# Effect of Titanium Dioxide on the Flame-Retardant Finishing of Cotton Fabric

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**ABSTRACT:** In this study, titanium dioxide ($TiO_2$) or nano titanium dioxide (nano-$TiO_2$) was used as a cocatalyst in the flame-retardant (FR) formulation of *N*-methylol dimethylphosphonopropionamide (Pyrovatex CP New, FR), melamine resin [Knittex CHN, crosslinking agent (CL)], and phosphoric acid (PA) for cotton fabrics to improve the treatment effectiveness and minimize the side effects of the treatment. For FR-treated cotton fabrics, the flame extinguished right after removal of the ignition source with no flame spreading. However, after neutralization and/or home laundering, FR–CL-treated specimens failed the flammability test, whereas the opposite results were obtained from FR–CL–PA-treated specimens. A noticeable result was that the $TiO_2$/nano-$TiO_2$ cocatalyst had a significant effect on decreasing the flame-spread rate. Thermal analysis found that the FR-treated specimens without wet posttreatment showed two endothermic peaks representing the phosphorylation of cellulose and acid-catalyzed dehydration. In addition, the treated fabrics showed some new characteristic peaks in their chemical structures; these were interpreted as carbonyl bands, $CH_2$ rocking bands, and $CH_3$ asymmetric and $CH_2$ symmetric stretching. The surface morphology of the FR–CL–PA-treated cotton specimens showed a roughened and wrinkled fabric surface with a high deposition of the finishing agent that had a lower breaking load and tearing strength, which resulted from the side effects of the CL used. However, the addition of a $TiO_2$ or nano-$TiO_2$ cocatalyst could compensate for the reduction in the tensile strength. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 267–278, 2011

**Key words:** catalyst; crosslinking; flame retardance

## INTRODUCTION

The flammability of fabrics varies dramatically between fibers, ranging from a very high flammability of cellulosic fibers to the inherent flame-retardant (FR) nature of synthetic fibers. Generally speaking, fabrics made from untreated natural fibers, such as cotton, linen, and silk, will burn easily with a high flame velocity. In addition to fibers, the flame-spread rate of fabrics is also dependent on the fabric density and structure; lightweight and loose fabrics are more prone to catching fire quickly.[1] Blended fabrics are considered to be less ignitable with slow flame spread as most synthetic fibers, such as nylon, acrylic, and polyester, resist ignition. However, once ignited, synthetic fabrics melt, and their hazard may increase because the high rate of burning, combined with the melting of the fabric, can result in even more serious burning. The fire hazard associated with blended fabrics may be greater than that of fabrics made of only synthetic or only cellulosic fibers. Reducing flammability of cellulosic fibers has then been one of the major challenges facing the textiles industry.

Many FR agents and methods of application have been developed in attempts to produce FR textile materials. Reactive organophosphorus chemicals, such as *N*-methylol dimethylphosphonopropionamide (e.g., Pyrovatex CP New), have been used as flame-retardant (FR) agents for treating cotton fabrics to impart effective FR properties. FR agents react with the 6-hydroxyl groups of cellulose under acid-catalyzed conditions to produce animal-linked structures without crosslinking.[1] However, the FR agents are not efficiently fixed to the cotton fibers unless they are used in combination with a melamine resin (Knittex CHN), a crosslinking agent (CL), as a binder. In addition, the use of phosphoric acid (PA) as the catalyst makes multiple launderings necessary after the treated fabric is cured.[1,2]

Furthermore, it may be necessary to add a suitable coreactant to enhance the crosslinking of components of the FR–CL–PA formulation. Several interesting developments have occurred recently that involve catalytic effects in various FR formulations.[3–9] In this study, titanium dioxide ($TiO_2$) or nano titanium dioxide (nano-$TiO_2$) was used as a cocatalyst to effectively minimize the side effects of FR treatment. The finishing formulation (recipe) proposed in this study was applied to textile materials by conventional

**TABLE I**
**FR Treatment Conditions**

| Sample abbreviation | Pyrovatex CP New (%) | Knittex CHN (%) | PA (%; 85%) | Micro-TiO$_2$ (%) | Nano-TiO$_2$ (%) |
|---|---|---|---|---|---|
| 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 |

The concentration percentage was measured on the basis of the weight of volume.

pad–dry–cure finishing techniques. The surface morphology of cotton was investigated to find evidence of the presence of FR agents and metal oxides on the fiber surface. The combustibility of the FR-treated fabrics, evaluated by a fabric 45° flammability test, was also studied. Apart from these, thermal and chemical structure analyses were performed by differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy. Grab and Elmendorf tearing tests were conducted to test the fabric strength.

## EXPERIMENTAL

### Material

Plain-weave 100% semibleached cotton fabric (58 ends/cm and yarn count = 40 tex in warp; 58 picks/cm and yarn count = 38 tex in weft; fabric weight = 175 g/m$^2$, 30 × 30 cm$^2$) was used. The FR agent and cellulose CL used were an organic phosphorus compound (Pyrovatex CP New, FR) and a melamine resin (Knittex CHN, CL), respectively, supplied by Huntsman, Ltd. (Singapore). Analytical-reagent-grade PA, which served as a catalyst, was supplied by Sigma-Aldrich Co. (St. Louis, MO, US). The cocatalysts used were micro titanium dioxide (micro-TiO$_2$; 2 μm in diameter) and nano-TiO$_2$ (100 nm in diameter) obtained from UniChem, Ltd. (Doha, Qatar), and International Laboratory, Ltd. (San Bruno, CA, US), respectively. Both had a purity of 99.5+%. The alkali was analytical-reagent-grade sodium carbonate, which was supplied by Sigma-Aldrich. All other chemicals used in the study were reagent grade.

### FR, two-bath, pad–dry–cure treatment

The 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 the FR agent (FR+CL+PA) until a wet pickup of 80% was achieved at 25°C. The fabrics were then dried at 110°C for 5 min. In the second bath, dipping and padding processes (80% wet pickup) were performed, with the TiO$_2$/nano-TiO$_2$ solution dispersed in 10% Matexil DN-VL (dispersing agent).

Subsequently, the padded fabrics were dried at 110°C for 5 min and then cured at 170°C for 1 min. After curing, the fabric specimens were (or were not) neutralized with 30 g/L sodium carbonate for 15 or 30 min 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 h before any further treatment.

### Scanning electron microscopy (SEM)

The surface morphology of cotton fibers was examined by a JEOL JSM-6490 scanning electron microscope (Peabody, MA, US) with an accelerating voltage of 20 kV and a current of 10 μA at a high-magnification power of up to 3000×.

