Development of Flame Retardancy Properties of New Halogen-Free Phosphorous Doped SiO$_2$ Thin Films on Fabrics

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ABSTRACT: In this study, flame retardancy properties of fabrics treated with phosphorous (P) doped and undoped SiO$_2$ thin films were developed by sol–gel technique. As to this aim, P-doped and undoped SiO$_2$ film were coated on cotton fabric from the solutions prepared from P, Si-based precursors, solvent, and chelating agent at low temperature in air using sol–gel technique. To determine solution characteristics, which affect thin film structure, turbidity, pH values, and rheological properties of the prepared solutions were measured using a turbidimeter, a pH meter, and a rheometer machines before coating process. The thermal, structural, and microstructural characterization of the coating were done using differential thermal analysis/thermograviometry, fourier transform infrared spectroscopy, X-ray diffractometry, and scanning electron microscopy. In addition, tensile strength, wash fastness, flame retandancy, and lightness properties of the coated fabrics were determined. To compensate the slight loss of tensile strength of samples, which occurred at the treated fabrics with P-doped Si-based solutions, the cotton fabrics were coated with polyurethane films during second step. In conclusion, the flame retardant cotton fabric with durability of washing as halogen-free without requiring after treatment with formaldehyde was fabricated using sol–gel processing for the first time. Moreover the cotton fabrics, which were treated with P-doped Si-based solutions and then coated with polyurethane at second step, still has got nonflammable property. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3747–3756, 2007

Key words: thin films; sol–gel; flame retardancy; nanolayers; thermal properties

INTRODUCTION

During the last 20 years, the perceived need for enhanced flame retardant performance at an acceptable cost, caused an increase of the studies aimed to enhancing the efficiency of presently used flame retardants and to developing the novel ways using known chemistry.[1] Notable issues include the increasing interest in enhancing char-forming efficiency both by durable intumescent systems as through increasing thermal barrier properties and invoking nanoparticle presence to assist this same process.[2]

Classical flame retardant processes for cellulosic materials are treatments with phosphorous–nitrogen-based compounds. Particularly, these are of interest for cotton where both the major durable finishes (THPC-based, e.g., Proban, Rhodia, and phosphonamide derivatives, e.g., Pyrovatex, Ciba) involves use of HCHO during manufacture or application with associated health risks during processing, and end-use. While there have been a number of recent attempts to find reactive alternatives to these commercially well-established treatments for cotton, formaldehyde-based chemistry is still required to ensure bonding to cellulose-OH moieties.[3–5] Unfortunately, Wu and Wang[6] demonstrates that if it is to achieve acceptable levels of multiple laundering durability, its application requires the presence of methylolated resin species like dimethylol dihydroxyethylene urea or methylated formaldehyde–urea. It is feasible, however, that the use of low formaldehyde resins in combination with these organophosphorus compound developments may provide successful retardants in the not-too-distant future. In spite of this, the application of sol–gel processing presents alternatively the new halogen-free flame retardancy finishing process with durability of washing for cotton fabric without requiring combination or after treatment with formaldehyde–urea resin.

Lecoeur et al.[7] treated cotton fabric with different formulations based on monoguanidine dihydrogen phosphate and 3-amino propylethoxysilane and

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evaluated as a flame retardant in padding for cotton. The thermal stability of the formulations is then examined using thermal analysis. While the degradation is initiated at lower temperatures for all padded fabrics when compared with untreated cotton, the residual amounts of char are higher at 800°C for formulations with phosphoric acid. Flame behavior of the treated cotton fabrics was evaluated using the electrical burner test and was studied with cone calorimeter as fire model. The rate of heat release (RHR) peak was decreased very much for all the formulations, when compared with the RHR peak of the virgin cotton. The highest decrease was achieved with the formulations at pH 4.[7]

In present study, we delved into development of flame retardancy properties of fabrics treated with pure and P-doped SiO_2 thin films. With this regard, pure and P-doped SiO_2 thin films were coated on cotton fabric using sol–gel method. The new halogen-free flame retardancy finishing process was presented for cotton fabric without requiring after treatment with formaldehyde with durability of washing inasmuch as sol–gel technique opens up a new approach for how to develop the flame retandancy of fabric textile materials. Depending on this purpose, turbidity, pH, and rheological properties of the prepared solutions were determined on account of the fact solution preparation and processing have a large influence on final properties of films. To define chemical structure and reaction type of intermediate temperature products and to use suitable process regime, Differential Thermal Analysis–Thermogravimetry (DTA-TG) and Fourier Transform Infrared (FTIR) devices were used in the film characterization. Structural analysis of the produced films was performed using multipurpose X-Ray Diffraction (XRD) and surface morphology was investigated using Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS). In addition, add-on value, tensile strength, wash fastness, contact angle, flame retandancy, and lightness properties of the coated fabrics were determined by means of standard method of add-on value calculation, Instron 4411 tensile tester, Linitest plus apparatus, KSV CAM 100 instrument ganiometer, vertical flammability test equipment and Minolta 3600 days spectrophotometer, respectively.

