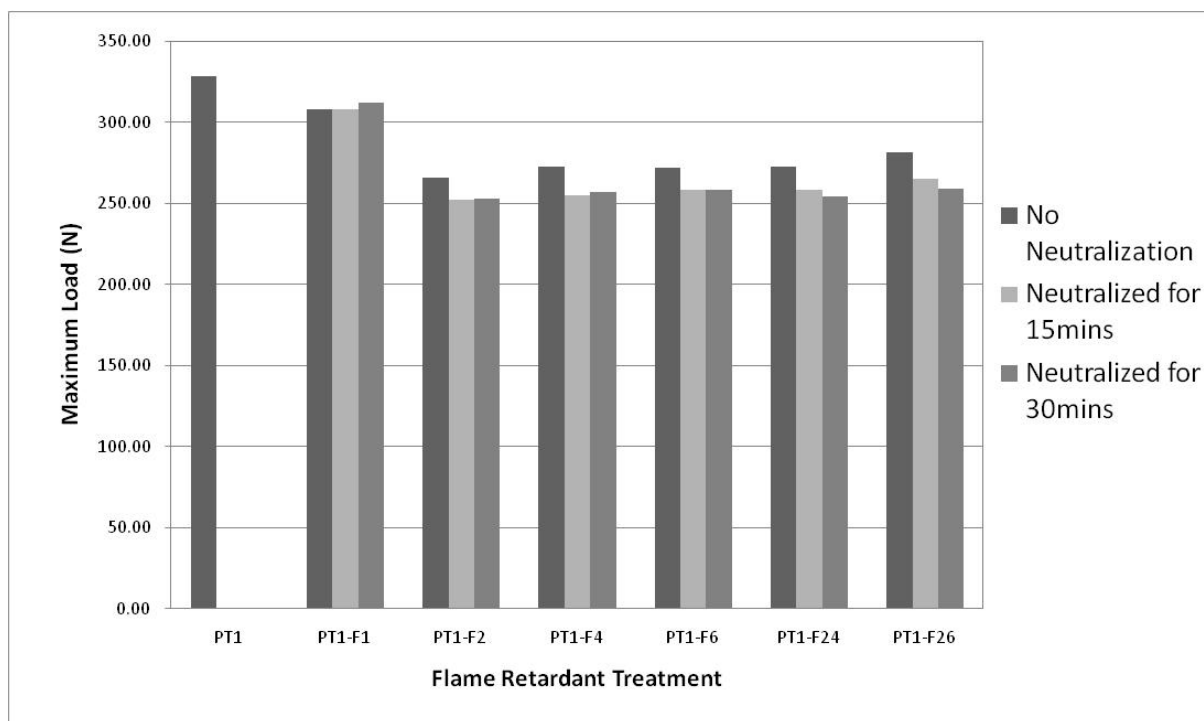
(a)

(b)

Fig. 2. Tensile strength of plasma pretreated cotton specimen subjected to flame-retardant treatment; (a) 0.2 L/min oxygen; (b) 0.4 L/min oxygen

As shown in Figs. 2a-2b, tensile strength of plasma pretreated cotton specimens subjected to FR-CL was slightly lower. One of the reasons is that the crosslinking agent, CL, reduces the strength of cotton fabrics (Kang et al. 1998; Yang et al. 2000, 2004). Moreover, the results also imply that the reduction of breaking loads is due to the strong acidity of the finishing bath, which severely tenderizes the fabric. The pH value of the FR-CL-PA finishing bath is even lower, and therefore, occurrence of the diminished breaking load is more significant for PT1-F2 and PT2-F2 specimens.

In the present study, the effectiveness of the TiO_2/nano-TiO_2 co-catalyst added in the finishing formulation was evaluated, i.e. whether it can promote formation of the crosslinked polymeric network between FR and cotton by the CL. From Figs. 2a-2b, the results show that 0.2% to 0.4% TiO_2 or nano-TiO_2 co-catalyst so added may compensate for the reduction in tensile strength caused by flame-retardant agents. This is attributed to the fact that the metal oxide co-catalytic effect dominated over the acid hydrolysis process. Hence, the metal oxide present minimizes the side-effects of the crosslinking process.

