

Flame-Retardant Finishing in Cotton Fabrics Using Zinc Oxide Co-Catalyst

Y. L. Lam, C. W. Kan, C. W. M. Yuen

Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

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ABSTRACT: In this article, *N*-Methylol dimethylphosphonopropionamide (FR) in combination with a melamine resin (CL), phosphoric acid (PA) catalyst and zinc oxide (ZnO) or nano-ZnO co-catalyst were used (FR-CL-PA-ZnO or nano-ZnO system) to impart flame-retardant property on cotton fabrics. FR-CL or FR-CL-PA-treated cotton specimen showed roughened and wrinkled fabric surface morphology, which was caused by the attack of the FR with slightly acidity. In addition, FTIR analysis showed some new characteristic peaks, carbonyl, CH₂ rocking and CH₃ asymmetric and CH₂ symmetric stretching bands, in the chemical structure of treated cotton specimens. Apart from these, the flame ignited on the flame-retardant-treated fabrics (without subjected to any post-wet treatment) extinguished right after the removal of ignition source. However, FR-CL treated specimens were

no longer flame-resistant when the specimens subjected to neutralization and/or home laundering, while FR-CL-PA treated specimens showed opposite results. By using 0.2% and 0.4% of ZnO or nano-ZnO as co-catalyst, the flame spread rate of neutralized and/or laundered test specimens decreased, even the specimens were undergone 10 home laundering cycles. Moreover, flame-retardant-treated cotton specimens had low breaking load and tearing strength resulting from side effects of the crosslinking agent used, while addition of ZnO or nano-ZnO co-catalyst could compensate for the reduction. Furthermore, the free formaldehyde content was dropped when ZnO and nano-ZnO co-catalyst was added in the treatment. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 612–621, 2011

Key words: flame-retardant; zinc oxide; co-catalyst; cotton

INTRODUCTION

In terms of flammability, cotton fabrics have a high burning rate in which the fabric construction and density may also affect the fabric combustibility in addition to its composition.^{1,2} Flame retardation serves a vital purpose in protection against textile related fires. It is an important property for textile products to ensure the safety of consumers. To reduce the flammability of cotton fabric, fiber blending with synthetic fiber is one of the options. Blends, such as cotton/polyester fabrics, are prone to ignition, since the non-thermoplastic component prevents the withdrawal of the fabric from the heat source.³ However, the thermoplastic fibers may melt upon progressive combustion, which can be dangerous. Hence, the problem can be alleviated by the application of flame-retardant chemical additives. In the textile industry, flame resistance property commonly imparted to cotton fabrics by means of chemical finishing.⁴ The use of flame retar-

dant chemicals enables the treated fabrics to meet stringent safety standards and regulations.

N-Methylol dimethylphosphonopropionamide (Pyrovatex CP New, FR) in combination with a bonding agent such as a melamine resin (KNITTEX CHN, CL) and a catalyst such as phosphoric acid (PA) has been one of the most commonly used durable flame retardant agents for cotton for many years.^{5,6} Development of new flame-retardant systems for cotton were mainly based on the way to reduce costs by using as little flame retardant as possible and to satisfy the ever-increasing demand for environmentally friendly flame retardants. In our other research, we developed a flame retardant finishing system for cotton based on FR-CL-PA-TiO₂ and FR-CL-PA-nano-TiO₂.⁷ Certainly, the selection of catalyst plays a significant role in influencing the bonding of the flame retardant agents to cotton. Researchers showed that nano-zinc oxide (nano-ZnO) coated on cotton fabrics could impart functional properties such as better strength properties, air permeability and UV-absorption property.⁸ Zinc oxide (ZnO) as catalyst could even help to enhance the flame-retardant action.⁹ Hence, we will investigate the bonding of FR-CL-PA flame retardant finishing agents, in the presence of ZnO or nano-ZnO as co-catalyst, to cotton in this article. The finishing system proposed is applied to textile materials by conventional pad-dry-cure finishing techniques. Surface

Correspondence to: Y. L. Lam (07901799r@polyu.edu.hk).

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TABLE I
Flame-Retardant Treatment Conditions

Sample Symbol	PYROVATEX CP NEW	KNITTEX CHN	Phosphoric Acid (85%)	Micro-Zinc Oxide	Nano-Zinc Oxide
F1	40%	5%			
F2	40%	5%	2.5%		
F44	40%	5%	2.5%	0.2%	
F46	40%	5%	2.5%	0.4%	
F64	40%	5%	2.5%		0.2%
F66	40%	5%	2.5%		0.4%

Concentration percentage measured based on weight of volume.

morphology of cotton specimens is investigated to find evidence of presence of flame-retardant agent crosslinks as well as ZnO or nano-ZnO on the fiber surface, while chemical structures analyses are performed by fourier transform infrared spectroscopy (FTIR). Combustibility of flame-retardant-treated fabrics, evaluated by fabric 45° flammability test and fabric thickness measurement upon wet treatment, is also studied. Apart from these, the grab test and Elmendorf tearing test are conducted to test whether the treatment will weaken the fabric. Formaldehyde content of the treated fabrics is also tested.

EXPERIMENTAL DETAILS

Material

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 175 g/m²), of size 30 × 30 cm² is used. The flame-retardant agent and cellulose crosslinking agent used are an organic phosphorus compound (PYROVATEX CP New, FR) and a melamine resin (KNITTEX CHN, CL), respectively, supplied by Huntsman Limited. Analytical reagent grade PA that served as catalyst was supplied by Sigma-Aldrich Co. Co-catalysts used were micro-zinc oxide (ZnO, 2 μm diameter) and nano-zinc oxide (nano-ZnO, 100 nm diameter) obtained from Fluka Chemical Corp. and Sigma-Aldrich, respectively, both having purity of 99+%. The alkali was analytical reagent grade sodium carbonate supplied by Sigma-Aldrich. All other chemicals used in the study were reagent grade.

Flame-retardant treatment

Cotton fabric samples were treated with different compositions of finishing agents as shown in Table I. A two-bath method was used for the treatments. In the first bath, the fabrics were dipped and padded with flame-retardant agent (FR-CL-PA) until 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, the dipping and padding processes (80% wet pick up) were performed, using ZnO or nano-ZnO 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 for neutralization. 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.