### Fabric 45° flammability test

The flammability of each specimen was measured in accordance with ASTM D 1230-94 with the 45° flammability test for apparel textiles (The Govmark Organization, Inc.). The specimens were tested after they were washed for 0, 1, 3, 5, or 10 home laundering cycles (12 min of washing and 6 min of final spinning) at 27 ± 3°C, according to AATCC 135-2004. The specimens were inserted into a frame and held in the flammability tester at an angle of 45°. A standardized flame, 16 mm in flame length, was applied to the fabric surface near the lower end for 4 s. The burning time (s), char length (cm), and burning speed (m/h) were then measured.

### Fabric thickness

A specimen was placed on the base of a thickness gauge (Hans Baer AG CH-Zurich Telex 57767) (Zurich, Switzerland), and a weighted presser foot was lowered. The displacement between them was measured in accordance with ASTM D 1777-96 as the thickness of specimen.

### DSC

DSC analysis was performed with a PerkinElmer DSC7 calorimeter (Massachusetts, US). All samples

were measured at 30–580°C at a heating rate of 10°C/min in a nitrogen environment. The sample weight was 12 ± 1 mg.

### FTIR spectroscopy

The chemical compositions of the cotton specimens were studied by with a PerkinElmer Spectrum 100 FTIR spectrophotometer, with scanning range between 4000 and 700 cm$^{-1}$, with attenuated total reflection (ATR). The average number of scans was 128; the area of the relevant signal in the zero-order derivative spectrum was measured.

### Grab test

The tensile properties were measured in accordance with ASTM D 5034-95 with a constant rate of extension Instron 4411 tensile testing machine (Norwood, MA, US).

### Elmendorf tearing test

Tearing strength was measured according to ASTM D 1424-96 with an Elmendorf tearing tester manufactured by Thwing-Albert Instrument Co (West Berlin, NJ, US).

## RESULTS AND DISCUSSION

### Morphological study

Figure 1(a) shows the morphological structure of the control (untreated) sample at magnification of 3000×. Without any treatment, the SEM image showed some integrity of cotton fibers with a normal spiral structure. The presence of natural folds running parallel to the cotton fiber axis was also observed. The untreated cotton fiber surface may be described as a smooth fiber surface. Figure 1(b,c) depicts the SEM images of the cotton sample treated with 40% FR and 5% CL in the absence or presence of 2.5% PA. SEM images showed that the surface roughness of the FR-treated fabric samples was higher than that of the untreated fabric. The results reveal that there was a high deposition of finishing agent on the thickened fiber surface. In addition, the appearance of the FR-treated fiber surface was slightly wrinkled; this implied that the fibers were damaged by FR treatment, as shown in Figure 1(b). This may have been caused by the slight acidity in the FR treatment formulation, that is, pH 5. On the other hand, Figure 1(c) shows remarkably wrinkled fiber surfaces compared to Figure 1(b). This is because the addition of 2.5% PA significantly lowered the pH values of the finishing bath, that is, pH 1–2. Therefore, the fiber surface was altered significantly because of the low pH of the finishing solution.

Figure 1(d,e) depicts the SEM images of the cotton specimen treated with 40% FR, 5% CL, and 2.5% PA in the presence of 0.2% TiO$_2$ and 0.2% nano-TiO$_2$. The images show that the metal oxide particles were attached to the cotton fabric during the padding process, but these particles were irregularly shaped. Figure 1(d) shows that clustered TiO$_2$ particles were unevenly distributed on the fiber surface and that the size of these particles varied greatly, with diameters in the range 0.5–3 μm. Moreover, Figure 1(e) shows that the nano-TiO$_2$ particles (with diameters of 0.05–0.2 μm) were agglomerated. The fabric surface was somewhat rough and uneven, with a certain degree of agglomeration of the particles; this was possibly due to the surface attraction between small nanoparticles.

### Flammability

All fabrics made of natural or cellulosic fibers are combustible. A *combustible textile* is defined as a textile material that will ignite and burn easily or that will produce vapors that ignite and burn when they are subjected to an external sources of ignition. Some combustible fabrics when used for clothing are potentially dangerous to the wearer. In this experiment, we measured two critical factors: (1) the ease of ignition and (2) the flame-spread speed. The ease of ignition and relative ability to sustain combustion measures the flammability characteristics of a material. The progressive burning of a fabric at a distance of 127 mm is recorded as fail resistance to burning, and the 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 II shows the burning characteristics measured with the flammability tests and the thickness of the unwashed and washed cotton specimens.

In Table II, the results show that the control fabric was burned to ashes vigorously at a speed of 30.24 m/h. For the nonneutralized FR-treated cotton fabrics, the flame was extinguished right after the removal of the ignition source with no flame spreading; this left fabric with only a spot of char formation. Therefore, the specimens were classified as flame-resistant fabrics. When the fabrics were subjected to thermal decomposition, FRs generally promote the formation of solid char; this leads to a catalytic dehydration degradation reaction, as shown in the following formula:[10–12]