As discussed, the drop of breaking load is mainly attributed to acidity of finishing agents and, therefore, neutralizing flame-retardant-treated cotton specimens with alkali is indispensable. However, an unanticipated result was observed, i.e. tensile strength of plasma pretreated cotton specimens subjected to flame-retardant treatment after neutralization was lower than before neutralization. This is probably due to the fact that wet neutralization treatment redevelops loose fibrils on the fabric surface. Nevertheless, the tensile strength of cotton specimens increased in the following order: only flame-
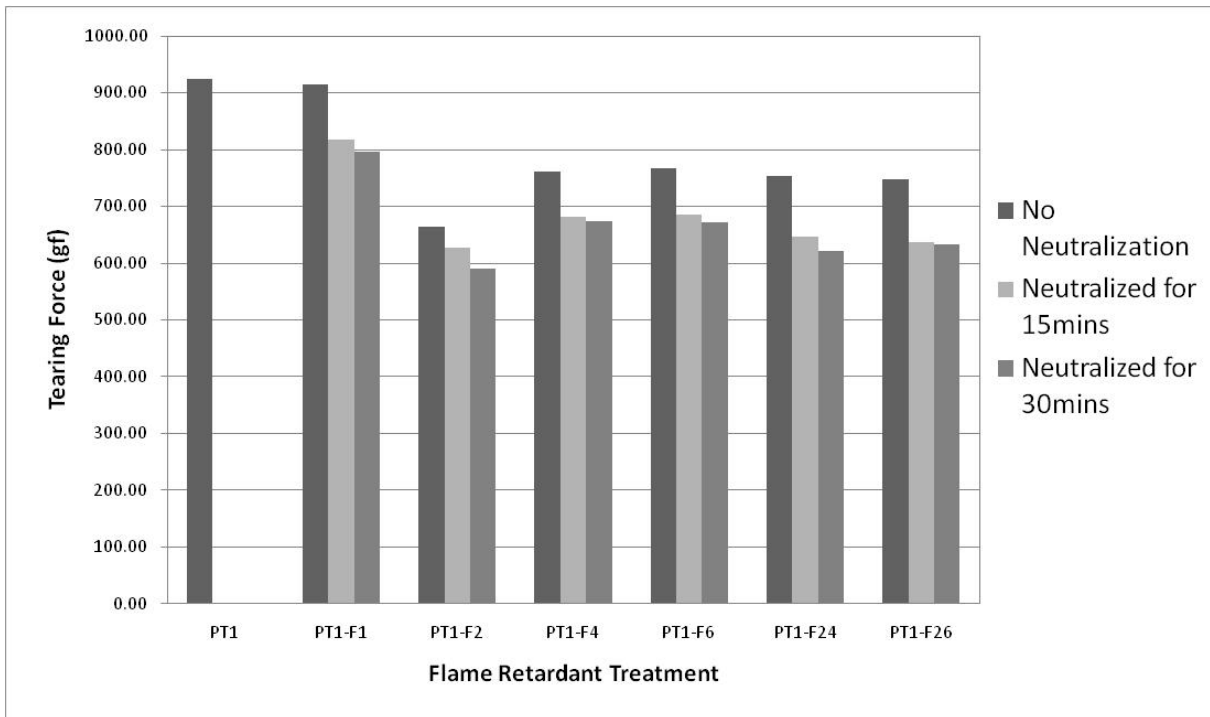
retardant-treated, flame-retardant-treated + neutralized, plasma pretreated + flame-retardant-treated + neutralized, and plasma pretreated + flame-retardant-treated. Hence, it is proven that plasma-treatment compensates for the loss in tensile strength caused by the flame-retardant treatment.