Scanning electron microscopy (SEM)

The surface morphology of cotton fibers was examined by the JEOL JSM-6490 Scanning Electron Microscope, with an accelerating voltage of 20 kV and a current of 10 μA at a high magnification power of up to 8000×.

Fourier transform infrared spectroscopy (FTIR)

Chemical compositions of cotton specimens were studied by the Perkin Elmer Spectrum 100 of Fourier Transform Infrared spectrophotometer, with scanning range between 4000 and 700 cm⁻¹, with attenuated total reflection (ATR). The average number of scans was 128; area of the relevant signal in zero-order derivative spectrum was measured.

Fabric thickness measurement

The fabric thickness of test specimens was measured by the Fabric Thickness Tester, Hans Baer AG Ch-Zurich Telex 57767 with the pressure of 10 g/cm². When compared to control fabric, positive change implies a gain in the fabric thickness while negative change indicates a loss in fabric thickness of the fabrics.

Fabric 45° flammability test

Flammability of all specimens was measured in accordance with ASTM D1230-94 by using a flammability tester for apparel textiles (The Govmark

Organization). The specimens were tested after washing for 0, 1, 3, 5, or 10 home laundering cycles at $27 \pm 3^\circ\text{C}$, 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 (modified from 1 to 4 seconds as per standard).

Grab test

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

Elmendorf tearing test

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

Determination of formaldehyde

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

RESULTS AND DISCUSSION

Morphological study

The untreated cotton fiber surface may be described as a smooth fiber surface. Without undergoing any damaging treatment, the integrity cotton fibers show normal spiral structure as proved in Figure 1(a). The morphological structure of control sample consists of natural folds running parallel to the fiber axis. Figure 1(b,c) show the SEM images of cotton sample treated with 40% FR and 5% CL in the absence or presence of 2.5% PA at the magnification of $2000\times$. When compared with Figure 1(a), the morphological structure of flame-retardant-treated specimens, illustrates in Figure 1(b,c), show rougher and more wrinkle fiber surface. The results revealed that the deposition of finishing agent on the fibers damaged its surface. This may have been caused by the slight acidity in the FR, that is, pH 5 as measured. As presented in Figure 1(c), the situation is even worse when 2.5% PA is added in the treatment. PA significantly lowers the pH values of the finishing bath, that is, pH 1–2 as measured, and so the fiber surface is altered remarkably given by the low pH catalyst.

Figure 1(d,e) depict SEM images of cotton specimen treated with 40% FR, 5% CL, and 2.5% PA in the presence of 0.2% ZnO and 0.2% nano-ZnO with a magnification of $2000\times$. The SEM images show that

the irregular-shaped metal oxide particles are attached to the cotton fabric during the padding process. Figure 1(d) clearly shows that clustered ZnO particles are unevenly distributed on the fiber surface and the size of these particles varies slightly, with diameters in the range of $0.4\text{--}1\ \mu\text{m}$. In addition, Figure 1(e) illustrates that the nano-ZnO particles are attached on the fiber surface or between the fibers, while only the existence of big agglomerated particles is observable. High magnification of SEM image showing the existence of nano-ZnO is illustrated in Figure 2. Figure 2 shows that nano-ZnO particles are being agglomerated together with the diameters $0.1\text{--}1.5\ \mu\text{m}$. Agglomeration of particles is observed due to the surface attraction between small nanoparticles.

Surface chemical analysis

FTIR-ATR analysis used to characterize the surface chemical composition of the substrate. Some characteristic bands associated with the cellulose structure in the cotton fibers was evaluated, that is, hydrogen bonded OH stretching centered at $3300\ \text{cm}^{-1}$, CO stretching centered at $1030\ \text{cm}^{-1}$, CH stretching centered at $2900\ \text{cm}^{-1}$, CH wagging centered at $1310\ \text{cm}^{-1}$, and peaks around $1640\ \text{cm}^{-1}$ corresponding to the absorbed water molecules. In addition, when the fabrics are treated with flame-retardant agents, new characteristic peaks are found, that is, carbonyl bands, CH_2 rocking band and CH_3 asymmetric and CH_2 symmetric stretching, as shown in Figure 3(a–d).

Figure 3(a) illustrates the full FTIR-ATR of flame-retardant-treated cotton fabric, showing new characteristics peaks such as CH_2 rocking, carbonyl, CH_3 asymmetric and CH_2 symmetric stretching bands. As illustrated in Figure 3(b), a prominent peak centered at $820\ \text{cm}^{-1}$, an indication of CH_2 rocking band for $\text{P}\text{--}\text{CH}_2$ bond, is observed from flame-retardant-treated specimens. The rocking band of $\text{--}\text{CH}_2$ is a characteristic strong–medium intensity band for phosphonate structures having $\text{P}\text{--}\text{CH}_2\text{--}\text{R}$ groups.^{10,11} The spectrum confirmed the existence of flame-retardant agents on the treated specimens.

Moreover, apart from the control cotton spectra, Figure 3(c) spectrum show strong and distinct absorption band at 1540 and $1750\ \text{cm}^{-1}$ that are attributed to the carbonyl ($\text{C}=\text{O}$) stretching bond due to the carbonyl stretching modes of carboxylate anion and ester respectively.^{12–14} A strong peak around $1670\ \text{cm}^{-1}$, corresponding to the absorbed water molecules, is also clearly shown in Figure 3(c). In general, CL forms a linkage between treated cotton cellulose and FR, which functions as a binder for FR and also as nitrogen provider to enhance the flame retarding performance of the treated cotton fabric.^{4,15} The carbonyls retained in cotton existed in three different