EXPERIMENTAL

Nanosol preparation

The sol–gel films were obtained by simplified sol–gel method using metal based precursors. For this process, all chemicals used were reagent grade. The precursors were weighed out in fume hood and the sols were then prepared using Si alkoxide and P salt pre-

cursors, solvent, and chelating agent. Tetra ethylorthosilicate (TEOS, $C_8H_{20}O_4Si$) (Fluka, 98%) as a precursor, ethanol (C_2H_5OH) (96%, Isik Chemistry, Turkey), and water as a solvent, HCl (0.01N) (37%, Atabay Chemistry) for acidic hydrolysis, H_3PO_4 (85%, Merck), or ethyldichloro phosphate ($CH_3CH_2OPOCl_2$, 96%, Aldrich, Germany) to provide flame retardant effect were used. The solution was prepared by mixing TEOS with ethanol and then adding HCl. After this process, the obtained solution was stirred at room temperature for 60 min in air to obtain transparent sols. The pH value of the solution was measured to be 2.8 at this stage using a standard pH meter (WTW Inolab, Germany). Following H_3PO_4 or ethyldichloro phosphate were added to the solution drop by drop at room temperature in air. After these solutions were stirred at 25°C for 30 min in air, the solvent is lost as the temperature is elevated. The pH value of the sol decreased to 1.25 and 0.75 by adding phosphoric acid and ethyl dichlorophosphate, respectively. The used recipes to prepare the sols were given in Table I. The molar ratio of TEOS : Ethanol : H_2O : HCl : H_3PO_4/ethyldichloro phosphate was 0.9 : 7.9 : 11 : 0.0016 : 0.74/0.4. The mixture was vigorously stirred for 30 min to provide transparent solutions. The stability of the process is set by control of the hydrolysis and condensation reactions such that, while the solutions are being dried, the solvent is lost or the temperature is elevated (see Fig. 1 for details).

Characterization of sols

To determine solution characteristics, which affect thin film structure, turbidity, pH values, and rheological properties of the prepared sols were measured by a turbidimeter, a pH meter, and a rheometer, respectively. Turbidity properties of the sols were measured using VELP TB1 Model turbidimeter. Measurement range was taken in the range of 0–1000 ntu (nephelometric turbidity unit). After preparation of transparent sols, their pH values were measured to determine their acidic and basis charac-

TABLE I
The Recipies, Final pH Values, Turbidities of Silica Sols and Add on Values of Treated Cotton Fabrics

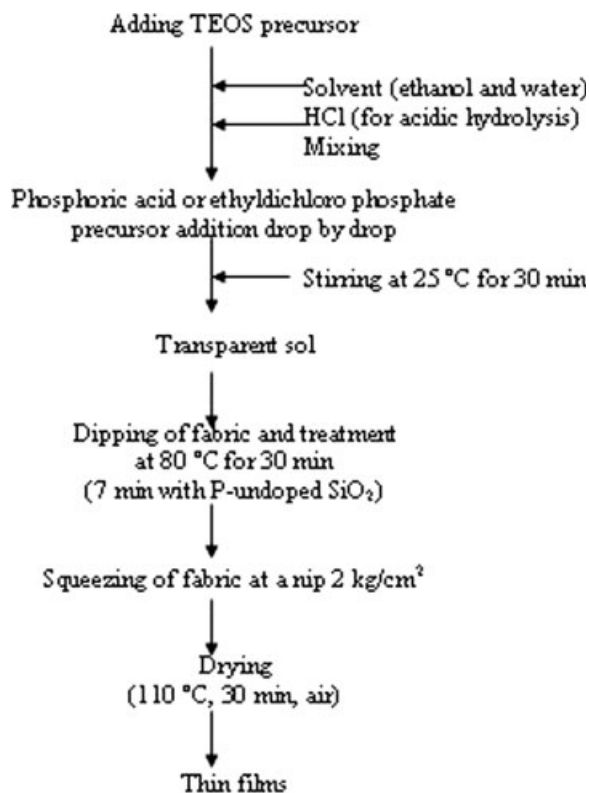| Chemicals	1st recipe	2nd recipe	3rd recipe
TEOS (mL)	22	22	22
Ethanol (mL)	46	46	46
H_2O (distilled) (mL)	20	20	20
HCl (mL)	15	15	15
H_3PO_4 (mL)	–	5	–
$CH_3CH_2OPOCl_2$ (mL)	–	–	5
Turbidity (ntu)	2.34	1.29	–
pH Values	2.8	1.25	0.75
Add-on value (%)	30.6	24.5	20.6

Figure 1 Flow chart for sol–gel processing.

teristics using a standard pH meter (WTW Inolab, Germany). The rheological properties of the sols were measured using a Bohlin Instruments CVO 100 Rheometer with 2° conic plate geometry 60 mm in diameter and 70-μm gap sizes between the plates The viscosity values of both doped and undoped sols were measured at constant 300 Hz frequency and at 25°C at single shear mode.