Furthermore, the overall tensile strength of PT1-treated specimens was higher than PT2-treated specimens, as shown in Figs. 2a-2b. Although plasma treatment increases inter-yarn and inter-fibre friction and develops a larger cohesive force, surface bombardment by electrons, ions, and excited atoms can cause polymer bonds' breakages. High oxygen concentration plasma treatment may result in formation of a brittle polymer layer (Wong et al. 1999). Hence, PT1 treatment is more effective than PT2 treatment.
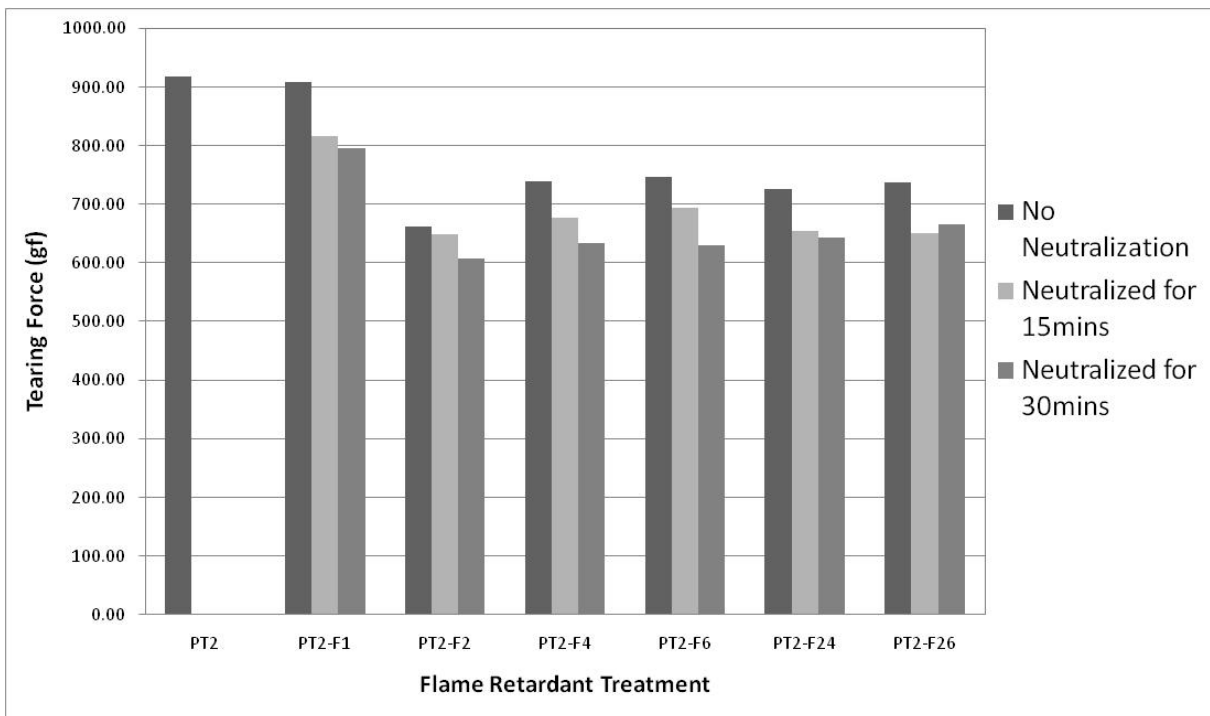
Tearing Strength

