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Effects of TiO_2 and curing temperatures on flame retardant finishing of cotton

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ABSTRACT

The performance of flame retardancy of cotton cellulose can be influenced by curing conditions. In this study, cotton cellulose was imparted durable flame retardant properties by a reaction between a flame retardant agent (Pyrovatex CP New) and a cross linking agent (Knittex CHN), in the presence of catalysts phosphoric acid and titanium dioxide (TiO_2). After treating cotton fabrics at different curing temperatures for different curing time, its flame retardant performance was evaluated by 45° fabric flammability standard test method. For cotton fabrics cured at 150 and 170 °C, good flame retardant characteristics were retained even after three home laundering cycles. The use of TiO_2 as a co-catalyst in the treatment improved the flame retardant properties and reduced the loss of tearing strength of cotton fabrics. No significant negative effect in the whiteness index was observed, as compared with conventional flame retardant treatment.

1. Introduction

Cellulosic fibre is an essential natural textile fibre and plays an important role in our daily lives because of its various applications. The large consumption of cotton fibre is due to its numerous advantages such as good water absorbance and breathability. Apart from the daily applications of cotton cellulose, other forms of cellulose, such as graft copolymers from cellulose and lignocellulosic polymers have been widely studied from biological and green aspects (Thakur, Thakur, & Gupta, 2014; Thakur, Thakur, & Gupta, 2013a,b). Although cellulosic fibre has supreme properties, one critical defect of cellulosic fibres is that these fibres are easily burnt and are susceptible to fire. Therefore, application of flame retardant materials on cotton cellulose is an essential issue in the textile industry (Lessan, Montazer, & Moghadam, 2011; Schindler & Hauser, 2004).

Cellulosic fabric is a highly flammable product which, once ignited, results in the flame spreading at a rate that is linked to fibre density and fabric structure (Weil & Levchik, 2008). Some other blended fabrics such as nylon, acrylic and polyester are considered as less ignitable fabrics. However, fire associated with these synthetic fibres is more dangerous since these fibres melt during burning, leading to severe skin burn (Lam, Kan, & Yuen, 2011a). In order to impart flame retardancy property, cotton fabrics are impregnated with flame retardant additives that prevent ignition. In textile industry, flame retardant finishing is widely applied in our daily life, protecting consumers from unsafe apparel.

Many flame retardant treatments, formulations and additives were developed in the 1950s–1980s (Horrocks, Kandola, Davies, Zhang, & Padbury, 2005; Horrocks, 1986). One of the effective durable flame retardant agents is called Pyrovatex CP New which is an *N*-methylol dimethylphosphonopropionamide, commonly used nowadays. It is an organic phosphorus compound. The flame retardant agent is applied together with melamine resins such as Knittex CHN. Melamine resin is a crosslinking agent forming linkages between cellulose and the flame retardant agent. In addition, phosphoric acid is used as the catalyst to initiate the reaction with lower activation energy. The chemistry of the Pyrovatex CP system is shown in Fig. 1. It can see that the melamine resin links the flame retardant agent and cellulose together. Melamine resin is mainly composed of nitrogen content. In combination of nitrogen with phosphorus has a synergistic effect on flame retardancy (Kaur, Jain, Gur, & Bhatnagar, 1980). The Pyrovatex CP conventional formulation achieves flame retardancy by condensed phase mechanisms (Gaan & Sun, 2007a), i.e. the pyrolysis reaction is altered to produce less flammable volatiles and more residual char while preventing the formation of levoglucosan. The amount of phosphorus content is the main factor to control the flame retardancy efficiency (Lessan et al., 2011; Schindler & Hauser, 2004).

In the present study, the conventional formulation of flame retardant finishing has been modified with the addition of metal oxides. The addition of metal oxides such as titanium dioxide (TiO_2) or zinc oxide (ZnO) as a co-catalyst in the formulation has been

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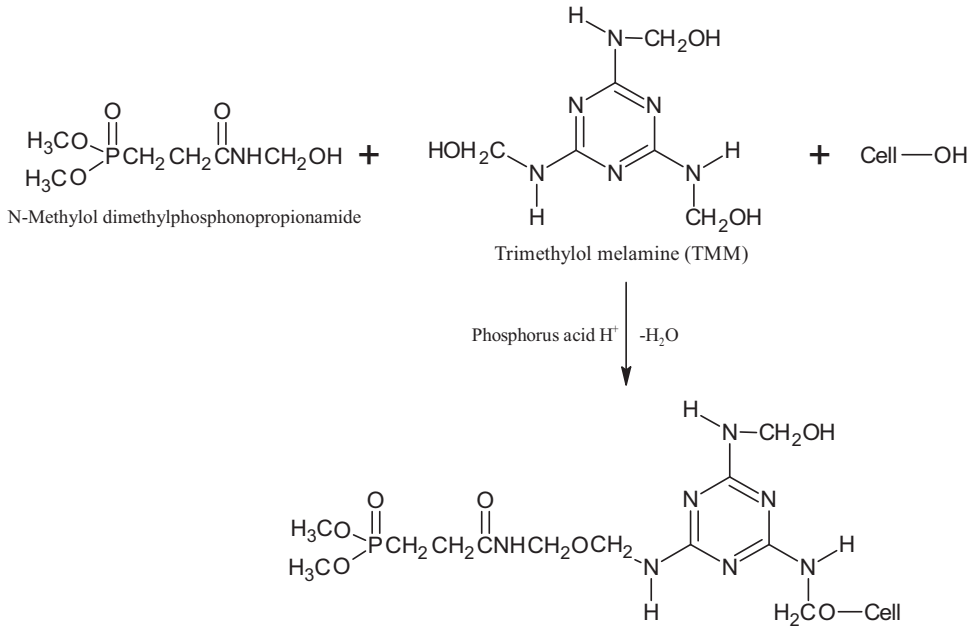

Fig. 1. The chemistry of the Pyrovatex CP system.

found to be useful for improving flame retardant properties of cotton materials (Lam et al., 2011a; Lam, Kan, & Yuen, 2011b). Moreover, TiO_2 and ZnO have been used separately as flame retardant agents to impart flame retardancy to cellulosic fabrics. (Fallah, Fallah, & Zanjanchi, 2011a,b). This shows that metal oxides have positive effects on flame retardant properties. In addition, the presence of metal oxides in the finishing treatment affords various advantages. The inclusion of nano-ZnO in the system gives additional functional properties such as improved strength and UV-absorption (Yadav et al., 2006). The use of TiO_2 also minimizes side effects of the flame retardant treatment such as compensation for the reduction in tensile strength (Lam, Kan, & Yuen, 2012). Moreover, TiO_2 may also serve as a heat sink in the flame retardant reaction in order to disrupt the combustion cycle of cellulosic fibres (Tan, Wang, & Zhang, 1996; Schindler & Hauser, 2004).

On one hand, applying flame retardant chemicals on fabrics results in excellent flame retardant properties and on the other hand, flame retardant chemicals may cause some harmful effects to the marine environment (Gutenmann & Lisk, 1975). Phosphorous compounds present in waste water lead to various environmental problems (Schindler & Hauser, 2004). Formaldehyde, which is known as carcinogenic, is released during curing process and arouses health concerns. Therefore, metal oxide is added in the formulation to minimize the side effects and improve flame retardant properties of cotton materials simultaneously. Lam et al. (2011b) study, addition of metal oxide in the formulation can inhibit formaldehyde release.