$$(C_6H_{10}O_5)_x \rightarrow 6C + 5H_2O$$
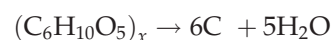
According to the reaction, the black carbonaceous residue that remains after the combustion process of the treated fabric is mainly due to the fact that water is removed from the material. Hence, the
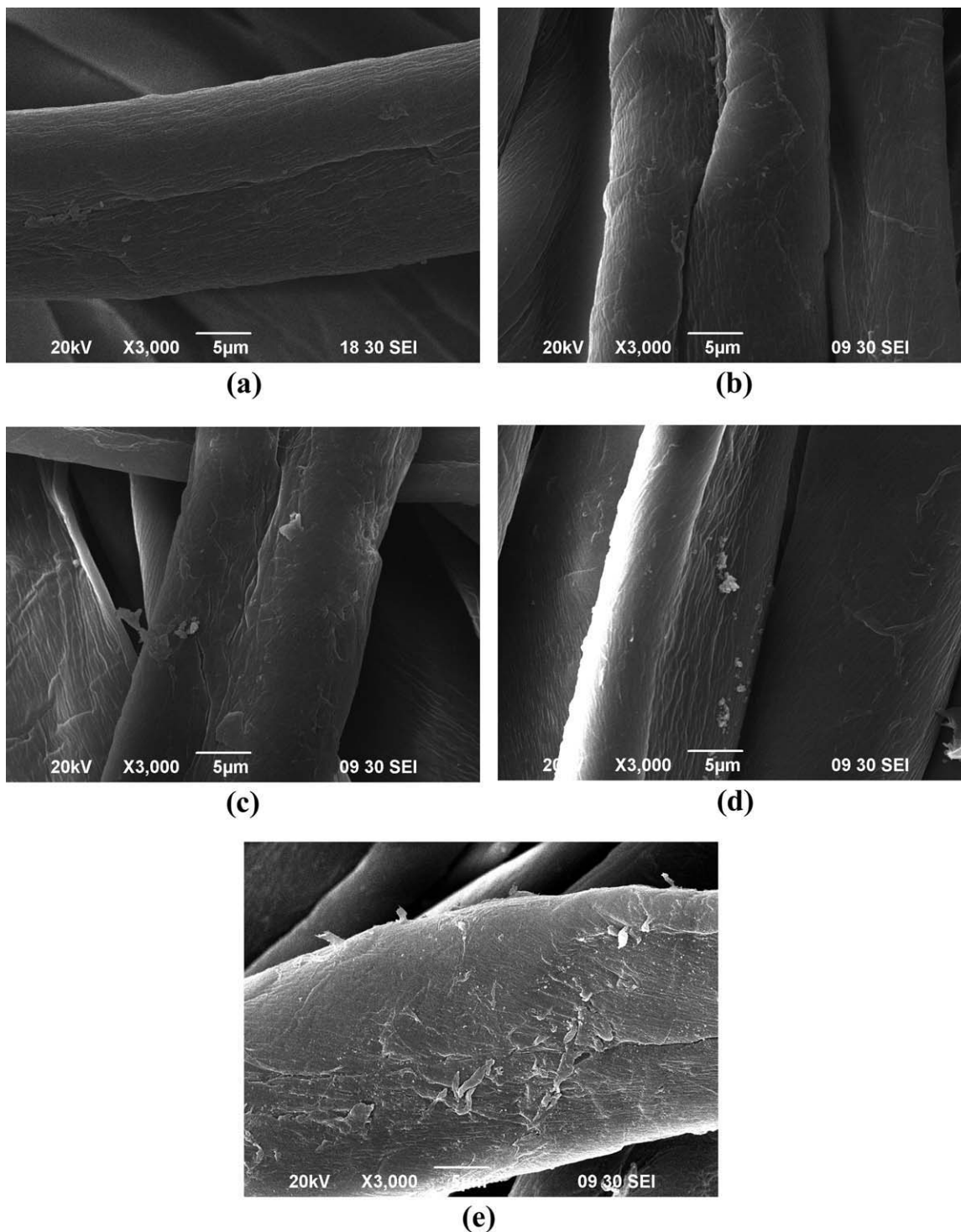
**Figure 1** SEM image of cotton specimens (a) without any finishing treatment, (b) treated with 40% FR and 5% CL; (c) treated with 40% FR, 5% CL, and 2.5% PA; (d) treated with 40% FR, 5% CL, 2.5% PA, and 0.2% TiO$_2$; and (e) treated with 40% FR, 5% CL, 2.5% PA, and 0.2% nano-TiO$_2$ at 3000X.

outstanding improvement in the flame retardance of the treated cotton could be explained by the presence of an insulating layer of char residual, which developed on the fabric surface during the burning process. The carbonaceous layer protected the fibers from heat and discouraged burning after the ignition source was removed.[10]

As Table II shows, all F1 specimens subjected to neutralization and/or home laundering failed the flammability test. Generally speaking, CL will form a linkage between treated cotton cellulose and FR. It functions as a binder for FR and also as a nitrogen provider to enhance the FR performance of treated cotton fabric.[13,14] However, the molecular

**TABLE II**
**Flammability of the Cotton Specimens**

| Sample abbreviation | Number of launderings | No neutralization | | | | | Neutralization for 15 min | | | | | Neutralization for 30 min | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Burning time (s) | Char length (cm) | Burning speed (m/h) | Pass/fail | Fabric thickness (mm) | Burning time (s) | Char length (cm) | Burning speed (m/h) | Pass/fail | Fabric thickness (mm) | Burning time (s) | Char length (cm) | Burning speed (m/h) | Pass/fail | Fabric thickness (mm) |
| Control | 0 | 17.86 | 15.00 | 30.24 | Fail | 0.46 | | | | | | | | | | |
| F1 | 0 | DNI | 0.93 | — | Pass | 0.41 | 43.77 | 12.70 | 10.44 | Fail | 0.46 | 44.24 | 13.00 | 10.58 | Fail | 0.49 |
| F2 | 0 | DNI | 0.89 | — | Pass | 0.41 | 6.01 | 1.64 | 9.81 | Pass | 0.46 | 7.11 | 1.81 | 9.18 | Pass | 0.46 |
| F4 | 0 | DNI | 0.89 | — | Pass | 0.40 | 14.23 | 3.03 | 7.65 | Pass | 0.44 | 40.18 | 8.49 | 7.60 | Pass | 0.44 |
| F6 | 0 | DNI | 1.00 | — | Pass | 0.39 | 7.66 | 1.56 | 7.35 | Pass | 0.44 | DNI | 0.75 | — | Pass | 0.47 |
| F24 | 0 | DNI | 0.70 | — | Pass | 0.41 | DNI | 0.73 | — | Pass | 0.45 | 14.02 | 3.00 | 7.71 | Pass | 0.45 |
| F26 | 0 | DNI | 0.85 | — | Pass | 0.41 | 8.41 | 1.74 | 7.44 | Pass | 0.46 | 9.04 | 1.94 | 7.74 | Pass | 0.44 |
| F1 | 1 | 45.72 | 13.00 | 10.24 | Fail | 0.45 | 37.72 | 13.00 | 12.41 | Fail | 0.49 | 37.49 | 13.00 | 12.48 | Fail | 0.51 |
| F2 | 1 | 10.90 | 2.60 | 8.59 | Pass | 0.44 | 4.99 | 1.29 | 9.28 | Pass | 0.50 | 5.85 | 1.43 | 8.77 | Pass | 0.50 |
| F4 | 1 | 15.82 | 3.10 | 7.05 | Pass | 0.54 | 5.58 | 1.28 | 8.23 | Pass | 0.49 | 8.00 | 1.91 | 8.60 | Pass | 0.49 |
| F6 | 1 | 45.01 | 9.34 | 7.47 | Pass | 0.46 | 6.21 | 1.59 | 9.20 | Pass | 0.49 | 10.50 | 1.91 | 6.56 | Pass | 0.49 |
| F24 | 1 | 10.66 | 2.43 | 8.19 | Pass | 0.53 | DNI | 0.96 | — | Pass | 0.49 | 13.12 | 2.76 | 7.58 | Pass | 0.48 |
| F26 | 1 | 12.34 | 2.53 | 7.36 | Pass | 0.53 | 6.71 | 1.53 | 8.19 | Pass | 0.50 | 8.10 | 1.94 | 8.61 | Pass | 0.49 |
| F1 | 3 | 42.38 | 13.00 | 11.04 | Fail | 0.49 | 32.58 | 13.00 | 14.36 | Fail | 0.51 | 35.96 | 13.00 | 13.01 | Fail | 0.54 |
| F2 | 3 | 13.43 | 3.05 | 8.18 | Pass | 0.47 | 7.76 | 1.94 | 8.99 | Pass | 0.50 | 5.55 | 1.45 | 9.40 | Pass | 0.52 |
| F4 | 3 | 19.18 | 3.73 | 6.99 | Pass | 0.58 | DNI | 1.05 | — | Pass | 0.54 | 7.38 | 1.83 | 8.90 | Pass | 0.53 |
| F6 | 3 | 30.20 | 5.86 | 6.99 | Pass | 0.55 | 20.88 | 4.66 | 8.04 | Pass | 0.47 | 10.18 | 2.41 | 8.53 | Pass | 0.51 |
| F24 | 3 | 20.10 | 3.79 | 6.78 | Pass | 0.58 | 7.03 | 1.49 | 7.62 | Pass | 0.49 | 7.61 | 1.89 | 8.93 | Pass | 0.49 |
| F26 | 3 | 9.19 | 2.04 | 7.98 | Pass | 0.63 | 4.75 | 0.99 | 7.49 | Pass | 0.53 | 13.92 | 3.30 | 8.54 | Pass | 0.50 |
| F1 | 5 | 41.75 | 13.00 | 11.21 | Fail | 0.51 | 32.28 | 13.00 | 14.50 | Fail | 0.56 | 30.88 | 13.00 | 15.16 | Fail | 0.54 |
| F2 | 5 | 14.28 | 3.57 | 9.00 | Pass | 0.50 | 6.40 | 1.56 | 8.80 | Pass | 0.54 | 4.20 | 1.18 | 10.07 | Pass | 0.54 |
| F4 | 5 | 20.88 | 4.38 | 7.55 | Pass | 0.58 | DNI | 1.15 | — | Pass | 0.56 | 4.90 | 1.25 | 9.18 | Pass | 0.53 |
| F6 | 5 | 19.78 | 3.68 | 6.70 | Pass | 0.54 | 22.16 | 4.39 | 7.13 | Pass | 0.53 | 8.10 | 2.04 | 9.06 | Pass | 0.53 |
| F24 | 5 | 12.38 | 2.57 | 7.47 | Pass | 0.60 | 4.86 | 1.05 | 7.77 | Pass | 0.54 | 36.36 | 7.03 | 6.96 | Pass | 0.50 |
| F26 | 5 | 18.68 | 3.88 | 7.48 | Pass | 0.62 | 7.88 | 1.40 | 6.40 | Pass | 0.56 | 25.27 | 5.40 | 7.69 | Pass | 0.52 |
| F1 | 10 | 32.86 | 13.00 | 14.24 | Fail | 0.51 | 27.88 | 13.00 | 16.79 | Fail | 0.55 | 26.39 | 13.00 | 17.73 | Fail | 0.54 |
| F2 | 10 | 13.88 | 5.38 | 13.95 | Pass | 0.50 | 5.80 | 2.38 | 14.77 | Pass | 0.54 | 5.24 | 1.16 | 7.98 | Pass | 0.53 |
| F4 | 10 | 13.25 | 4.59 | 12.47 | Pass | 0.57 | 8.80 | 1.78 | 7.28 | Pass | 0.55 | 24.69 | 4.78 | 6.96 | Pass | 0.50 |
| F6 | 10 | 12.36 | 3.25 | 9.47 | Pass | 0.53 | 15.80 | 3.28 | 7.47 | Pass | 0.53 | 22.50 | 2.85 | 4.56 | Pass | 0.51 |
| F24 | 10 | 29.25 | 7.68 | 9.45 | Pass | 0.59 | 18.50 | 2.88 | 5.60 | Pass | 0.54 | 18.14 | 3.79 | 7.52 | Pass | 0.50 |
| F26 | 10 | 15.36 | 3.52 | 8.25 | Pass | 0.62 | 15.69 | 2.65 | 6.08 | Pass | 0.55 | 14.83 | 2.96 | 7.19 | Pass | 0.51 |