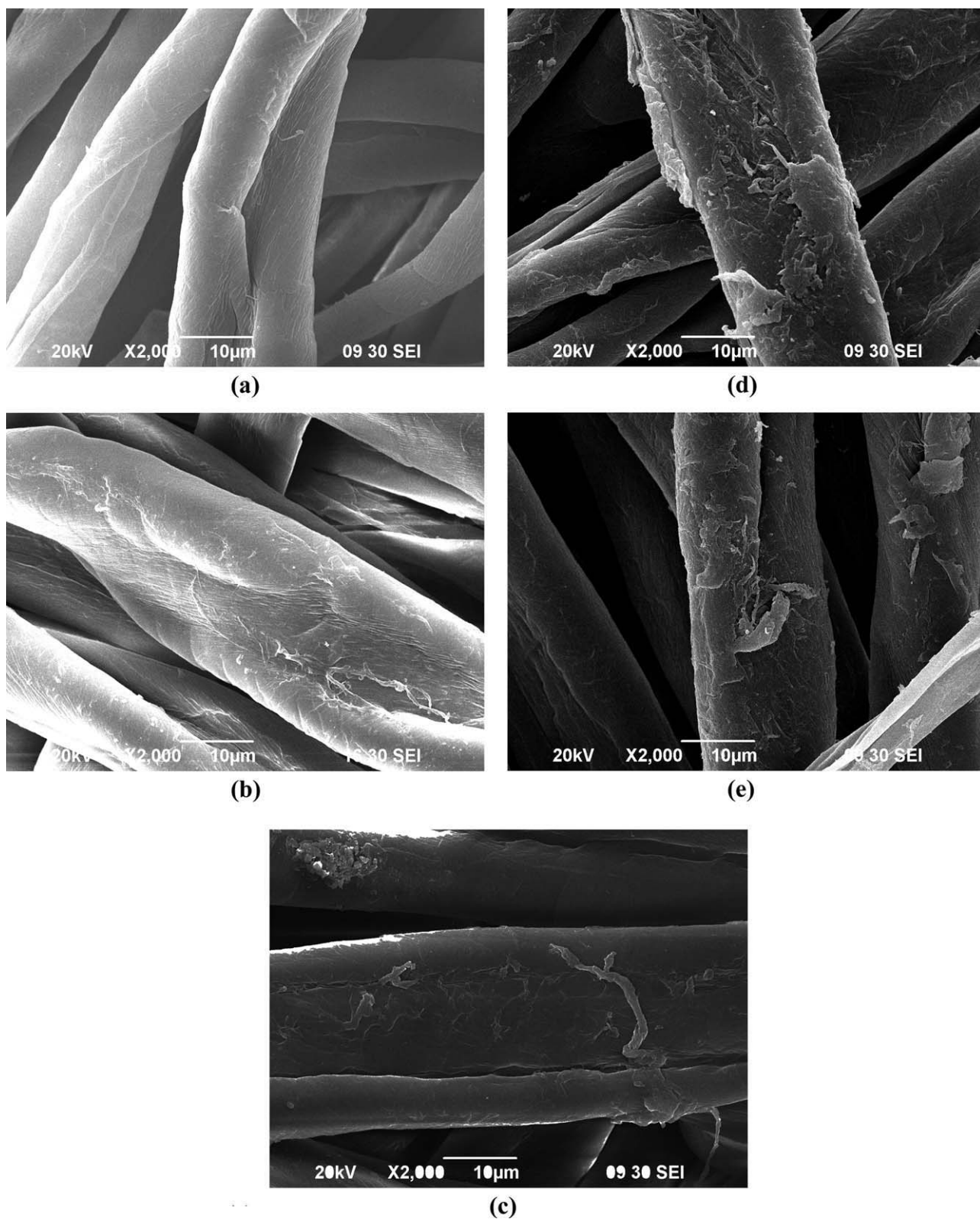


Figure 1 SEM image of (a) control, (b) FR-CL, (c) FR-CL-PA, (d) FR-CL-PA-ZnO, and (e) FR-CL-PA-nano-ZnO treated cotton specimen at $\times 2000$.

forms, which are intermolecular ester linkage, carboxyl and carboxylate anion, when esterification occurs between PA and cotton.^{16,17} FTIR-ATR is used

to characterize the intermolecular ester crosslinkages in flame-retardant-treated cotton fabric and thus all specimens show the $C=O$ stretching bond due to the

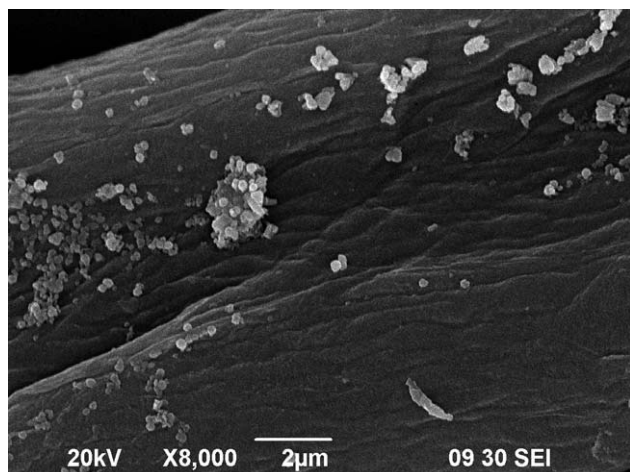


Figure 2 SEM image of F66 specimen at $\times 8000$.

carbonyl stretching modes of ester except F1 specimen without treating with PA.

Figure 3(d) demonstrates the absorption band centered at 2855 cm^{-1} , which is attributed to CH_3 asymmetric and CH_2 symmetric stretching of FR.¹³ Moreover, it is difficult to identify the presence of

phosphorus bonding as phosphorus bond overlaps with characteristic absorption peaks of primary and secondary OH deformation of cotton.¹³ In addition, the ester carbonyl band transmittance is inversely proportional to the amount of ester crosslinkage and the performance of the treated fabric. From Figure 3(a–d), the spectrum show that the percentage of transmittance of F1 specimen of the characteristics peaks is the lowest when compared to other flame-retardant-treated specimens.