In this study, the effect of TiO_2 as the co-catalyst and of the curing conditions collectively (i.e. curing temperature and curing time) on the flame retardant finishing of cotton was studied. Different concentrations of TiO_2 were added into the conventional flame retardant formulation and the reaction conditions were optimized. The flammability, tearing strength, fabric whiteness, surface morphology as well as thermal behaviour of the treated fabrics were evaluated after the finishing treatment.

2. Experimental

2.1. Materials

One hundred percent semi-bleached plain woven cotton fabric purchased from Lai Tak Enterprise Limited (14 ends/cm, yarn count 74 tex, in warp; 14 picks/inch, yarn count 93 tex, in weft; fabric weight 226 g/m^2) was used. Fabric samples were cut into size 30 cm × 30 cm for the finishing treatment. Pyrovatex CP New, and Knittex CHN (melamine resin) provided by Huntsman Limited served as the durable flame retardant agent and the crosslinking agent, respectively. Catalyst, 85% phosphoric acid supplied by Sigma-Aldrich Co., was added. TiO_2 (effective diameter = 444 nm) supplied by Accuchem (purity ≥ 99.8%) was employed as co-catalyst in the treatment. Sodium carbonate used for neutralization was supplied by Sigma-Aldrich.

2.2. Methods

The composition of the flame retardant formulations used for the treatment is shown in Table 1. One bath pad-dry-cure method was used to carry out the flame retardant finishing. The fabrics were impregnated and padded with the prepared formulations to achieve a wet pick up of 75–80% at room temperature. Then, the samples were dried in oven at 110 °C for 5 min followed by curing at four different temperatures of 110, 130, 150 or 170 °C and different times of 1, 2 or 3 min. Half of the samples prepared from each condition were subjected to further neutralization. The

Table 1
The formulations of flame retardant solution with different concentrations of TiO_2.

Formulation	Pyrovatex CP new (%)	Knittex CHN (%)	Phosphoric acid (85%) (%)	TiO_2 (%)
Z (conventional formulation)	40	5	25	0
X	40	5	25	0.2
Y	40	5	25	0.4

Concentration percentage measured based on weight of volume

fabrics were sequentially neutralized in 30 g/L sodium carbonate at 50 °C for 30 min. Then, the fabrics were rinsed under running warm water, about 50 °C. After rinsing, the fabrics were dried completely in the oven at 80 °C. Finally, the fabrics were conditioned at 21 ± 1 °C and 65 ± 5% for 24 h before any test. Curing at 170 °C for 1 min was the conventional flame retardant finishing condition for counter comparison.

2.3. 45° Fabric flammability test

Flammability of fabrics was tested in accordance with Standard 16 CFR Part 1610. The test was performed using a 45° flammability tester for apparel textiles manufactured by the Govmark Organization Inc. In order to demonstrate the performance of the flame retardant finishing after usual home laundering, three home laundering cycles at 27 ± 3 °C according to AATCC 135-2004 were completed before carrying out the flammability test. A 16 mm standardized flame length was applied on the specimens for 4 s (instead of 1 s to increase the burning chance of a fabric sample during testing) (Lam et al., 2011a; Lam, Kan, & Yuen, 2011c). The flammability characteristics were evaluated by two important factors, burning time and char length. The burning time shows the ease of ignition and the ability to sustain the combustion process. Char length or char residue refers to the burn mark on the fabric samples. If the progressive burning of a fabric at a distance of 127 mm is recorded or the flame travels up the specimen and the stop thread is broken, the fabric is assumed to have failed the test. If the flame self-extinguishes when travelling along the fabrics without breaking the stop thread, the fabrics are said to be pass. Five specimens were tested and the average burning time was calculated.

2.4. Tearing strength

Tearing strength of fabrics was assessed by the Elmendorf test following BS EN ISO 13937 (Elmatear Digital Tear Tester manufactured by James H. Heal & Co. Ltd., Halifax England). Standard weight with 3200 g was mounted on the tester for the measurement. The average tearing force was calculated from all warp and weft measurements.

2.5. Whiteness

Whiteness of the fabric was measured in accordance with AATCC Test Method 110-2005 in order to demonstrate how white the textile materials appear to average viewers. Each sample was measured 3 times using a spectrophotometer (GretagMacbeth Color-Eye 7000A) with D_{65} standard illuminant and 10° observer.

2.6. Fabric thickness

A specimen was placed on the base of a thickness gauge (Hans Baer AG CH-Zurich Telex 55767) (Zurich, Switerland), and a weighted presser foot was lowered. The displacement between them was measured according to ASTM D1777-96 as the thickness of specimen.

2.7. Characterization techniques

Scanning electron microscopy was used to investigate the surface morphology of the cotton fibres before and after treatment. The specimens were investigated by a Hitachi TM3000 Tabletop Microscope with 15 kV accelerating voltage and 1750 mA filament current under a high magnification. Energy dispersive X-ray analysis (EDX) was performed by JEOL JSM-6490 Scanning Electron Microscope. It was used to collect the elemental information of cotton species. Moreover, in order to investigate the thermal behaviour of samples, thermogravimetric analysis was performed by using Mattler-Toledo thermogravimetric analyser. Weighed about 5 mg fabrics samples in an alumina crucible. The analysis was performed under oxygen atmosphere where the flow rate was set to 50 mL/min. The temperature range for the analysis was 30–800 °C and the heating rate was 10 °C per minute. Besides, the chemical composition of the samples were studied by Fourier transform infrared–attenuated total reflection (FTIR-ATR) spectroscopy. The analysis was done by a PerkinElmer Spectrum 100 FTIR spectrophotometer with scanning range from 4000 cm^{-1} to 650 cm^{-1}. The average number of scan was 8.

3. Results and discussion

3.1. Flame retardancy analysis

3.1.1. Effect of curing temperature and curing time on the flammability

Cotton is a kind of combustible textile material which burns easily when there is an external source of ignition. Levoglucosan is one of extremely flammable materials formed by thermal degradation of cellulosic fibres and causes cellulose combustion (Schindler & Hauser, 2004). In the experiment, the effect of curing temperature was investigated. The flammability characteristics were evaluated by two important factors, burning time and char length. Table 2 shows the results of fabric flammability test with three home laundering cycles after the flame retardant treatment.

Selected sample of treated fabrics after flammability test are demonstrated in Fig. 2. The control fabric burned vigorously and entirely. The burning time was found to be 22.01 s. The control fabric was described as failed and not flame resistant. In Table 2, for the treated fabrics cured at high temperatures of 150 and 170 °C, the performance of flame resistance was better than that cured at lower temperatures of 110 and 130 °C. It can also be observed by comparing the sample A and B, and sample C and D in Fig. 2. The crosslinking agent formed linkages between the cotton cellulose and flame retardant agent and enhanced the flame resistance (Lam et al., 2011a,b; Wu & Yang, 2004a; Wu & Yang, 2004b). When the curing temperature was increased from 110 to 170 °C, the burning time and char length of the fabrics were reduced. This indicated that the fabrics were more resistant to the spread of flame. Higher curing temperatures result in better reaction efficiency for the crosslinking reaction involved. For some conditions such as Z2170, Z2150, Z3170 and Z3150, the flame extinguished promptly after the removal of ignition source without spreading of the flame. The char length, ranging from 0.7–0.93 cm, remained on each fabric. These fabrics were classified as flame-retarded fabric. The char residue was caused by thermal decomposition of fabrics. Eq. (1) shows the one of pyrolysis route of cotton which is dehydration process. Dehydration of cellulose occurs and carbonaceous residue is left. The process favours at lower temperature (Lam et al., 2011a; Siriviriyanun, O'Rear, & Yanumet, 2008).

$$(C_6H_{10}O_5)_x \rightarrow 6xC + 5x{\cdot}H_2O \quad (1)$$

Another pyrolysis route can proceed via the formation of levoglucan which further breakdown to flammable volatiles at higher temperature. In order to prevent from forming levoglucan, phosphorus-based flame retardant treatment facilitated dehydration of cotton at lower temperatures during the degradation of cotton. Thus, the treatment can improve flame retardancy of the cotton. (Lam et al., 2011b; Siriviriyanun et al., 2008). Moreover, by comparing the non-neutralized samples with the neutralized one, flame retardancy of the neutralized sample was enhanced. There were more fabrics which were not ignited, as shown in Table 2. In addition, the effect of neutralization by sodium carbonate (Na_2CO_3)

Table 2
Flammability of the cotton specimen.