DNI, did not ignite. Laundering was done in accordance with AATCC test method 135-2004 under a washing temperature of $27 \pm 3°C$.

rearrangement after the combustion process, that is, the formation of the carbonaceous insulating layer, was catalyzed by PA. The results reveal that CL, without proceeding to complete esterification of cotton, was not effective in reducing the flammability of the cotton fabric. On the other hand, with the addition of PA in the finishing formulation, all F2 specimens subjected to neutralization and/or home laundering demonstrated the opposite results. Table II indicates that use of PA as a catalyst in FR finishing increased the percentage fixation of FR on the fabric, even after multiple laundering cycles or neutralization.

Moreover, the durability of the FR properties of the FR-treated cotton fabrics to multiple home launderings was also studied. Although the treated specimens burned and charred from 2.43 to 9.34 cm after one home laundering cycle, Table II shows that the specimens still passed the flammability test. The FR coating was able to react directly with cellulose through its N-methylol group to form a crosslinked polymeric network, and the bonding was highly resistant to hydrolysis during multiple home launderings. Consequently, more FR molecules were able to bind to the cotton through the CL crosslinking bridges.[15,16] Moreover, the superior performance of PA as a catalyst in the formation of stable crosslinked polymeric networks helped to maintain the durability of the FR properties of the treated fabric; that is, only the F1 specimens failed the flammability test after laundering.

Both the compression in the padding process and natural fabric shrinkage under wet conditions competed to change the fabric thickness. It is believed that the fabric thickness is reduced after padding (contributed by the pressure between two rolling padders), and thus, Table II shows that the fabric thickness of the FR-treated specimens dropped by 10.58–14.91%. However, fabric shrinkage dominated over the pressure applied on the fabrics after laundering or neutralization. In comparison with those nonwashed FR-treated fabrics, Table II shows that the thickness of the treated specimens increased (8.92–35.22% after one home laundering cycle), and the changes remained steady after three home laundering cycles. In the meantime, neutralization in 50°C alkali also increased the fabric thickness slightly, that is, by 6.10–19.75% (when compared to the nonneutralized FR-treated fabrics). The change in the fabric thickness and the loss of FR chemicals occurred simultaneously with the home launderings, whereas the increase in the fabric thickness slightly increased the inherent FR properties. Therefore, the flame-spread rate remained unchanged or even decreased after home laundering.
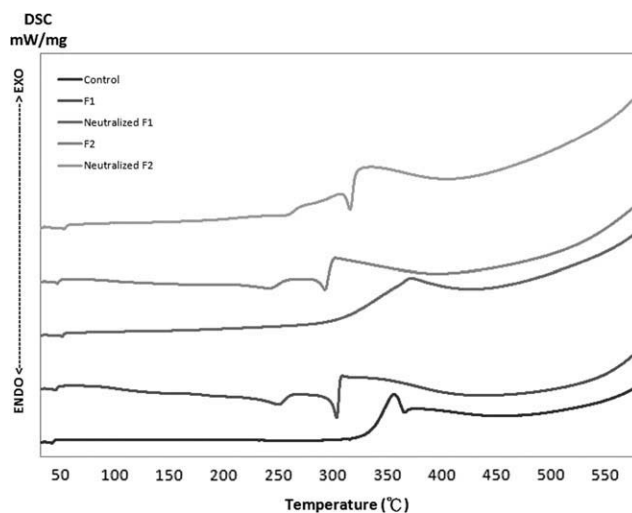
**Figure 2** DSC thermal diagram of the FR-treated cotton specimen.