Change in fabric thickness

The SEM images, as discussed in Section “Morphological Study”, showed that FR-CL-ZnO flame-retardant system roughened the fiber surface due to the attack of acidic FR and CL. In this study, neutralization for 0, 15, and 30 minutes after flame-retardant treatment is studied. Moreover, the durability of the flame-retardant-treated cotton fabrics to multiple home launderings is also studied. However, fabrics may exhibit shrinkage upon wet treatment due to the release of tensions developed during yarn spinning, fabrication, and finishing.¹⁸ Fabric with poor dimensional stability, refers to the fabric ability to resist a

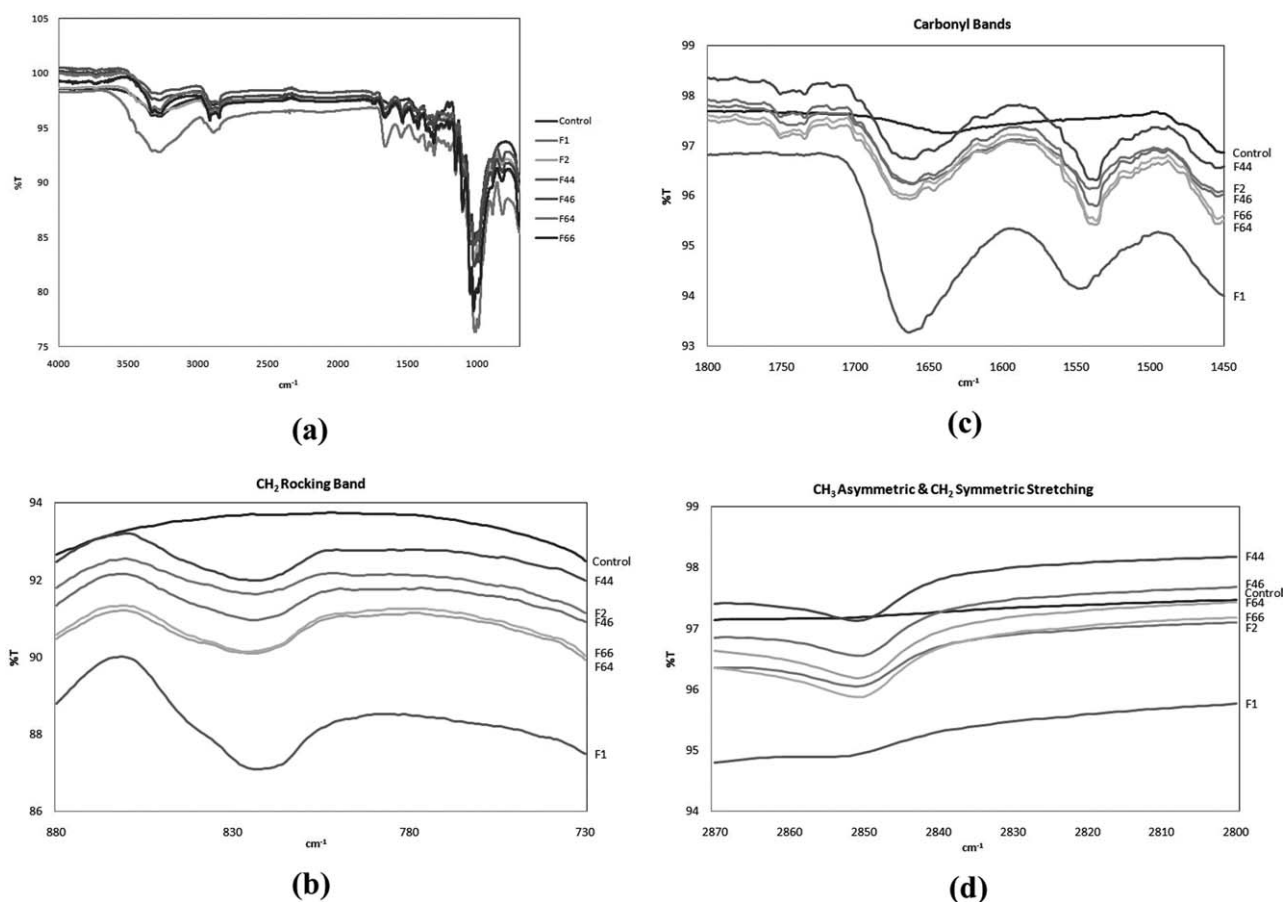


Figure 3 FTIR-ATR spectra of flame-retardant-treated cotton specimens at (a) $4000\text{--}700\text{ cm}^{-1}$, (b) $880\text{--}730\text{ cm}^{-1}$, (c) $1800\text{--}1450\text{ cm}^{-1}$, and (d) $2870\text{--}2800\text{ cm}^{-1}$.

TABLE II
Fabric Thickness of Flame-Retardant-Treated Cotton Fabrics

Sample No.	Neutralization after pad-dry-cure (min)	Fabric Thickness (mm)	Fabric Thickness after 1 laundering cycle (mm)	Fabric Thickness after 3 laundering cycles (mm)	Fabric Thickness after 5 laundering cycles (mm)	Fabric Thickness after 10 laundering cycles (mm)					
Control	0	0.46	–	–	–	–					
F1	0	0.41	(–10.6%)	0.45	(–1.6%)	0.49	(6.8%)	0.51	(10.6%)	0.51	(10.6%)
F2	0	0.41	(–11.9%)	0.44	(–4.1%)	0.47	(2.7%)	0.50	(8.4%)	0.50	(8.4%)
F44	0	0.42	(–8.9%)	0.47	(2.4%)	0.52	(12.2%)	0.53	(15.4%)	0.52	(13.2%)
F46	0	0.40	(–13.3%)	0.46	(0.3%)	0.49	(5.4%)	0.52	(11.8%)	0.52	(13.4%)
F64	0	0.40	(–13.0%)	0.47	(2.8%)	0.52	(13.6%)	0.53	(15.7%)	0.53	(15.6%)
F66	0	0.41	(–10.6%)	0.48	(3.7%)	0.48	(3.6%)	0.55	(18.5%)	0.54	(16.2%)
F1	15	0.46	(0.5%)	0.49	(7.0%)	0.51	(9.5%)	0.56	(20.6%)	0.55	(19.2%)
F2	15	0.46	(–1.4%)	0.50	(8.1%)	0.50	(8.9%)	0.54	(17.1%)	0.54	(16.5%)
F44	15	0.45	(–1.6%)	0.49	(6.2%)	0.52	(13.3%)	0.55	(18.2%)	0.55	(19.0%)
F46	15	0.46	(–0.7%)	0.49	(7.0%)	0.49	(6.8%)	0.55	(20.0%)	0.55	(19.2%)
F64	15	0.45	(–1.9%)	0.47	(2.7%)	0.50	(7.9%)	0.55	(20.2%)	0.56	(21.4%)
F66	15	0.45	(–1.9%)	0.47	(1.1%)	0.50	(9.2%)	0.56	(21.4%)	0.54	(18.0%)
F1	30	0.49	(6.0%)	0.51	(11.4%)	0.54	(17.3%)	0.54	(17.9%)	0.54	(17.1%)
F2	30	0.46	(–0.3%)	0.50	(8.4%)	0.52	(13.0%)	0.54	(16.8%)	0.53	(15.4%)
F44	30	0.46	(–0.8%)	0.49	(6.8%)	0.55	(18.2%)	0.53	(13.8%)	0.55	(18.2%)
F46	30	0.45	(–1.9%)	0.50	(7.9%)	0.49	(6.5%)	0.55	(20.0%)	0.55	(19.7%)
F64	30	0.44	(–4.3%)	0.47	(1.9%)	0.50	(8.1%)	0.55	(19.0%)	0.55	(20.1%)
F66	30	0.46	(–1.4%)	0.49	(5.1%)	0.50	(7.6%)	0.56	(21.3%)	0.56	(20.6%)