Sample code[b]	No. of launder-ing	Burning time (s)	Char length (cm)	Pass/fail	Fabric thickness (mm)	Burning time (s)	Char length (cm)	Pass/fail	Fabric thickness (mm)
Control	–	No neutralization				30 min Neutralization			
		22.01	Entirely burned	Fail		–	–	–	
Z1170	3	39.58	8.43	Pass	0.51	DNI[a]	0.78	Pass	0.53
Z1150	3	38.63	9.13	Pass	0.51	DNI	0.80	Pass	0.52
Z1130	3	46.18	11.00	Fail	0.50	49.30	10.78	Fail	0.52
Z1110	3	45.93	12.25	Fail	0.50	37.40	10.45	Fail	0.51
Z2170	3	DNI	0.93	Pass	0.51	DNI	0.73	Pass	0.53
Z2150	3	DNI	0.75	Pass	0.50	DNI	0.60	Pass	0.52
Z2130	3	45.38	9.00	Pass	0.50	DNI	0.83	Pass	0.53
Z2110	3	39.88	10.78	Fail	0.50	38.73	10.25	Fail	0.52
Z3170	3	DNI	0.70	Pass	0.50	DNI	0.65	Pass	0.53
Z3150	3	DNI	0.71	Pass	0.51	DNI	0.73	Pass	0.52
Z3130	3	51.23	11.38	Pass	0.50	DNI	0.79	Pass	0.52
Z3110	3	43.08	9.83	Pass	0.50	50.23	11.10	Fail	0.51
X1170	3	DNI	0.75	Pass	0.52	DNI	0.85	Pass	0.52
X1150	3	DNI	0.70	Pass	0.50	DNI	0.64	Pass	0.52
X1130	3	33.40	5.83	Pass	0.51	DNI	1.30	Pass	0.52
X1110	3	48.78	11.38	Fail	0.50	39.75	10.48	Fail	0.52
X2170	3	DNI	0.75	Pass	0.51	DNI	0.68	Pass	0.52
X2150	3	DNI	0.83	Pass	0.51	DNI	0.78	Pass	0.52
X2130	3	15.48	2.53	Pass	0.50	DNI	0.76	Pass	0.52
X2110	3	55.13	11.35	Fail	0.51	41.78	10.95	Fail	0.53
X3170	3	DNI	0.90	Pass	0.51	DNI	0.70	Pass	0.52
X3150	3	DNI	0.95	Pass	0.51	DNI	0.78	Pass	0.52
X3130	3	DNI	1.00	Pass	0.50	DNI	0.53	Pass	0.53
X3110	3	53.85	11.65	Fail	0.51	42.73	10.83	Fail	0.51
Y1170	3	DNI	0.83	Pass	0.51	DNI	0.74	Pass	0.53
Y1150	3	DNI	0.85	Pass	0.50	DNI	0.64	Pass	0.51
Y1130	3	45.93	11.20	Fail	0.51	30.23	5.88	Pass	0.52
Y1110	3	43.88	11.43	Fail	0.50	38.60	10.50	Fail	0.52
Y2170	3	DNI	0.86	Pass	0.51	DNI	0.81	Pass	0.53
Y2150	3	DNI	0.78	Pass	0.51	DNI	0.71	Pass	0.53
Y2130	3	DNI	0.70	Pass	0.51	DNI	0.84	Pass	0.52
Y2110	3	37.43	12.50	Fail	0.50	46.88	10.98	Fail	0.53
Y3170	3	DNI	0.79	Pass	0.51	DNI	0.78	Pass	0.53
Y3150	3	DNI	0.65	Pass	0.50	DNI	0.65	Pass	0.52
Y3130	3	DNI	0.75	Pass	0.51	DNI	0.79	Pass	0.52
Y3110	3	50.05	11.53	Fail	0.51	40.25	10.70	Fail	0.51

[a] DNI: Did not ignite.
[b] "*Z*" refers to the padding solutions without TiO_2. "*X*" and "*Y*" refer to the padding solutions with 0.2% and 0.4% TiO_2, respectively. More information about padding solutions is shown in Table 1. The first number digit of the code refers to curing time in minute, and the last three digits refers to curing temperature in degree Celsius.

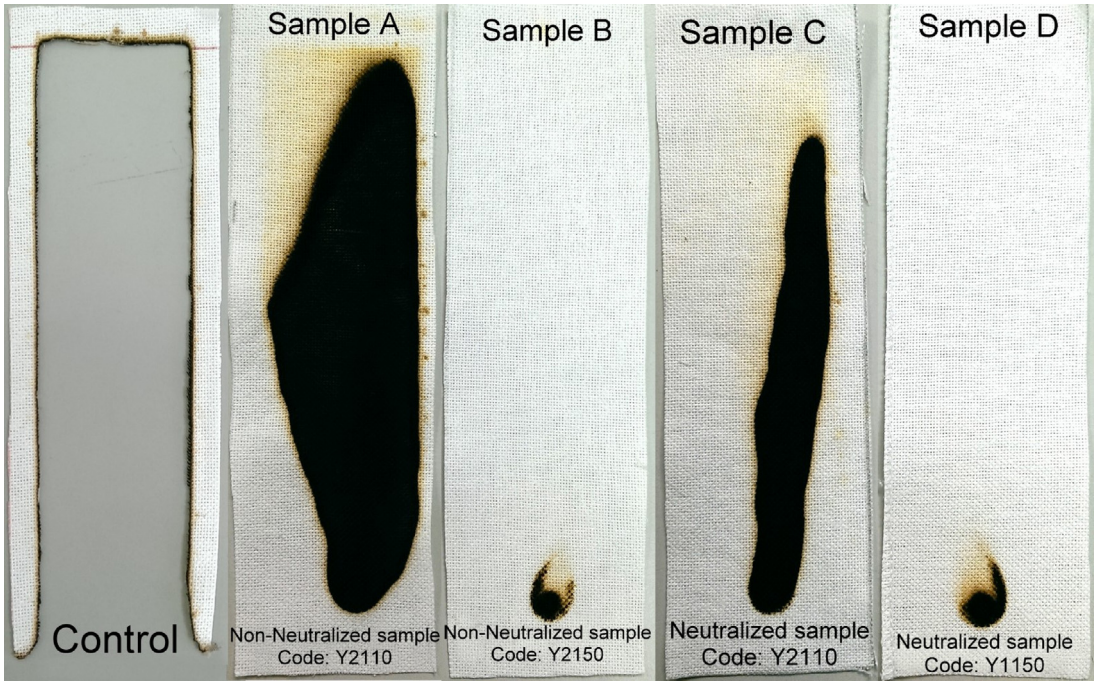

Fig. 2. Selected sample of treated fabrics after flammability test.