Furthermore, $TiO_2$/nano-$TiO_2$ imparted a significant effect on the FR efficiency, as demonstrated in Table II. When 0.2 and 0.4% $TiO_2$ were used as cocatalysts, the flame-spread rate of the posttreated (neutralized and laundered) FR–CL–PA-treated test specimens decreased by 1.94–50.71 and 0.86–49.42%, respectively, compared to the respective F2 specimens. On the other hand, in comparison with the respective F2 specimens, the flame-spread rate decreased from 4.66 to 62.09 and 1.82 to 58.84% when the neutralized and laundered test specimens were subjected to FR finishing (FR–CL–PA) in the presence of 0.2 and 0.4% nano-$TiO_2$ cocatalyst, respectively. In both cases, the maximum decline in flame-spread rate occurred when the treated specimens underwent 15 min of neutralization together with 10 home laundering cycles. The reason for the diminished flame-spread rate may have been the catalytic effects in the crosslinking and dehydration reactions.[4,8,9] Therefore, we proved that the selection of catalyst for the FR finishing formulation apparently played an important role in influencing the bonding of the chemicals to cotton for effective flame retardance, that is, a slow flame-spread rate. In this study, both $TiO_2$ and nano-$TiO_2$ showed excellent catalytic effects on the FR–CL–PA formulation.

## Thermal analysis

We used DSC to examine the thermal behavior of the fabrics under a nitrogen gas environment. In this study, thermal analysis was conducted on the control and FR-treated (FR–CL and FR–CL–PA) cotton fabrics, as depicted in Figure 2, which shows that the control fabric demonstrated two endothermic peaks. The first small endothermic peak, around 40–50°C, was ascribed to moisture desorption, and the second endotherm,

between 330 and 340°C, occurred when the decomposition of cellulose occurred with the formation of levoglucosan and other decomposition products.[17,18] The exotherm right after the second endoderm corresponded to char crosslinking reactions.[18]

The FR we used was an effective FR that could promote char formation. It required the absorption of heat by the release of nonflammable molecules during char formation. In addition, the char behaved as a carbonized replica of the original fabric, which continued to function as a thermal barrier.[19] The F1 and F2 specimens, without neutralization, showed similar thermal behaviors, as shown in diagrams in Figure 2. The spectra showed weak and strong endothermic peaks at 240–260 and 290–310°C, respectively. The first peak was interpreted as the phosphorylation of cellulose, and the second strong peak was considered to be acid-catalyzed dehydration. The FR-treated fabric revealed a broad peak at 240–260°C, which represented the efficient phosphorylation of cellulose. The phosphorylation of cellulose could have prevented the formation of levoglucosan, that is, the fuel formed during the thermal decomposition of cellulose, and, thus, improved its thermal stability.[18] On the other hand, the strong peak indicated the presence of FR agents that lowered the decomposition temperature and enhanced the formation of char after pyrolysis of the specimens.[16]

Figure 2 also shows the thermal diagram of the FR-treated fabrics neutralized with hot alkali after curing. The neutralized F1 specimen subjected to FR treatment without the PA catalyst showed the same poor FR properties as that of the control fabric. In general, the CL formed a linkage between the treated cotton cellulose and FR as a binder and also as a nitrogen provider to enhance the FR performance of the treated cotton fabric.[13,14] However, the molecular rearrangement after the combustion process was catalyzed by PA. The DSC thermal diagram revealed that the CL, without proceeding to the complete esterification of cotton, was not effective in reducing the flammability of the cotton specimens. However, the neutralized F2 specimen subjected to FR treatment with the PA catalyst showed a spectrum similar to F2. The thermal analysis data demonstrated that the FR applied to the cotton fabrics was retained on the fabric after neutralization. We proved that the use of PA as a catalyst in FR finishing increased the percentage fixation of FR on the fabric even after wet treatment; this demonstrated good laundering durability.

## Chemical structure analysis

FTIR–ATR spectroscopy is a surface-sensitive technique that is used to characterize the chemical structure of a substrate.[20,21] This analysis was performed on the control cotton fabric, and the spectrum at 4000–700 cm$^{-1}$ is illustrated in Figure 3(a). The spectra about the characteristic bands related to their chemical structure were the hydrogen-bonded OH stretching centered at 3300 cm$^{-1}$, the CO stretching centered at 1030 cm$^{-1}$, the CH stretching centered at 2900 cm$^{-1}$, and the CH wagging centered at 1310 cm$^{-1}$,[20–22] as illustrated in Figure 3(b–e). In addition, a peak around 1640 cm$^{-1}$, corresponding to the absorbed water molecules, is clearly shown in Figure 3(f).[20,21] All of these intense peaks were associated with the cellulose structure of the cotton fibers.

In addition, when the fabrics were treated with FR agents, new characteristic peaks, represented as carbonyl bands, CH$_2$ rocking bands, and CH$_3$ asymmetric and CH$_2$ symmetric stretching, were formed. Figure 4(a–d) illustrates the FTIR–ATR spectra of the FR-treated cotton fabric. In Figure 4(b), a strong peak around 1660 cm$^{-1}$, corresponding to the absorbed water molecules, is clearly shown. Also, the spectra showed distinct and strong absorption bands at 1740 and 1550 cm$^{-1}$; these were attributed to the carbonyl (C=O) stretching bond due to the carbonyl stretching modes of ester and carboxylate anions, respectively.[2,10,23] FTIR–ATR spectroscopy was also used to characterize the intermolecular ester crosslinkages in the FR-treated cotton fabric. When esterification occurred between the CL and cotton cellulose, the carbonyls retained in the cotton existed in three forms, that is, intermolecular ester linkages, carboxyls (the acidic form of the free carboxyls), and carboxylate anions (the basic form of the free carboxyl).[24,25] Moreover, the ester carbonyl band transmittance was inversely proportional to the amount of ester crosslinkages and the performance of the treated fabric. The spectrum showed that the percentage transmittance of the F1 specimen at 1740 and 1550 cm$^{-1}$ was the lowest compared to the other FR-treated specimens shown in Figure 4(b). However, the durability of the FR–CL linkage on the cotton fabric was impermanent with wet treatment, as proven in the flammability test, which we discussed earlier. Furthermore, TiO$_2$/nano-TiO$_2$ catalyzed the crosslinking process of FR–CL, and hence, the overall transmittance shifted downward and implied a more effective process, as presented in Figure 4(b). The FTIR–ATR spectra clearly demonstrated that the metal oxide participated in the esterification of CL onto cotton under the curing conditions.