Coating process

Scoured and bleached 100% plain-weave cotton fabric (weight 126 g/m², 17 picks/cm, 21 ends/cm) was used in this research. WB 14 Model-Memmert water bath machine was used for treatment of cotton fabric at 80°C for 30 min with P- and Si-based sols. Then the fabrics were squeezed using a Rapid Fulard (Model P-A1, Labortex, Taiwan) for 87% A_F (take up) at a nip pressure of 2 kg/cm². The drying process was done using Nüve KD400 Oven (Turkey) at 110°C for 30 min in air. In the second step, some fabrics which were treated with P-doped Si-based solutions at 25°C for 30 min in air were coated with polyurethane solution (Tubicoat PU, CHT R. Beitlich GmbH) and then dried at 110°C for 30 min in air. The compensation of loss of tensile strength of the samples was aimed, while coating polyurethane during second step. Tubicoat PU 80 (CHT) which is very soft, elastic polyurethane for fine coatings was used. In this case, it gives sealing, light-absorbing or light-reducing coatings in cloth, domestic textiles, and geotextiles sector.[8] The coatings were carried out with knife over roll method by Atac coating machine (Serial no. 014, Turkey).[9]

Film characterization

Small aliquots from Si-, P-based sols were dried at 150°C during 1 h in air for film characterization. Thermal behavior of P- and Si-based xerogel powders was studied by heating rate of 10°C/min to gain decomposition and phase formation from room temperature to 550°C under oxygen atmosphere using DTA/TGA analyzer (DTG-60H Shimadzu). Al$_2$O$_3$ powder was used as a reference material. FTIR absorption spectra of gels dried at 150°C for 1 h were taken over the range 400–4000 cm^{-1} at room temperature using a Perkin–Elmer FTIR spectrophotometer. Powders were mixed with potassium bromide (KBr) and pressed to form appropriate tablets. Fluka library supplied by Perkin–Elmer was used for analyzing the spectra obtained.

XRD patterns of untreated (bare) fabric and thin films on fabrics were determined to indentify phase structure by means of a Rigaku (D/MAX-2200/PC) diffractometer with a Cu K$_\alpha$ irradiation (wavelength, λ = 0.15,418 nm) by both θ-2θ mode and 2θ scan mode with a scan speed of 8°/min. Thin-film XRD geometry where incident angle was fixed at 1° was used to collect data from only thin films. The diffracted X-ray beam was collected by scanning the detector between 2θ = 15° and 60°. The surface topographies and qualities of untreated fabric and SiO$_2$-based films on the fabrics were comparatively examined using SEM (JEOL JSM 6060) operating at 3 kV with 2000× magnification.

Textile characterization

To emphasize textile characteristics of the coated fabrics, add-on value, tensile strength, wash fastness, contact angle, flame retandancy, and lightness properties of the coated fabrics were investigated through standard method of add-on value calculation, Instron 4411 tensile tester, Linitest plus apparatus, KSV CAM 100 instrument ganiometer, vertical flammability test equipment and Minolta 3600d spectrophotometer, respectively. The add-on values of the coated fabric were calculated according to eq. (1).

$$W_{\text{add-on}}(\%) = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where W_1 is the dry weight of the untreated fabric and W_2 is the dry weight of the treated fabric. Since both the cotton and silica absorb moisture, untreated

and coated fabrics were also dried under the same conditions with treated fabrics. In add-on-value calculation, moisture absorbing properties of coated and uncoated fabrics were taken into consideration during weighing. The treated and untreated fabrics were conditioned at standard atmosphere of $(20 \pm 2)°C$ and $(65 \pm 2)\%$ relative humidity before weighing. Thus the dry weights of fabrics were determined.

The tensile properties (in warp direction) of treated and untreated fabrics were determined, using an Instron 4411 tester according to ASTM D 5035-90 (strip test). Tensile strength and extension of the fabrics were evaluated with this respect. The wash fastness was tested by washing conditions according to TS EN ISO 105-C06-A1S without balls, using Linitest plus apparatus (Atlas, Germany). Washing process was repeated 10 times. Contact angle of the fabrics were determined by measuring their contact angle using KSV CAM 100 Instrument Contact Angle Goniometer.