can be observed by comparing Sample A and C in Fig. 2. The char residue formed in Sample C is obviously narrower than that of sample A which indicates that sample C burned less vigorously. Furthermore, comparing the neutralized Y1130 with the non-neutralized Y1130, the flame retardant properties of neutralized ones were slightly improved. The burning time and the char length of Y1130 specimen were reduced 35% and 46%, respectively, after neutralization. When cotton fabrics are immersed in the Na_2CO_3 solution, swelling occurs. After neutralization with Na_2CO_3 at 50 °C, thickness of the fabrics increased averagely about 3.19% reported in Table 2. Fabric thickness has a positive correlation with protection from flame of a material (Song & Yu, 2013). Thus, increase in fabric thickness can enhance the inherent flame retardant properties even though there may be some loss of flame retardant chemicals during neutralization. Sequentially, the fibres had more contact with each other and less air was trapped in the fabrics, resulting in increased conductive heat loss due to increased conductivity (Song & Yu, 2013). Therefore, the flame retardant properties of the treated fabrics were found to be superior after neutralization. In short, the flame retardant treated fabrics cured at 150 and 170 °C were well equipped with flame retardant properties. Curing temperature of 150 °C was found to be better because less heat energy was consumed in the finishing process.

Apart from curing temperature, curing time is another factor that influences flame retardant properties. As shown in Table 2, fabrics treated for a longer curing time yielded better performance. For the Z1110, Z2110 and Z3110 specimens, the char length of Z1110 specimen cured for 1 min was 12.25 cm. The char length was reduced to 10.78 cm and 9.83 cm under the condition of Z2110 cured for 2 min and Z3110 cured for 3 min, respectively. A longer curing time allowed more heat energy transfer for the crosslinking reaction. From the results, a combination of curing time of 1 min and curing temperature of 110 °C was not efficient to equip the fabrics with significant flame retardant performance.

3.1.2. *Effect of titanium dioxide on the flammability*

TiO_2 was added to the formulation in order to improve the flammability characteristics of the product. Adding TiO_2 as a co-catalyst has been found feasible in previous studies (Lam et al., 2011a, 2012). The number of "do not ignite (DNI)" specimens was increased with the inclusion of TiO_2 as the co-catalyst. There were 7 out of 12 "DNI" specimens for those treated in the presence of 0.2% and 0.4% TiO_2 whereas there were only 4 out of 12 "DNI" specimens for those treated without addition of TiO_2. For the Z2130, X2130 and Y2130 specimens, the burning time of Z2130 was 45.4 s which was greatly reduced by 65% to 15.5 s compared to X2130. Further increasing the concentration of TiO_2 to 0.4% halted Y2130 specimen from ignition. Meanwhile, the char length was reduced by 72% when the concentration of TiO_2 increased from 0% to 0.2%. According to the wall theory (Jolles & Jolles, 1972), if the concentration of dust presents in the air is high enough, no flame can propagate. Therefore, if there is sufficient amount of TiO_2 impregnated onto the fabric, TiO_2 may inhibit propagation of flame. Moreover, the flame retardant performance was satisfactory for all specimens cured at 150 °C and 170 °C in the presence of 0.2% and 0.4% TiO_2. However, the improvement of flammability for samples cured at 110 °C in the presence of TiO_2 was not significant. One possible postulation for such phenomenon was that the crosslinking reaction may not be fully activated at a low temperature. In short, the presence of TiO_2 gave a significant improvement on the flame retardant properties. However, the effect of TiO_2 on flammability might be less effective after neutralization since the content of TiO_2 remained on the fabrics should be decreased. However, the flammability performance remained unchanged or even improved because of the effect of neutralization. There are two factors affecting the performance of flammability based on the discussions. If the fabrics was carried out neutralization after curing process, the factor altering flammability performance was dominant by neutralization effect rather than the presence of TiO_2. Therefore, the effect of TiO_2 on flammability after neutralization become less significant.

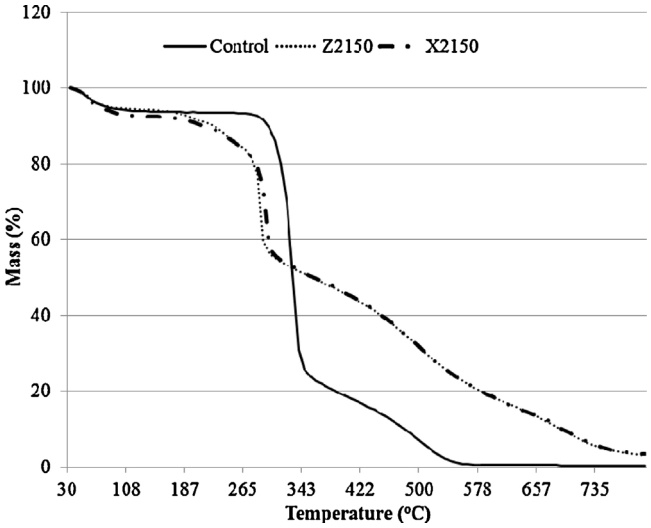

Fig. 3. TG comparative curves of untreated (control) and treated cellulosic fabric with different flame retardant formulation.

To summarize, the effects of curing temperature, curing time and concentration of TiO_2, the best conditions for imparting effective flame retardant properties were deduced. Cotton fabrics should be treated with the formulation X (in the presence of 0.2% TiO_2) and cured at 150 °C for 1 min. Compared with the conventional flame retardant finishing conditions, a reduction of 20 °C in temperature was achieved at the curing step, in the presence of 0.2% TiO_2.

3.1.3. *Thermogravimetric analysis*

In order to investigate the effect of TiO_2 on flame retardancy, thermogravimetric analysis was performed. Thermogravimetric analysis (TG) was used to investigate the thermal decomposition process of polymers by continuously recording the mass changes of a sample of material as a function of a combination of temperature and time. The relative thermal stability, combustion pathway and pyrolysis process were evaluated. In Fig. 3, the solid line represents the TG curve of the control sample. The dotted line and the dashed line represent treated samples Z2150 and X2150, respectively. The TG curve of the control sample shows three stages of cellulosic pyrolysis, initial, main and char decomposition steps (Fallah et al., 2011a; Zhu, Sui, Wang, Sun, & Gang, 2004). For the control sample, temperature at the initial stage was below 300 °C. The curve is flat with a minimal mass loss. There were changes in physical properties of the cellulose and the damage to cellulose occurred mostly in amorphous region, in the initial stage (Fallah et al., 2011a; Zhu et al., 2004). In the range of 300 °C to 350 °C, the curve drops suddenly, indicating the main pyrolysis stage. The mass loss was significant and rapid. Pyrolysis took place in crystalline region and the pyrolysis products were mainly produced in this stage. Glucose and all kinds of combustible gases were the main pyrolysis products. Char decomposition stage refers to a temperature beyond 350 °C. In this stage, dehydration and charring reactions compete with the production of non-volatile liquid L-glucose by depolymerization (Fallah et al., 2011a; Zhu et al., 2004). The latter is more obvious. The mass decreased gradually, due to dehydration and decarboxylation, by release of water and carbon dioxide molecules and production of carbonyl products. The remaining mass was only 0.35% at the end of series of reactions.