For FR-treated specimens, a prominent peak centered at 820 cm$^{-1}$ was observed, as illustrated in Figure 4(c). The peak was the contribution of the CH$_2$ rocking band for the P—CH$_2$ bond and indicated that FR–CL crosslinks appeared on the cotton
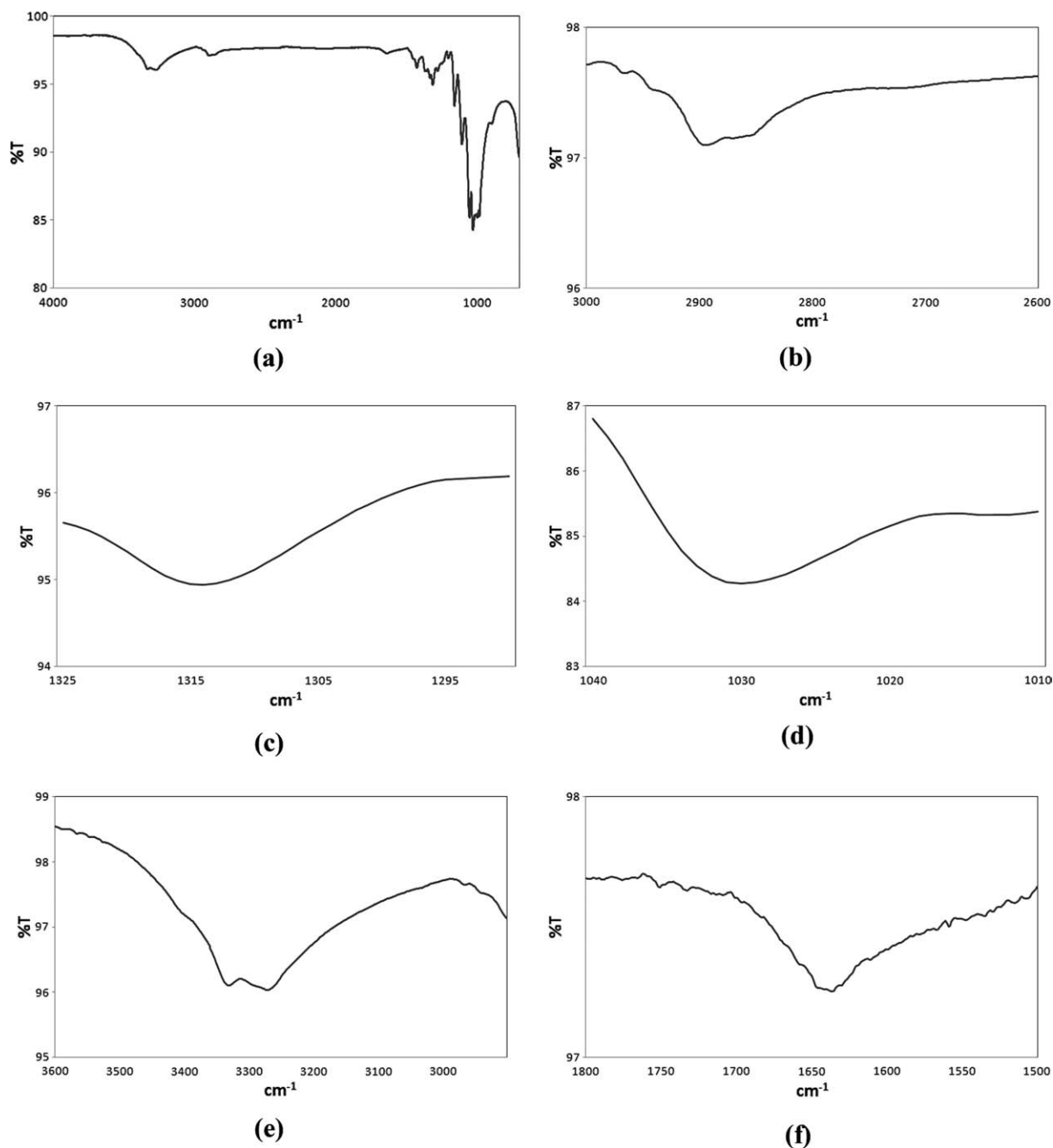
**Figure 3** FTIR–ATR spectra of the control cotton specimen at (a) 4000–700 cm$^{-1}$, (b) 3000–2600 cm$^{-1}$ (CH stretching), (c) 1325–1290 cm$^{-1}$ (CH wagging), (d) 1040–1010 cm$^{-1}$ (CO stretching), (e) 3600–2900 cm$^{-1}$ (OH stretching), and (f) 1800–1500 cm$^{-1}$ (absorbed H$_2$O).

fabric. The rocking band of —CH$_2$ is a characteristic strong–medium intensity band for phosphonate structures having P—CH$_2$—R groups.[18,19] Figure 4(d) demonstrates the absorption band centered at 2850 cm$^{-1}$, which was attributed to the CH$_3$ asymmetric and CH$_2$ symmetric stretching of FR.[10] In addition, it was difficult to identify the presence of phosphorus bonding as the phosphorus bond overlapped with the characteristic absorption peaks of the primary and secondary OH deformation of cotton.[10]