Figures 3a and 3b show the tearing force of cotton fabrics plasma pretreated with 0.2 L/min oxygen and 0.4 L/min oxygen concentration (subjected to different flame-retardant formulations in accordance with Table 2), respectively. The results obviously show that the tearing strength of PT1 and PT2 pretreated cotton specimens subjected to different flame-retardant systems dropped to a great extent, in the order PT1, PT1-F1, PT1-F6, PT1-F4, PT1-F24, PT1-F26, PT1-F2 and PT2, PT2-F1, PT2-F6, PT2-F4, PT2-F26, PT2-F24, and PT2-F2, respectively. As per the previous study, the control sample (without plasma pretreatment and flame-retardant treatment) had 917.6 gf tearing strength, and the flame-retardant-treated cotton specimens had even lower tearing strength because of the side effects of the finishing agent used (Lam et al. 2010a). Compared to the control cotton specimen, tearing strength of PT1 and PT2 pretreated cotton specimens (without flame-retardant treatment) increased by 0.79% and 0.22%, respectively, as shown in Figs. 3a-3b. The increased inter-yarn and inter-fibre friction because of surface modification by plasma treatment (Kan et al. 2006) restricts the sliding action of yarns during tearing and thereby increases the fabric's tearing strength. Moreover, differences between tearing strengths of PT1-treated specimens and PT2-treated specimens subjected to different flame-retardant formulations were small. Hence, oxygen flow rates of 0.2 to 0.4 L/min were satisfactory to modify the fabric's surface.

Tearing strength of plasma pretreated cotton specimens dropped slightly after being subjected to FR-CL treatment, and a further decrease occurred when PA was added in the flame-retardant treatment. In the presence of PA catalyst in the FR-CL finishing bath, the pH value of the solution was changed from pH 5 to pH 1-2 (strongly acidic), which may reduce fabric strength. Besides, the high temperature curing treatment also increases brittleness of cotton fibres. In order to remove residual acidic chemicals on treated specimens, washing flame-retardant-treated cotton specimens with alkali is essential. The results, as shown in Figs. 3a-3b, highly correlate to the tensile strength. Tearing strength of plasma pretreated cotton specimens subjected to flame-retardant treatment was lower after neutralization than before neutralization, especially in the case of a relatively longer neutralization process. This is mainly attributable to the high temperature neutralization process, i.e. 50°C, which reduces the tearing strength of the treated specimens and the effect is more serious in case of prolonged washing process, i.e. 30 minutes. Nevertheless, plasma-treatment still compensates the loss in tearing strength caused by the flame-retardant treatment.

(a)

(b)

Fig. 3. Tearing strength of plasma pretreated cotton specimen subjected to flame-retardant treatment; (a) 0.2L/min oxygen; (b) 0.4L/min oxygen

In addition, the results showed that either 0.2% to 0.4% TiO_2 or nano-TiO_2 co-catalyst may compensate for the reduction in tensile strength caused by flame-retardant agents, as demonstrated in Figs. 3a-3b. The metal oxide present promotes formation of the crosslinked polymeric network by the CL, between FR and cotton, due to the co-cocatalytic effect. Hence, the metal oxide present minimizes the side-effects of the crosslinking process. Moreover, metal oxide particles attached to the fabric surface or filled between the fibres increase yarn friction, which can help resist yarn slippage, i.e. the more are the TiO_2 particles attached on the fabric surface, or filled between the fibres, the higher is the friction, and by implication, tearing strength. However, when nano-TiO_2 was added in flame-retardant treatment, there was only a slight enhancement of tearing strength of plasma pretreated cotton, as shown in Figs. 3a-3b. The results are mainly attributed to the fact that the smaller nano-particles can increase yarn friction to a lesser extent than micro-TiO_2.

Formaldehyde Content

Many of the current flame retardant finishing processes are toxic and cause environmental concerns. Durable phosphorus-based flame retardant agents contain significant levels of carcinogenic formaldehyde, though it is still the most popular flame-retardant treatment in the textile industry. Free formaldehyde was extracted from treated cotton fabric with water at 40 ^{o}C, and the quantity was then determined colorimetrically. The procedure is used when free and hydrolysed formaldehyde on the treated fabric is in the range of 20ppm to 3500 ppm; results below 20 ppm are reported as 'non-detectable'. Table 5 shows the quantity of formaldehyde content on fabric treated with different plasma treatments and flame-retardant formulations.