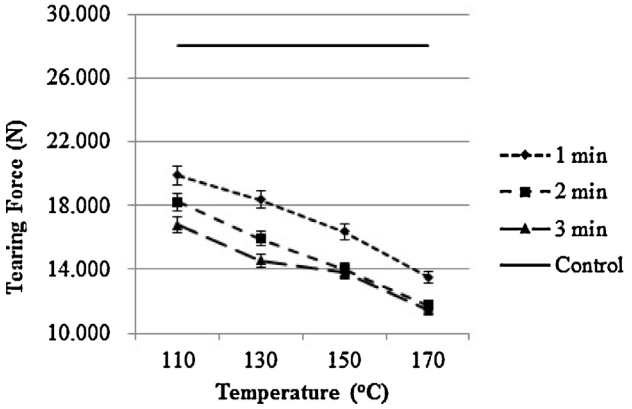

Fig. 4. Tearing force of the treated fabrics in the absence of TiO_2 with different curing temperatures and times.

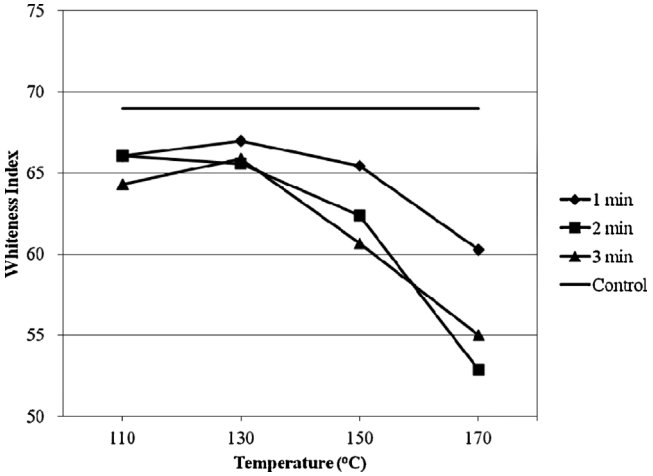

Fig. 6. Whiteness Index of the treated fabrics in the absence of TiO_2 with different curing temperatures and curing times.

For the TG curves of samples Z2150 and X2150, the shape of the curves is similar to that of the control sample with the three stages clearly defined. The treated samples show a lower decomposition temperature and mass loss. These stages happened well below the temperature for thermal degradation of the untreated cellulose (Fallah et al., 2011a). Decomposition temperatures of the treated samples were obviously lower than the control samples. Such difference is a result of the presence of flame retardant agent. The sudden drop of the mass began at about 280 °C. The differences in decomposition temperature between the treated sample and the untreated (control) sample was caused by the postponed formation of volatile pyrolysis products when the polymer was subjected to thermal degradation (Fallah et al., 2011a; Zhu et al., 2004). Approximately 3.0–3.4% mass remained at the end of the series of reactions. A significantly larger amount of solid residues was produced from the flame-retardant treated samples. This indicates that more charred products were produced after the treatment. TG curves of samples Z2150 and X2150 are highly similar to each other. At the end of the series reactions at 800 °C, the remaining mass of Z2150 was about 3.07% and X2150 was about 3.33% which is higher than that of Z2150 because there was a small amount of TiO_2 still remaining at the end of series of reactions in sample X2150.

3.2. Tearing strength

The tearing strength performance measured in units of Newton (N) of the fabrics after the flame retardant finishing is shown in Figs. 4 and 5. Fig. 4 shows the tearing force of the fabrics treated in the absence of TiO_2 while Fig. 5(a) and (b) illustrate the tearing behaviour in the presence of 0.2% and 0.4% TiO_2, respectively. The black horizontal solid line represents the control sample, which was not subjected to any pre-treatment, and 28 N tearing force was recorded. In Figs. 4 and 5, the tearing force of the flame retardant treated samples is lower than that of the control sample. After the flame retardant treatment, tearing strength drops due to fabric stiffening, caused by high levels of phosphorus by weight of fabrics and the accompanying flame retardancy. Stiffening lowers the tearing strength (Lam et al., 2012). Another reason for the drop in tearing strength is the highly acidic condition of pH 1–2 with the presence of phosphoric acid. Cotton fibres get tendered and damaged by acid hydrolysis resulting in breaking down of cellulose chains.

In Fig. 4, a decreasing trend of the tearing force with respect to the change in curing temperature from 110 to 170 °C is observed. After curing at a high temperature, cotton fibres are damaged by heat and become brittle. When the curing time is increased, a lower tearing force is obtained. The number of crosslinks formed is expected to be greater at a higher curing temperature and for longer curing time. Thus, the higher curing temperature and longer curing time caused a more significant loss of tearing strength.

The shape of Fig. 5(a) is similar to Fig. 4. When the fabrics were treated in the presence of TiO_2 at high curing temperatures of 150 °C and 170 °C, the loss of tearing strength was less serious than when treated in the absence of TiO_2. Such discrepancy is probably caused by the change of efficiency of crosslinking reaction. TiO_2 in the finishing solution might boost the crosslinking reaction as a co-catalyst to enhance the crosslinking performance. However, at lower curing temperatures of 110 °C and 130 °C, the tearing forces of fabrics treated in the presence of 0.2% TiO_2 were superior to the fabric treated in the absence of TiO_2. At the low curing temperature, the crosslinking reaction may not be fully activated. TiO_2 particles

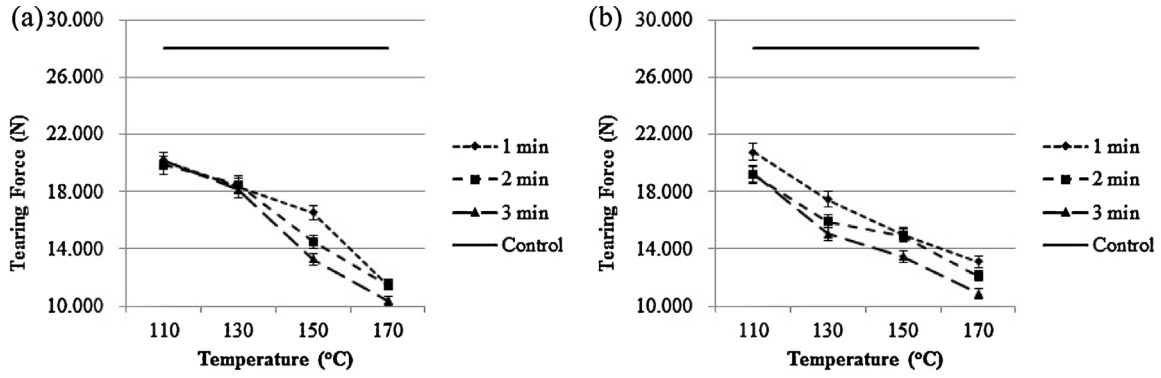

Fig. 5. Tearing force of the treated fabrics in the presence of (a) 0.2% and (b) 0.4% TiO_2 with different curing temperatures and curing times.