change in its dimensions, may become more compact and stiff. Therefore, the fabric thickness varies after each individual treatment.

In general, the major flame protection property of cotton fabric is thermal resistance, which, is approximately related to fabric thickness.¹⁹ Hence, it is important to study the change in fabric thickness upon post-wet treatment, that is, neutralization and laundering. Table II presents the change in fabric thickness of flame-retardant-treated cotton fabrics.

From Table II, the results showed that the fabric thickness decreased from 8.9–13.0% after flame-retardant finishing without neutralization and laundering process. This is attributed to the fact that the fabrics are compressed during the padding process. However, the extent of change in fabric thickness minimized after neutralization in 50°C alkali. In addition, with both neutralization and home laundering cycles, the fabrics shrink from 1.9–21.4% as shown in Table II. The results also showed that the change in fabric thickness steady after five home laundering cycles. For this reason, the change in fabric thickness, leading to the change in thermal resistance, on the improvement of flame-retardant property of treated fabrics should be considered.

Flammability

On the whole, cotton fabrics ignite and burn easily when subjected to external sources of ignition. When fabrics were subjected to thermal decomposition, flame retardants generally promoted formation of

solid char, leading to a catalytic dehydration degradation reaction.^{13,20,21} Black carbonaceous residue that remained after the combustion process of treated fabric is mainly attributed to the fact that water is removed from the material. Table III shows the burning characteristics, ease of ignition, and burning speed, in the flammability tests of flame-retardant-treated cotton fabrics. The ease of ignition and relative ability to sustain combustion measures the flammability characteristics of a material. Moreover, burning 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. In this experiment, progressive burning of a fabric at a distance of 127 mm is recorded as “fail” resistance to burning.

Table III shows that, the entire control cotton fabric is burnt to ashes vigorously at a quick speed of 30.24 m/hr. The result shows that the control fabric is failed in the flammability test. Without post-wet treatment, the flame ignited on the flame-retardant-treated fabrics was extinguished right after removal of the ignition source, leaving fabric with only a spot of char formation. It is mainly attributed to the presence of char insulating layer, which developed on the fabric surface during the burning process. The carbonaceous layer protected the fibers from heat, discouraging burning after the ignition source is removed.¹³ The fabrics without flame spreading after the ignition source has been removed are classified as flame-resistant fabrics. In addition, F1 specimens are no longer flame-resistant when the

TABLE III
Flammability of Flame-Retardant-Treated Cotton Fabrics

Sample No.	Neutralization after pad-dry-cure (minutes)	Burning Speed (m/hr)		Burning Speed after 1 laundering cycle (m/hr)		Burning Speed after 3 laundering cycle (m/hr)		Burning Speed after 5 laundering cycle (m/hr)		Burning Speed after 10 laundering cycle (m/hr)	
Control	0	30.24	(Fail)	–	–	–	–	–	–	–	–
F1	0	DNI	(Pass)	10.24	(Fail)	11.04	(Fail)	11.21	(Fail)	14.24	(Fail)
F2	0	DNI	(Pass)	8.59	(Pass)	8.18	(Pass)	9.00	(Pass)	13.95	(Pass)
F44	0	DNI	(Pass)	7.39	(Pass)	7.73	(Pass)	8.26	(Pass)	8.04	(Pass)
F46	0	DNI	(Pass)	8.04	(Pass)	7.97	(Pass)	6.43	(Pass)	12.72	(Pass)
F64	0	DNI	(Pass)	6.87	(Pass)	7.19	(Pass)	7.64	(Pass)	10.61	(Pass)
F66	0	DNI	(Pass)	6.51	(Pass)	7.80	(Pass)	8.46	(Pass)	8.62	(Pass)
F1	15	10.44	(Fail)	12.41	(Fail)	14.36	(Fail)	14.50	(Fail)	16.79	(Fail)
F2	15	9.81	(Pass)	9.28	(Pass)	8.99	(Pass)	8.80	(Pass)	14.77	(Pass)
F44	15	8.46	(Pass)	8.01	(Pass)	6.03	(Pass)	6.53	(Pass)	9.26	(Pass)
F46	15	7.15	(Pass)	8.25	(Pass)	8.43	(Pass)	7.35	(Pass)	12.26	(Pass)
F64	15	DNI	(Pass)	8.97	(Pass)	8.43	(Pass)	7.54	(Pass)	12.00	(Pass)
F66	15	7.62	(Pass)	8.97	(Pass)	8.00	(Pass)	8.46	(Pass)	11.29	(Pass)
F1	30	10.58	(Fail)	12.48	(Fail)	13.01	(Fail)	15.16	(Fail)	17.73	(Fail)
F2	30	9.18	(Pass)	8.77	(Pass)	9.40	(Pass)	10.07	(Pass)	7.98	(Pass)
F44	30	8.63	(Pass)	8.09	(Pass)	8.00	(Pass)	7.39	(Pass)	7.72	(Pass)
F46	30	7.20	(Pass)	7.73	(Pass)	7.59	(Pass)	6.99	(Pass)	7.86	(Pass)
F64	30	7.81	(Pass)	8.11	(Pass)	7.29	(Pass)	8.28	(Pass)	6.33	(Pass)
F66	30	8.08	(Pass)	7.31	(Pass)	8.27	(Pass)	8.00	(Pass)	6.16	(Pass)

DNI stands for "Did Not Ignite."