**Tensile strength and elongation**

Figure 5(a,b) shows the tensile strength and elongation at break, respectively, of cotton fabrics after treatment with different FR formulations, in accordance with Table I. The control sample demonstrated the highest tensile strength [Fig. 5(a)]. In comparison with the control sample, the FR-treated cotton specimens had lower breaking loads; this resulted from side effects of the CL used. Figure 5(a) indicates that the breaking load of samples treated
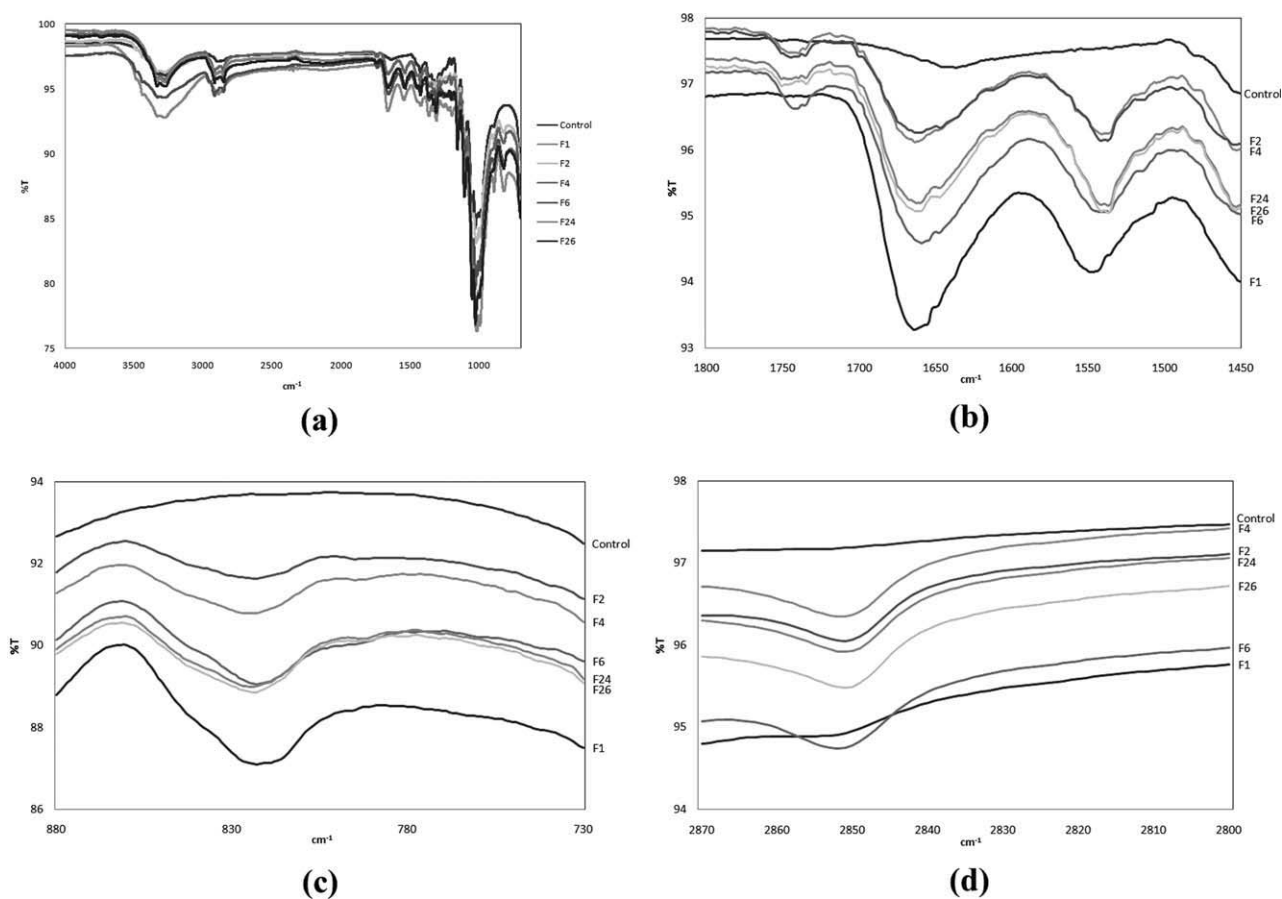
**Figure 4** FTIR–ATR spectra of the FR-treated cotton specimen at (a) 4000–700 cm$^{-1}$, (b) 1800–1450 cm$^{-1}$ (carbonyl bands), (c) 880–730 cm$^{-1}$ (CH$_2$ rocking band), and (d) 2870–2800 cm$^{-1}$ (asymmetric CH$_3$ and symmetric CH$_2$ stretching).

with the FR agents decreased in the order F24, F4, F26, F6, F1, and F2. Moreover, the tensile strength and elongation at break of the fabrics were highly correlated. Figure 5(b) shows a pattern similar to Figure 5(a).

A CL composed of melamine and formaldehyde was used. It was proven that crosslinking of cotton cellulose molecules reduced the strength of the crosslinked cotton fabric.[26–28] The results in Figure 5(a) imply that the reduction of breaking loads was also due to the strong acidity of the finishing bath, which severely decreased the fabric strength. In the absence of a metal oxide cocatalyst in the finishing formulation, the occurrence of a diminished breaking load was significant for the FR-treated cotton specimen F2 because of the presence of 2.5% PA with a pH of only 1–2. The results prove that the catalyst of PA increased the fabric FR, whereas it reduced the tensile strength. Therefore, the neutralization of the FR-treated cotton specimens with alkali was indispensable for the removal of PA from the substrate. As shown in Figure 5(a), the tensile strength of the neutralized cotton specimens increased obviously, no matter if they were neutralized for 15 or 30 min.

The acidity of the FR agent has a significant effect on the reduction of the tensile strength of treated cotton, and the magnitude of the tensile strength loss was enhanced with increasing degree of crosslinking. As shown in Figure 5(a), the results show that the addition of the TiO$_2$ or nano-TiO$_2$ cocatalyst, especially 0.2% nano-TiO$_2$, may have compensated for the reduction in the tensile strength caused by the FR agents. The effectiveness of the crosslinked polymeric network formation between FR and cotton by CL was enhanced by the metal oxides. Hence, the metal oxide minimized the side effects of the crosslinking process. In addition, the nano-TiO$_2$ cocatalyst gave a better overall improvement in the tensile strength because the nanoparticles (1) possessed high surface areas that had a large surface-to-bulk ratio; (2) had large pore volumes, and thus, bulky organic molecules could be easily adsorbed; and (3) possessed an unusual morphology and a high number of reactive sites, which imparted an intrinsically higher surface reactivity.[29] Furthermore, the increase in the amount of catalysts, which promoted the reversible crosslinking of cellulose molecules, resulted in less improvement in the tensile strength.[30]
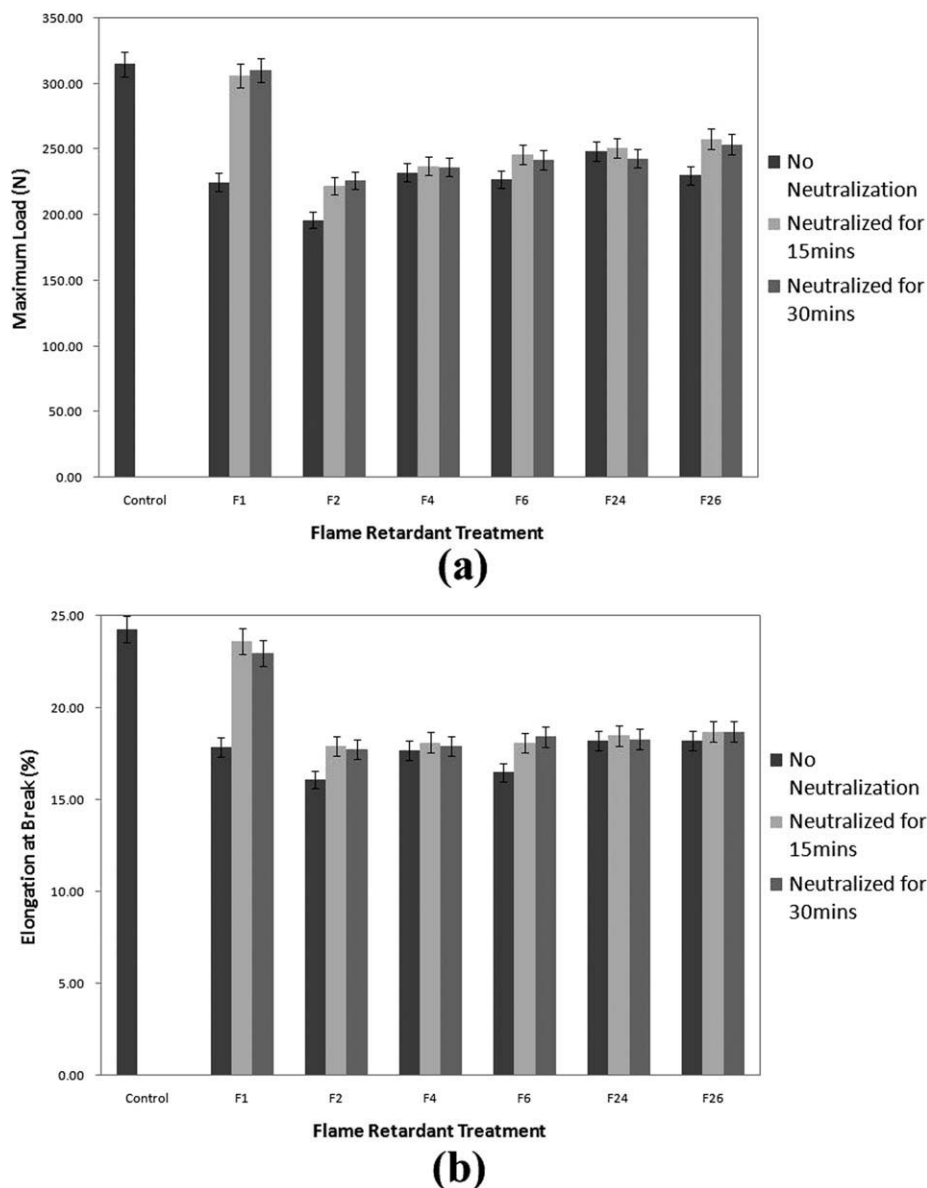
**(a)**