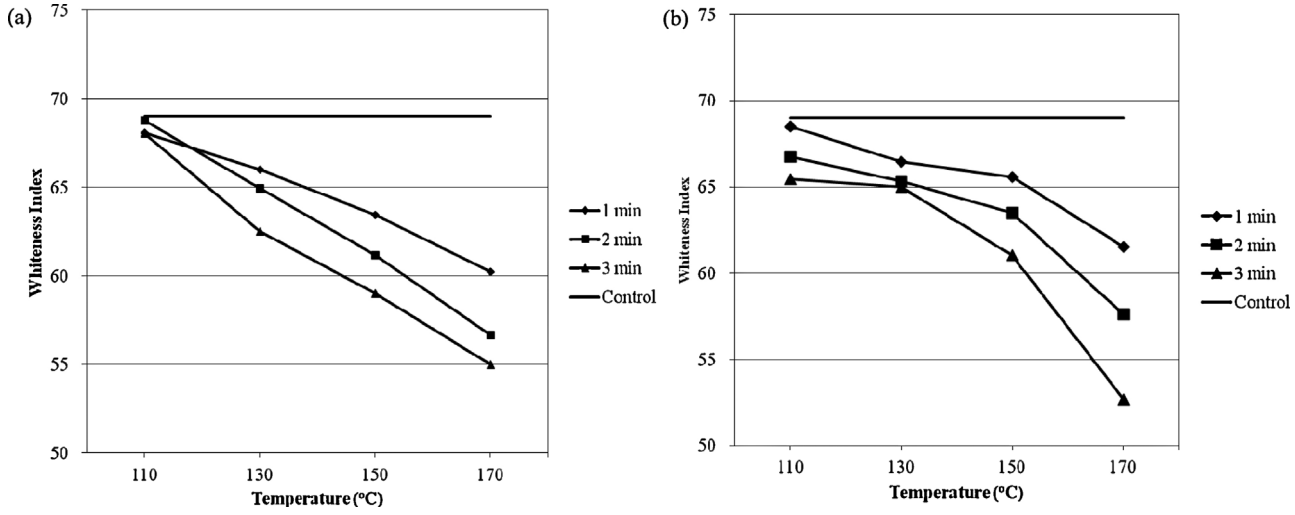

Fig. 7. Whiteness Index of the treated fabrics in the presence of (a) 0.2% and (b) 0.4% TiO_2 with different curing temperatures and curing times.

attached on the surface increase the yarn friction resulting in a better tearing force. However, further increase to 0.4% TiO_2 induced a similar result as 0.2% TiO_2 (Fig. 5(b)). The flame retardant finishing reduces the tearing strength of the fabric unavoidably. In the present study, the addition of 0.2% TiO_2 reduced the loss of tearing strength when compared with the conventional flame retardant treatment. Thus, TiO_2 helps minimise the major side effect of the flame retardant treatment, i.e. loss in tearing strength.

3.3. Whiteness

The whiteness of textile fabric is expressed as whiteness index which refers to the attribute of colour perception by which an object colour being judged to approach the preferred white. Figs. 6 and 7 illustrate the whiteness indexes of cotton fabrics in the presence of 0%, 0.2% and 0.4% TiO_2 under different conditions, respectively. The whiteness indexes fall in a range between 50 and 70. The black horizontal solid line represents the control sample without any pretreatment where the whiteness index is recorded as 69. Figs. 6 and 7 show a decreasing trend when the curing temperature increases from 110 °C to 170 °C. The 1-min line lies on the top and the 3-min line lies at the bottom. The decrease in whiteness index at a

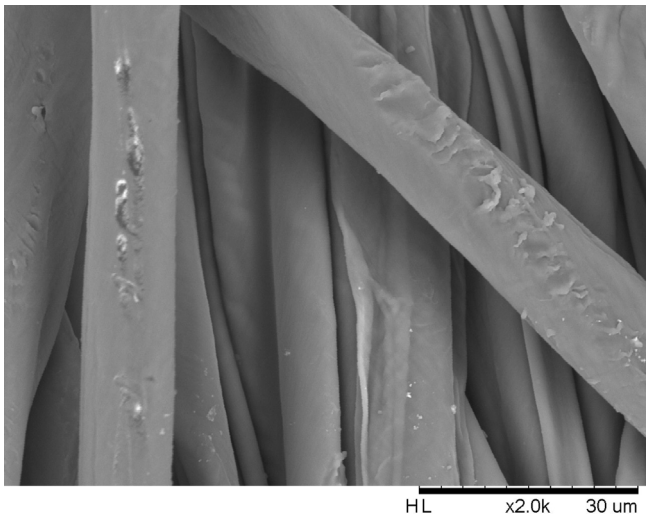

Fig. 9. SEM images of treated cotton cellulose in the absence of TiO_2 at a magnification of 2000×.

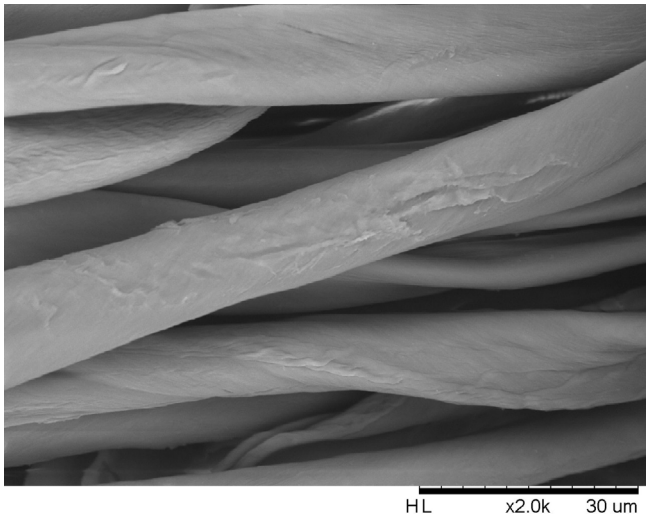

Fig. 8. SEM images of pure untreated (control) cotton cellulose at a magnification of 2000×.

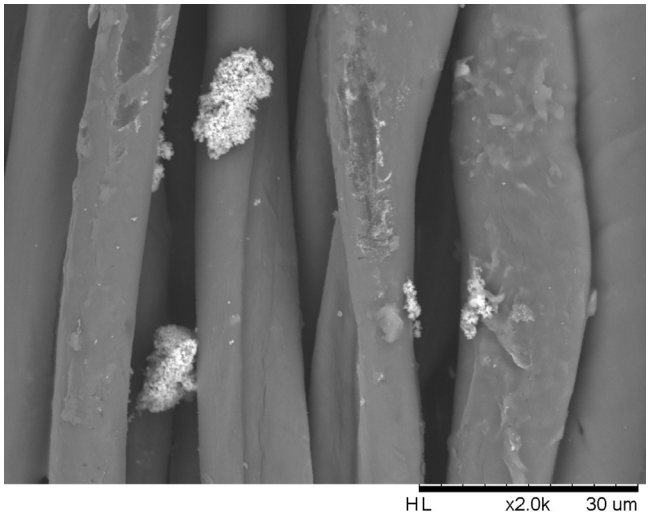

Fig. 10. SEM images of treated cotton cellulose in the presence of 0.2% TiO_2 at a magnification of 2000×.