Laundering was done in accordance with the AATCC Test Method 135–2004, under $27 \pm 3^\circ\text{C}$ washing temperature.

specimens subjected to neutralization and/or home laundering as presented in Table III. CL acts as nitrogen provider to enhance the flame retarding performance and forms a linkage between treated cotton cellulose and FR.^{4,15} However, post-wet treatment breaks the weak linkage of incomplete esterification of cotton and thus the specimens are failed in the flammability test. However, crosslinking agent with proceeding to complete esterification of cotton is effective in reducing flammability of cotton fabric. With addition of PA in the finishing system, all F2 specimens subjected to neutralization and/or home laundering demonstrate the opposite results. It is mainly attributed to the fact that use of PA as a catalyst in flame retardant finishing increases the percent fixation of FR on the fabric even after multiple laundering cycles or neutralization. Also, the molecular rearrangement after the combustion process, that is, formation of carbonaceous insulating layer, is catalyzed by PA.

In this study, durability of flame-retardant-treated cotton fabrics to multiple home launderings is also studied. After 1–10 home laundering cycles, the flame-resistant-treated specimens (F2, F44, F46, F64, and F66; without undergoing neutralization process) burned and charred in small area at a speed of 6.43–13.95 m/hr, while they are still passed in the flammability test. In general, FR coating is able to react directly with cellulose through its *N*-methylol group to form a crosslinked polymeric network and

more FR molecules are able to bind to cotton through the CL crosslinking bridges.^{6,22} The bonding is highly resistant to hydrolysis during multiple home launderings and the durability of flame-retardant properties is enhanced by PA as catalyst in forming stable crosslinked polymeric networks. In the meantime, the change in fabric thickness, leading to the change in thermal resistance, may also improve flame-retardant property of treated fabrics. As discussed in Section "Change in Fabric Thickness," fabrics may exhibit shrinkage upon wet treatment, which becomes more compact and stiff and the results showed that the change in fabric thickness steady after five home laundering cycles. The change in fabric thickness and the loss of flame retardant chemicals occurs simultaneously after home launderings, while the increase in fabric thickness drastically increases fabric inherent flame-retardant property. Therefore, the flame spread rate remains unchanged or even decreased after home launderings. Besides, neutralization in 50°C alkali also slightly increased the fabric thickness and the results showed that the flame-resistant-treated specimens subjected to both neutralization and home laundering cycles burned and charred while they are still passed in the flammability test.

In other study,⁷ a noticeable result is that TiO_2 or nano- TiO_2 has a significant effect on flame-retardant efficiency. Table III shows that, ZnO or nano-ZnO also diminishes the flame spread rate. By using

0.2 and 0.4% of ZnO as co-catalyst, the flame spread rate of neutralized and/or laundered test specimens decreased from 3.24 to 42.41% (maximum decrement occurs when the FR-CL-PA-0.2% ZnO-treated specimens are undergone 10 home laundering cycles) and 1.55–30.56% (maximum decrement occurs when the FR-CL-PA-0.4% ZnO-treated specimens are undergone 30 minutes neutralization and five home laundering cycles) respectively. However, the flame spread rate decreased from “Did Not Ignite” to 23.97% and 3.35 to 38.25% when the neutralized and/or laundered test specimens subjected to flame-retardant finishing in the presence of 0.2 and 0.4% nano-ZnO co-catalyst respectively. In the FR-CL-PA-nano-ZnO system, the maximum decline in flame spread rate occurs when the flame-retardant-treated specimens undergo 10 home laundering cycles. The diminishing of flame spread rate is mainly attributed to the fact that catalytic effects occur in crosslinking and dehydration reactions.^{23–25} Therefore, it is proved that selection of catalyst for the flame retardant finishing system apparently plays an important role in influencing bonding of the chemicals to cotton for effective flame retardance, that is, slow flame spread rate.

Tensile strength

Figure 4 shows the tensile strength of cotton fabrics, after treatment with different flame-retardant composition in accordance with Table I. As demonstrated in Figure 4, the control sample has highest maximum load at 315.0N, representing strong tensile strength. CL, a crosslinking agent in the flame-retardant system, is composed of melamine and formaldehyde that may reduce the strength of the crosslinked cotton fabric.^{26–28} Therefore, in comparison with the control sample, F1 specimens have lower breaking load resulted from the side effects of crosslinking agent used. Also, the reduction of breaking loads is attributed to the strong acidity of FR, which severely tenders the fabric strength. However, the problem can be minimized by the neutralization of the treated specimens. As presented in Figure 4, the tensile strength of the neutralized cotton specimens (both treated with 15 and 30 minutes) increased obviously. However, F2 specimens dropped remarkably due to the presence of 2.5% PA with pH only 1–2. The PA catalyst in the flame retardant finishing increases the percent fixation of FR on the fabric. The formation of carbonaceous insulating layer is also catalyzed by PA, so that the fabric flame retardancy is enhanced as discussed in Section “Flammability.” The results proved that the catalyst of PA increases the fabric flame retardancy whereas it reduces the tensile strength.