**(b)**

**Figure 5** (a) Tensile strength and (b) elongation at break of the FR-treated cotton specimen.

**Tearing strength**

Figure 6 shows the tearing force of the cotton fabrics after treatment with different FR formulations (Table I). The results obviously show that the tearing strength of the cotton specimens treated with diffe-rent FR formulations dropped significantly according to the following sequence: control, F1, F6, F4, F26, F24, and F2. In the absence of the PA catalyst in the bath, the pH value of the FR solution was pH 5, which was slightly acidic and may have tendered the fabric strength. On the other hand, there was a signi-ficant reduction in the tearing force because of the strong acidity of the finishing bath in the presence of the PA catalyst, that is, pH 1–2. The acidity of the treatment had a severe effect on the tearing strength of the treated cotton fabrics because of the tendering

of the fibers. Also, the treatment at high-temperature curing also caused brittleness in the cotton fibers.

Figure 6 also shows that the $TiO_2$ or nano-$TiO_2$ cocatalyst may have compensated for the reduction in the tearing strength caused by the FR agents, especially when a high concentration of metal oxide was used. This was probably due to the increased yarn friction, which helped to resist yarn slippage. When more particles were attached to the fabric surface or filled between the fibers, the friction to resist yarn slippage was higher. In addition, when nano-$TiO_2$ was added in the FR treatment, there was only a slight enhancement of the tearing strength of cotton, as shown in Figure 6. The results were mainly attributed to the fact that small nano-$TiO_2$ increased the yarn friction to a lesser extent
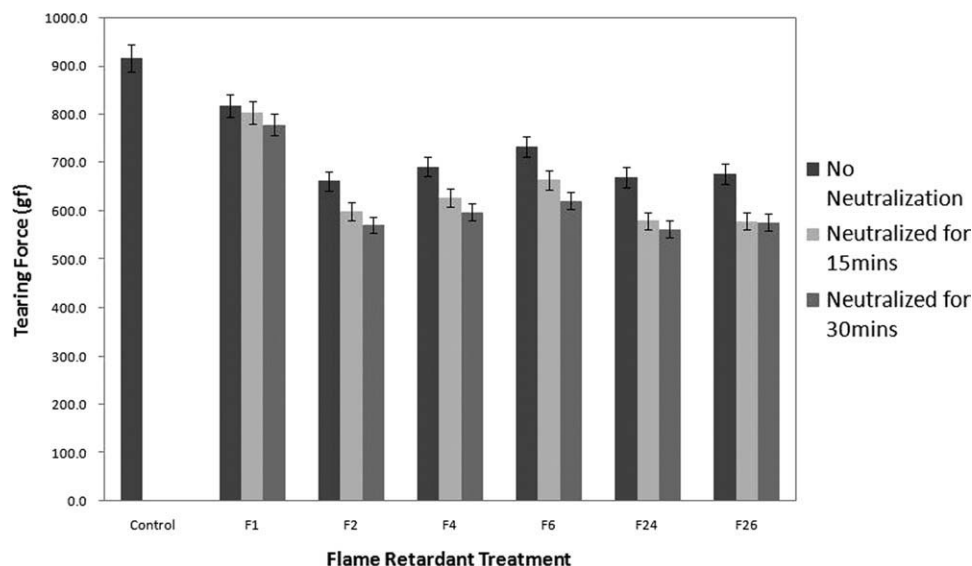
**Figure 6** Tearing strength of the FR-treated cotton specimen.

compared with micro-$TiO_2$. Moreover, washing the FR-treated cotton specimens with alkali helped to neutralize the acidic PA catalyst. However, the high-temperature neutralization process, that is, 50°C, deteriorated the tearing strength of the treated specimens. The effects were more serious in the case of the prolonged washing process, that is, the 30-min washing process.

## CONCLUSIONS

FR–CL, in the presence of a PA catalyst and/or a $TiO_2$/nano-$TiO_2$ cocatalyst, was used to impart FR properties to the cotton fabrics. The surface morphology of the FR-treated cotton specimens showed a roughened and wrinkled fabric surface with a high deposition of the finishing agent and agglomerated metal oxide. The combustion properties of the FR-treated fabrics were evaluated, and the non-neutralized FR-treated cotton fabrics showed no flame spreading. However, after neutralization and/or home laundering, the FR–CL-treated specimens failed the flammability test, whereas the opposite results were obtained with the FR–CL–PA-treated specimens. Furthermore, a noticeable result was that the $TiO_2$/nano-$TiO_2$ cocatalyst had a significant effect on decreasing the flame-spread rate. Apart from these, the FR-treated specimens without wet posttreatment showed endothermic peaks at 240–260 and 290–310°C, and the treated fabrics showed some new characteristic peaks in the chemical structure, interpreted as carbonyl bands, $CH_2$ rocking bands, and $CH_3$ asymmetric and $CH_2$ symmetric stretching. The effectiveness of the crosslinked polymeric network formation

between FR and cotton by CL was enhanced by the metal oxides. Also, the particles attached to the fabric surface or filled between the fibers increased the yarn friction; this helped to resist yarn slippage. In comparison with the control sample, the FR-treated cotton specimens had a lower breaking load and tearing strength, whereas the addition of the $TiO_2$ or nano-$TiO_2$ cocatalyst may have compensated for the reductions in the tensile and tearing strengths caused by the FR agents.

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