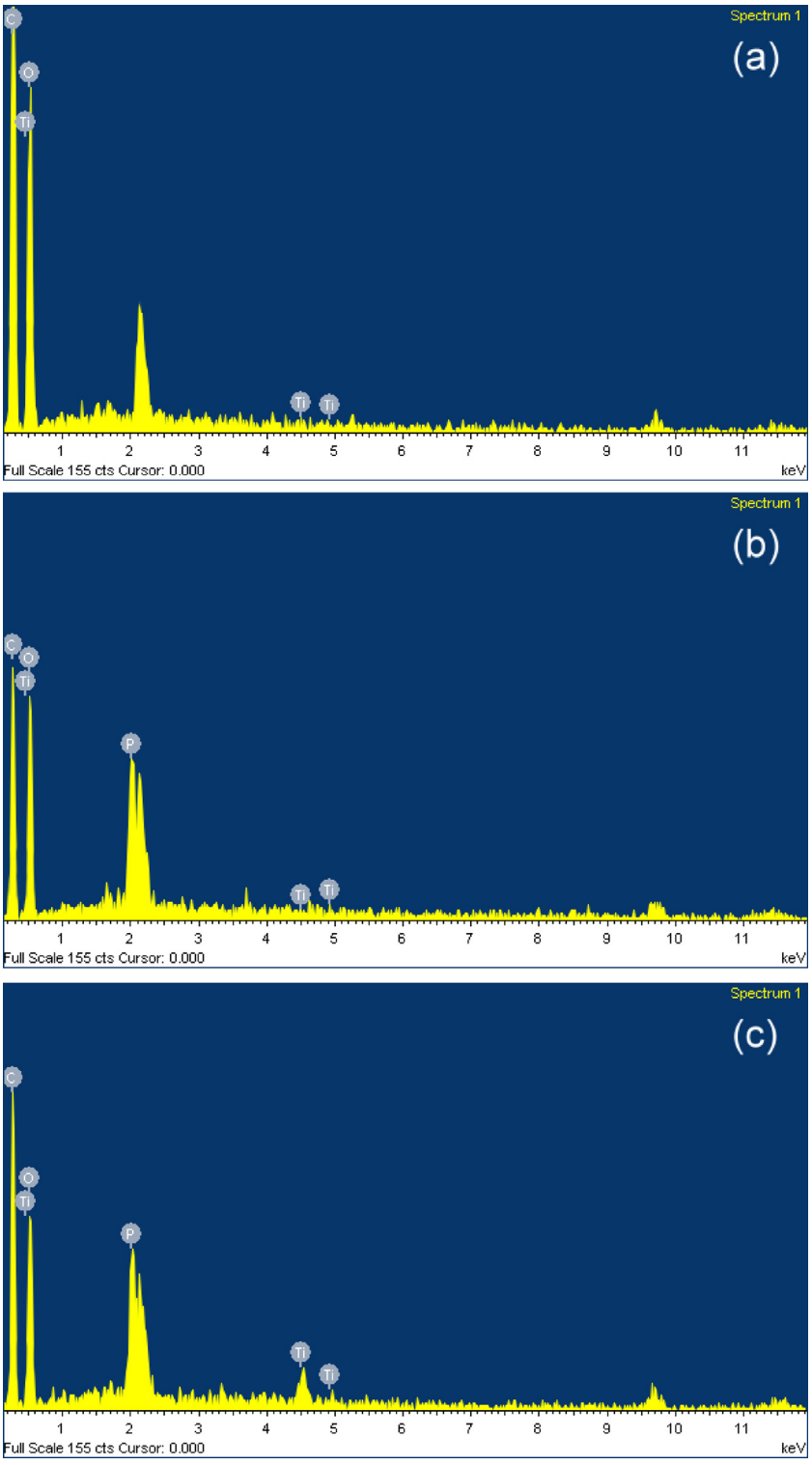

Fig. 11. EDX spectrum of (a) pure untreated (control) cotton cellulose (b) treated cotton cellulose in the absence of TiO_2 (c) treated cotton cellulose in the presence of 0.2% TiO_2.

higher temperature is because of thermal degradation of cotton. When cotton fabric is heated above 140 °C or even higher temperatures, cellulose breaks down into small carbon substances with carbonyl functionalities, resulting in the fabric yellowing (Schindler & Hauser, 2004; Horrocks, 2003). Higher curing temperatures and longer curing time cause more serious yellowing. Therefore, fabrics treated at the highest curing temperature and the longest curing time exhibit the lowest whiteness index.

On the whole, there are no obvious differences among Figs. 6 and 7. In Fig. 6, the whiteness index is similar to curing temperatures of 110 and 130 °C as the reaction may not have been fully activated and favourable. In Fig. 7(a) and (b), the highest whiteness index points are observed at curing temperature of 110 °C. It may be due to the presence of white TiO_2 particles causing whitening of the fabrics. No significant variation of whiteness is observed, in relation to the concentration of TiO_2 when the curing temperature

Fig. 12. The FTIR-ATR spectrum of untreated (control) sample.

increases from 130 °C to 170 °C. Thus, the addition of TiO_2 does not impose negative effects to the whiteness of fabric when compared with conventional flame retardant treatment, i.e. curing temperature of 170 °C and curing time of 1 min.

3.4. Scanning electron microscopy and energy-dispersive X-ray spectroscopy

Fig. 8 shows the untreated (control) cotton fibre surface at a magnification of 2000×. The surface of the fibre is smooth, with some wrinkles. The cotton fibres have a twisted ribbon-like structure caused by spiralling of cellulose fibrils. The direction of wrinkles on the fibre represent the fibrillar directional changes. Moreover, there are natural folds running parallel to the fibre axis. The normal spiral structure is clearly defined. Fig. 9 shows the cotton fibre surface after treatment with flame retardant finishing in the absence of TiO_2 at a magnification of 2000×. The treated cotton fibres are rougher than the control sample. Some cracks and damages are observed on the fibre surface, probably caused by the highly acidic padding bath in the treatment. The presence of phosphoric acid significantly lowers the acidity of the bath to about pH 1–2. The cotton fibres were damaged through acid hydrolysis of glycosidic linkages resulting in the cracks. Fig. 10 is the SEM image of cotton fibre surface after being treated with flame retardant finishing in the presence of 0.2% TiO_2 at a magnification of 2000×. Cracks and damage are observed. In addition, some irregular TiO_2 particles are found to be attached on the fibre surface. The irregular shape of the TiO_2 particles is due to formation of clusters. TiO_2 particles are unevenly distributed on the cotton fabrics surface. The particles have diameters of up to 10.5 μm. According to the SEM images of cotton fibres, the structure and characteristics of cotton fibre are found to be influenced by the finishing treatment.

In order to confirm the TiO_2 particles adhered on the cotton fabrics surface, EDX was used to collect the elemental information of cotton fabrics. Fig. 11(a)–(c) shows the EDX spectra of pure untreated (control) cotton cellulose, treated cotton cellulose in the absence of TiO_2 and treated cotton cellulose in the presence of 0.2% TiO_2, respectively. The atomic percentages of carbon (C), oxygen (O), phosphorus (P), and titanium (Ti) are shown in Table 3. The signal of the cotton species was dominant by C and O as cellulose is a carbohydrate compound. In Fig. 11(a)–(c), the signal near 2.2 keV is responsible for the gold element as the sample was coated with gold before performing analysis in order to increase the conductivity of the sample. About 2% phosphorus content was successfully added after flame retardant treatment. In addition, EDX analysis also confirmed that there is TiO_2 particles attached on the cellulose fibrils after treatment.

3.5. FTIR-ATR spectroscopy

FTIR-ATR spectroscopy is a surface-sensitive technique that can characterize the chemical structure of a substrate (Chung, Lee, & Choe, 2004; Lam et al., 2011a). The analysis has been done on the control sample and the treated samples. Fig. 12 illustrates the spectrum of control samples. The characteristic peaks and bands of the spectra were identified that were associated with cellulose

Table 3
The atomic percentage of different elements present in the cotton fabrics.