In addition, Figure 4 indicates that the breaking load of samples treated with flame-retardant agents,

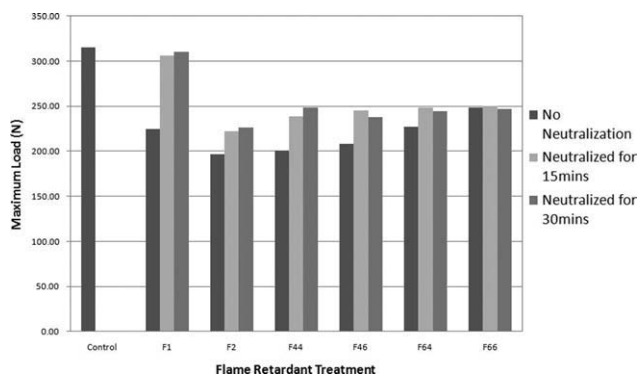


Figure 4 Maximum load of flame-retardant-treated fabrics.

in the presence or absence of ZnO or nano-ZnO co-catalyst, decreased according to the sequence of F66, F64, F46, F44, F2. As discussed, the acidity of flame-retardant agent has a dramatic effect on the reduction of tensile strength of the treated cotton and the magnitude of the tensile strength loss is enhanced with the increase in degree of crosslinking. From Figure 4, the results showed that adding ZnO or nano-ZnO co-catalyst may compensate for the reduction in tensile strength caused by flame-retardant agents because the metal oxide enhanced the effectiveness of the crosslinked polymeric network formation between FR and cotton by the CL. Hence, metal oxide minimizes side-effects of the crosslinking process. In addition, the nano-ZnO co-catalyst gives better overall improvement in tensile strength, especially when 0.4% nano-ZnO co-catalyst is used. It is attributed to the fact that nanoparticles (i) possess high surface areas which have a large surface to bulk ratio, (ii) have large pore volumes and thus bulky organic molecules can be easily adsorbed, and (iii) possess unusual morphology and high number of reactive sites that impart an intrinsically higher surface reactivity.²⁹

Tearing strength

Figure 5 illustrates the tearing force of cotton fabrics, after treatment with different flame-retardant composition in accordance with Table I. The control sample has strongest tearing strength with 917.6 gf tearing force. The results obviously show that tearing strength of flame-retardant-treated (without ZnO or nano-ZnO co-catalyst in the system) cotton specimens dropped significantly according to the sequence of control, F1, F2. In the absence of PA catalyst in the bath, pH value of the flame-retardant solution is pH 5, which is slightly acidic and may reduce the fabric strength, that is, F1 specimen has 818.4 gf tearing force. However, there is a significant reduction of tearing force due to the strong acidity of the finishing bath in the presence of PA catalyst,

that is, pH 1–2. Acidity of the treatment has a severe effect on tearing strength of treated cotton fabrics due to the tendering of fibers, that is, F2 specimen has 663.0 gf tearing force. Besides, the treatment at high temperature curing also causes brittleness in cotton fibers.

In addition, Figure 5 shows that the ZnO co-catalyst may compensate for reduction in tearing strength caused by flame-retardant agents, especially when high concentration of metal oxide is used. This is probably due to increased yarn friction, which resists the yarn slippage. The more are particles attached on the fabric surfaces or filled between the fibers, the higher will be the friction to resist yarn slippage. However, when nano-ZnO is added in the flame-retardant treatment, there is no improvement of tearing strength of cotton as illustrated in Figure 5. The results are mainly attributed to the fact that low concentration of small particles cannot increase yarn friction when compared with micro-ZnO. Moreover, high temperature neutralization process, that is, 50°C, deteriorates tearing strength of the treated specimens and the effects are more serious in the case of prolonged washing process, that is, 30 minutes.

Formaldehyde content

The reactive organophosphorus flame retarding system contains significant levels of formaldehyde, a known carcinogen, while it is still the most popular flame-retarding treatment in textile industry.^{10,14} This is a consequence of increasing commercial demands in terms of cost-effectiveness coupled with increasing concerns for the environmental and general toxicological character of these materials, and treatments.^{4,30} Formaldehyde is classified as a probable human carcinogen based on animal studies with neoplastic lesions at the point of contact, the respiratory tract, and limited evidence of human respiratory tract carcinogenicity.³¹ Table IV shows the formaldehyde content existed on the fabric

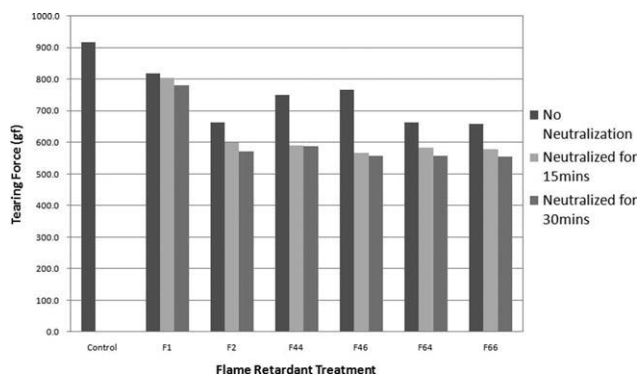


Figure 5 Tearing force of flame-retardant-treated fabrics.

TABLE IV
Formaldehyde Content of Flame-Retardant-Treated Cotton Fabrics

Sample Symbol	Formaldehyde Content (ppm)
F1	33
F1 (Neutralized for 15 min)	15
F1 (Neutralized for 30 min)	14
F2	30
F2 (Neutralized for 15 min)	9
F2 (Neutralized for 30 min)	9
F44	9
F46	8
F64	7
F66	4

treated with different flame-retardant composition in accordance with Table I.

Most *N*-methylol functional phosphorus chemistry is based on the use of FR in conjunction with a melamine formaldehyde resin, CL, to enhance its flame resistance. However, both of FR and CL contribute to the emission of formaldehyde, that is, F1 specimen shows formaldehyde content of 33 ppm. The result shows that the F1 specimen contains small quantity of free formaldehyde which can be toxic and allergenic. F2 specimen treated with FR-CL-PA shows lesser formaldehyde content, that is, 30 ppm. FR-CL system is based on formaldehyde as the bonding agent for cotton.¹⁴ The PA catalyst in the flame retardant finishing increases the percent fixation of FR on the fabric and therefore, lesser free formaldehyde is emitted. In addition, when compare to F2 specimen, the free formaldehyde content is significantly dropped from 70.10 to 74.42% and 77.74 to 87.71% when ZnO and nano-ZnO co-catalyst is added in the treatment respectively. When compared to other flame-retardant agents, FR is a low cost chemical with superior results. Metal oxide acting as co-catalyst in the FR-CL-PA treatment which assists in the crosslinking process, which remarkably minimizes the formation of free formaldehyde and allow the use of FR in the industry. Moreover, the results also show that the higher the concentration of catalyst, that is, 0.4%, added in the treatment, and smaller the co-catalyst particles size, the lower the release of free formaldehyde. Furthermore, neutralization helps to remove the unfixed flame-retardant agents and thus the free formaldehyde emission is minimized.