Table 5. Formaldehyde Content of Flame-Retardant-Treated Cotton Fabrics

Sample Symbol	Formaldehyde Content (ppm)		
	Without plasma treatment	PT1-treated	PT2-treated
F1	33	19	19
F2	30	17	16
F4	27	16	14
F6	27	15	14
F24	24	14	12
F26	22	13	12

FR is a low cost chemical that offers superior results, compared to other flame-retardant agents. Use of formaldehyde-based flame retardant agents in conjunction with CL is very common in the textile industry, though both FR and CL contribute to emission of formaldehyde; the F1 specimen showed a formaldehyde content of 33 ppm, which can be toxic and allergenic. The results revealed that the FR-CL system is based on formaldehyde as the bonding agent for cotton (Yang et al. 2007). Moreover, FR with PA catalyst in the formulation showed a free formaldehyde content of only 30 ppm in the F2

specimen (Table 5). The PA catalyst in flame retardant finishing enhanced the percent fixation of FR on the fabric and, therefore, free formaldehyde was reduced.

Metal oxide, acting as co-catalyst in the FR-CL-PA treatment, assists in the crosslinking process through effective catalytic reaction, which minimizes formation of free formaldehyde. TiO_2 or nano-TiO_2 not only enhance mechanical properties of flame-retardant treated specimens, but also minimize emission of the toxic free formaldehyde. Compared to the F2 specimen, free formaldehyde content dropped to 9.97-11.96% when TiO_2 was added as co-catalyst, and to 19.93-25.58% when nano-TiO_2 was the co-catalyst. The results also show that the higher the concentration of catalyst (0.4%) added in the treatment, and the smaller the co-catalyst particles size, the lower was the release of free formaldehyde. These results can be explained by the fact that increasing metal oxide concentration and decreasing particles size of TiO_2 leads to a more effective crosslinking process.

Table 5 also shows that plasma treatment significantly lowered free formaldehyde emission from FR-CL-treated and FR-CL-PA-treated specimens. The reduction in formaldehyde content caused by plasma treatment can be explained by the etching effect on the fabric surface, which removes weak boundary layers and organic contamination from fibre surface, thus avoiding interference in bonding between fibre and FR-CL-PA-linkages. Superior crosslinking between FR and cellulose decreases the release of free formaldehyde (Wang et al. 2004), especially after PT2 treatment. This is attributed to the severe etching effect produced by high oxygen flow rate, which alters the material's surface characteristics. Moreover, formaldehyde content of plasma pretreated specimens further dropped after FR-CL-PA-TiO_2 or FR-CL-PA-nano-TiO_2 treatment.

CONCLUSIONS

Cotton fabrics are highly combustible, and application of FR-CL, in the presence of PA catalyst and/or TiO_2/nano-TiO_2 co-catalyst, is used to impart flame-retardant properties to plasma pretreated cotton fabrics. Surface morphology of plasma pretreated cotton specimens subjected to flame-retardant treatment showed roughened and wrinkled fabric surfaces with high deposition of the finishing agent, caused by the plasma etching effect and application of acidic FR. Combustibility of FR-CL-PA-TiO_2 and FR-CL-PA-Nano-TiO_2 treated fabrics was evaluated by a fabric 45° flammability test. FR-CL-PA-treated specimens showed superior flame-retardant properties, which was further improved by plasma pretreatment and use of metal oxide co-catalyst. However, in comparison with the control sample, flame-retardant-treated cotton specimens had lower breaking load and tearing strength, caused by side effects of the crosslinking agent used, while plasma pretreatment may compensate for the reduction in tensile strength caused by flame-retardant agents. In addition, both plasma pretreatment and metal oxide co-catalyst improved the process of crosslinking between FR and cotton fabric, which minimises formation of free formaldehyde, thereby facilitating the use of FR in the industry.

ACKNOWLEDGMENTS

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