Sample	C (%)	O (%)	P (%)	Ti (%)
Control	54.68	45.32	–	–
Z	53.72	44.19	2.1	–
Y	56.97	40.34	1.88	0.81

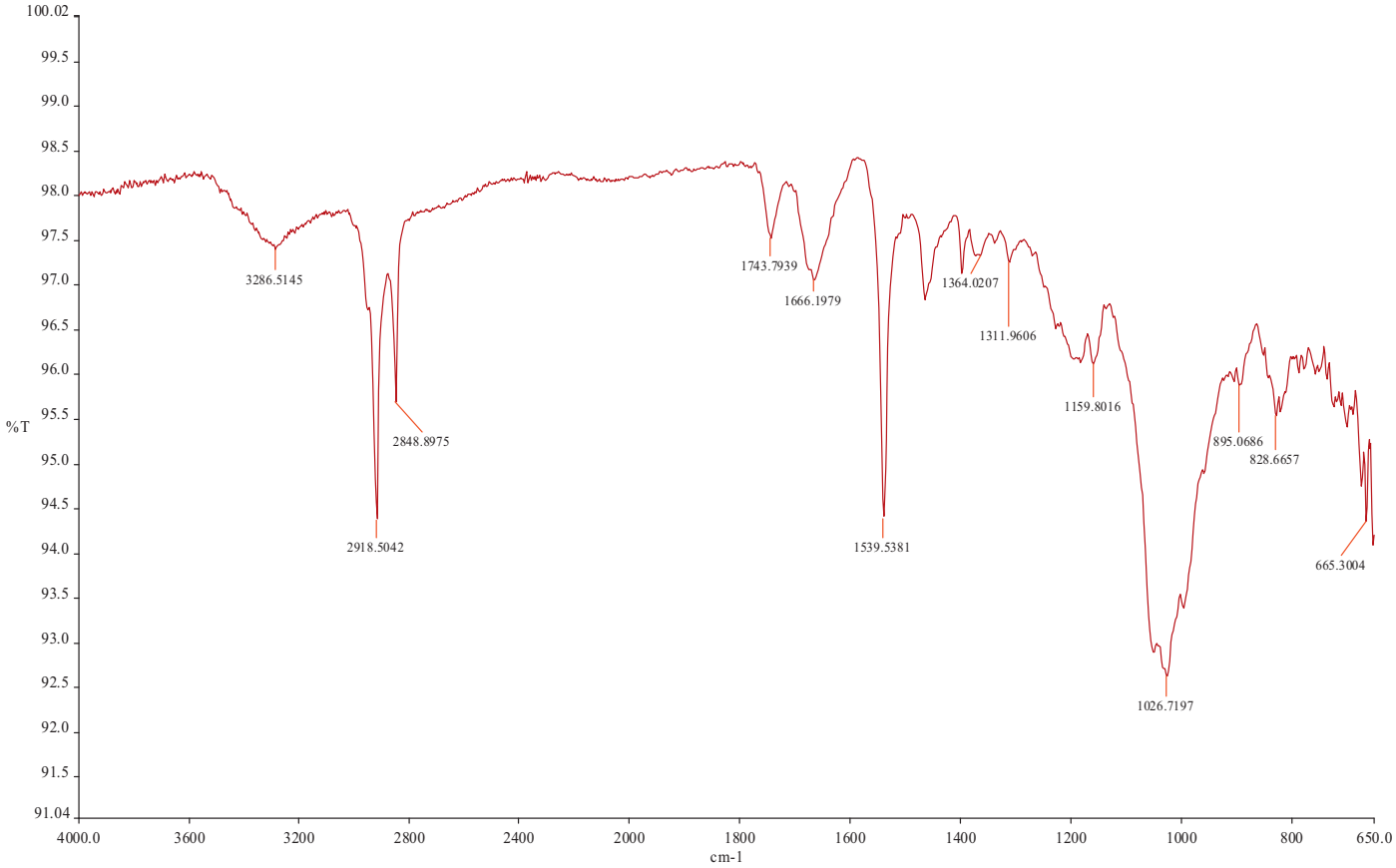

Fig. 13. The FTIR-ATR spectrum of treated samples with code X1150.

structure of cotton fibre with reference to the previous studies (Chung et al., 2004; Fan, Dai, & Huang, 2012; Hartzell-Lawson & Hsieh, 2000; Lam et al., 2011a). There are characteristic peaks or bands. Here listed out some major peaks. There are OH stretching centred at 3284 cm^{-1}, CH stretching centred at 2889 cm^{-1}, CH_2 symmetric bending centred at 1419 cm^{-1}, CH wagging centred at 1313 cm^{-1}, C—O—C non-symmetric bridge centred at 1200 cm^{-1}, CO stretching centred at 1027 cm^{-1}, non-symmetric out-of-phase ring stretching centred at 893 cm^{-1}, and OH out-of-phase bending centred at 665 cm^{-1}. The absorbed water molecules vibrated at about 1640 cm^{-1}. When the fabrics were treated with flame retardant treatment, there were some new characteristic peaks found such as carbonyl bands, CH_2 rocking bands, and CH_3 asymmetric and CH_2 symmetric stretching (Lam et al., 2011a). The spectrum of treated samples with code X1150 is demonstrated in Fig. 13. A much stronger peak is observed at 1660 cm^{-1}. This peak was dominant by C=O stretching of amide that is present at the flame retardant agent instead of absorbed water vibration. The non-cyclic secondary amide group (O=C—NH—C) not only had a C=O stretch at 1670 cm^{-1}, but another strong band in the IR spectrum near 1550 cm^{-1} involving the CNH bending and the C—N stretching (El-Bahy, 2005; Larkin, 2011). Furthermore, for the peaks centred at 826 cm^{-1}, it was contributed by CH_2 rocking band for P—CH_2. The rocking band of —CH_2 is a characteristic strong-medium intensity band for phosphonate structures that have P—CH_2-R groups (Gaan & Sun, 2007b; Gaun & Chen, 2006; Lam et al., 2011a). However, the vibration of phosphorus bonding (P=O) occurring usually at 1320–1140 cm^{-1} is difficult to identify as a result of overlapping with the characteristic absorption peaks of the primary and secondary OH deformation of cotton (Lam et al., 2011a; Siriviriyanun et al., 2008). The spectra of other samples treated under different curing conditions were similar to each other. From the evidence provided from the FTIR-ATR spectra, it can show that the flame retardant agent accompanying with crosslinker was successful adhered on the cellulose surface.

4. Conclusion

The effects of flame retardant treatment of fabric on tearing strength and whiteness of textiles obtained by applying Pyrovatex CP New in relation to various curing conditions in the presence of different concentrations of TiO_2 were examined. It was found that the flame retardant treated fabrics cured at 150 and 170 °C achieved good flame retardant characteristics. If there was TiO_2 in the formulation, an improvement of the flame retardant properties was observed since the presence of TiO_2, acting as a co-catalyst, enhanced the crosslinking reaction efficiency. In the conventional flame retardant finishing, there was a great drop in tearing strength after finishing, especially at a high curing temperature and long curing time. However, tearing strength was not affected dramatically with the presence of TiO_2. Thus, the addition of TiO_2 in the conventional flame retardant formulation can reduce the loss of tearing strength. Finally, with the use of TiO_2 as a co-catalyst, no significant negative effects were observed in fabric whiteness. Concerning the effect of curing temperature, curing time and the concentration of TiO_2, the cotton fabrics should be treated with the flame retardant formulation in the presence of 0.2% TiO_2 and cured at 150 °C for 1 min in order to impart flame retardant properties efficiently and effectively. Such conditions reduce the traditional curing temperature from 170 °C to 150 °C. And so, energy can be saved during the finishing treatment, leading to a more environment-friendly process.

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