CONCLUSION

Cotton fabrics have played a major role in the manufacture of clothing and furniture; however, they will burn easily. Hence, reducing flammability of cotton fibers by the application of flame retarding agents is

critical. In this article, FR-CL, in the presence of PA catalyst and/or ZnO or nano-ZnO co-catalyst, has been used to treat cotton fabrics to impart flame-retardant property. Surface morphology of cotton specimens subjected to FR-CL or FR-CL-PA systems shows roughen and wrinkled fabric surface with high deposition of finishing agent, which is caused by the attack of the FR with slight acidity. In the presence of ZnO or nano-ZnO, the SEM images proved that agglomerated metal oxide particles are attached on cotton fabric in irregular shape. In addition, the treated fabrics show some new characteristic peaks in its chemical structure, interrupted as carbonyl bands, CH₂ rocking band and CH₃ asymmetric and CH₂ symmetric stretching.

Apart from these, the results showed that the change in fabric thickness only steady after five home laundering cycles. Fabric with poor dimensional stability may become more compact and stiff, leading to the change in thermal resistance, that is, improvement of flame-retardant property of treated fabrics. In the flammability test, the entire control cotton fabric is burnt to ashes vigorously which is failed in the flammability test. Without post-wet treatment, the flame ignited on the flame-retardant-treated fabrics extinguished right after the removal of ignition source. However, FR-CL-treated specimens are no longer flame-resistant when the specimens subjected to neutralization and/or home laundering. With the addition of PA in the finishing system, even after 1–10 home laundering cycles, all the specimens subjected to neutralization and/or home laundering demonstrate opposite results. By using 0.2 and 0.4% of ZnO or nano-ZnO as co-catalyst, the flame spread rate of neutralized and/or laundered test specimens decreased, even the specimens are undergone 10 home laundering cycles.

In comparison with the control sample, the flame-retardant-treated cotton specimens have lower breaking load and tearing strength resulted from the side effects of crosslinking agent used. ZnO co-catalyst so added compensates for the reduction in tensile and tearing strength caused by the flame-retardant agents, while nano-ZnO co-catalyst demonstrates positive effect to tearing strength only. In addition, both of FR and CL contribute to the emission of formaldehyde, while the free formaldehyde content is dropped

when ZnO and nano-ZnO co-catalyst is added in the treatment. Furthermore, neutralization helps to remove the unfixed flame-retardant agents and thus the free formaldehyde emission is minimized.

References

1. Price, D.; Horrocks, A. R.; Akalin, M.; Daroq, A.A. *J Anal Appl Pyrolysis* 1997, 40-41, 511.
2. Yang, C.Q.; Qiu, X.Q. *Fire Mater* 2007, 31, 67.
3. Wakelyn, P. J.; Adair, P. K.; Barker, R. H. *Fire Mater* 2004, 29, 15.
4. Wu, W. D.; Yang, C. Q. *J Fire Sci* 2004, 22, 125.
5. Wu, X. L.; Yang, C. Q. *J Fire Sci* 2008, 26, 351.
6. Wu, W. D.; Yang, C. Q. *Polym Degrad Stab* 2006, 91, 2541.
7. Lam, Y. L.; Kan, C. W.; Yuen, C. W. M. *J Appl Polym Sci*, to appear.
8. Yadav, A.; Prasad, V. A.; Kathe, A. A.; Raj, S.; Yadav, D.; Sundaramoorthy, C.; Vigneshwaran, N. *Bull Mater Sci* 2006, 29, 641.
9. Well, E. D.; Levchik, S. *J Fire Sci* 2004, 22, 251.
10. Gaan, S.; Sun, G. *J Anal Appl Pyrolysis* 2007, 78, 371.
11. Guan, J. P.; Chen, G. Q. *Fire Mater* 2006, 30, 415.
12. Wu, X. L. *J Fire Sci* 2009, 27, 431.
13. Siriviriyanun, A.; O'Rear, E. A.; Yanumet, N. *Cellulose* 2008, 15, 731.
14. Yang, H.; Yang, C. Q. *J Fire Sci* 2007, 25, 425.
15. Wu, W. D.; Yang, C. Q. *Polym Degrad Stab* 2004, 85, 623.
16. Yang, C. Q. *Textile Res J* 1991, 61, 298.
17. Yang, C. W.; Bakshi, G. D. *Textile Res J* 1996, 66, 377.
18. Topalbekiroğlu, M.; Kaynak, H. K. *Int J Clothing Sci Technol* 2008, 20, 281.
19. Raheel, M. *Protective clothing systems and materials*; Marcel Dekker, Inc., New York 2004, p 1.
20. Mostashari, S. M.; Mostashari, S. Z. *Asian J Chem* 2005, 17, 2331.
21. Mostashari, S. M.; Mostashari, S. Z. *J Appl Fire Sci* 2004, 13, 329.
22. Yang, H.; Yang, C. Q. *Polym Degrad Stab* 2005, 88, 363.
23. Lewin, M. *Polym Adv Technol* 2001, 12, 215.
24. Lewin, M.; Endo, M. *Polym Adv Technol* 2003, 14, 3.
25. Wang, J. S.; Liua, Y.; Zhaoa, H. B.; Liua, J.; Wang, D. Y.; Songa, Y. P.; Wang, Y. Z. *Polym Degrad Stab* 2009, 94, 625.
26. Yang, C. Q.; Wu, W. D.; Xu, Y. *Fire Mater* 2004, 29, 109.
27. Kang, I.; Yang, C. Q.; Wei, W.; Lickfield, G. C. *Textile Res J* 1998, 68, 865.
28. Yang, C. Q.; Wei, W.; Lickfield, G. C. *Textile Res J* 2000, 70, 910.
29. Sun, J.; Gao, L.; Zhang, Q. H. *J Am Ceram Soc* 2003, 86, 1677.
30. Horrocks, A. R.; Kandola, B. K.; Davies, P. J.; Zhang, S.; Padbury, S. A. *Polym Degrad Stab* 2005, 88, 3.
31. Collins, J. J.; Esmen, N. A.; Hall, T. A. *Am J Ind Med* 2001, 39, 336.