Flame spread (in warp direction) times of the cotton fabrics were evaluated according to TS 5569 EN ISO 6941 with vertical flammability test equipment before and after 10 times washing. The lightness and whiteness properties of the coated fabrics were determined by means of Minolta 3600d spectrophotometer according to Stensby (D65-10°). Yellowness index values of the coated fabrics were measured using ASTM D 1925 and ASTM E 313 standards (C-10°) by means of Minolta 3600d spectrophotometer.

RESULTS AND DISCUSSION

Solution characteristics

The turbidity of solutions

With turbidity experiments, whether sols are dissolved very well is understood as ntu values before coating process. It is interpreted that powder based precursors are completely dissolved as turbidity value approaches to 0 ntu and they are not dissolved and some powder particles are suspended in a sol as it approaches to 1000 ntu. The fabrication of homogeneous, continuous and thin film is directly related to turbidity value, which is 0 ntu. In this experiment turbidity values of the P-doped and undoped Si-based sols were found to be 2.34 and 1.29, respectively, as shown in Table I. According to the turbidity values, it can be pointed out that powder based precursors are completely dissolved in the sols and thus transparent sols were obtained. Since very low turbidity values were measured, the sols had very small silica particles. Moreover, these values present an important clue for further processing. Notably, films prepared from sols containing larger particles are not homogeneous, continuous and thin.

The pH values of solutions

Now that pH value of silica sols is an important factor influencing the formation of the polymeric three-dimensional structure of the gel during the gelation process, it should be taken into consideration, while preparing solutions. While ramified structure is randomly formed in acidic conditions, separated clusters are formed from the solutions showing basic characters as explained in Ref. [10]. The pH values of the transparent sols prepared from three recipes were given in Table I. According to these results, it is clear that acidity of the solutions increases with increasing concentrations of H_3PO_4 and ethyl dichlorophosphate.

The effects of pH on the hydrolysis and condensation of Si-based precursors, such as TEOS, have been extensively investigated. More details on pH values of silica sol can be found in previous reports[11,12] and the references therein. As for these research results, the silica precursor TEOS was rapidly hydrolyzed, but condensation was restricted in our experimental conditions (pH < 3), because of the high relative rates of hydrolysis relative to condensation. We have a good agreement with a research of Cui et al.[12] Besides, the rates of hydrolysis of TEOS increased when the pH value decreased in the range of pH 2.8 and 0.75. When H_3PO_4 and ethyl dichlorophosphate precursors are incorporated into the solutions, the pH value decreased under acidic conditions. Compared with the solution with H_3PO_4, the pH value of the solution having ethyl dichlorophosphate was found to be 0.75, indicating that the pH value decreased.

It is worth noticing that the pH of silica sols and gelation times (or called gel point) is related with isoelectric value of silica particles. The silica particles are positively and negatively charged above and below their isoelectric pH of 1.4–2.0. It can be considered that at pH 2.8 particles are negatively charged and at pH 1.25 and 0.75 the silica particles are positively charged. Nevertheless, since only TEOS was used in the solution in the first recipe, which was listed in Table I, we have similar results with the mentioned values in the literature.[13] According to Ref. 13, gelling time is longest near the isoelectric point at pH 2 and rapid gelling occurs in the region of very low pH (<1) or above the isoelectric point, resulting in more porous structures. In the second and third recipes, P-based precursors were separately added to the solution. To illustrate, P-doped sols are viscous, not dilute, as shown in Figure 2 and thus pH value is lower than the isoelectric point.

The viscosity of solutions

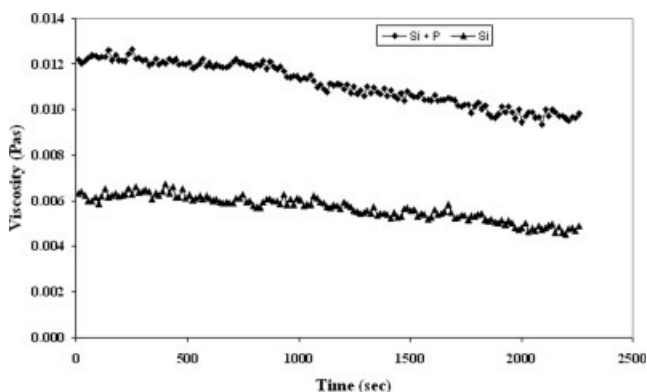Gelation occurs when aggregation of particles or molecules takes place in a liquid, under the action of

Figure 2 The viscosity versus time plots of P-doped and undoped Si-based solution with phosphoric acid.

van der Waals forces or via the formation of covalent or noncovalent bonds. The process can be investigated using rheological measurement techniques.[14] Figure 2 shows rheological properties, such as viscosity for the prepared solutions. While the viscosity values of the P-doped Si-based solutions with phosphoric acid were about 11.8 mPa s, the viscosity values of the undoped Si-based solution were approximately 5.5 mPa s. As well-documented elsewhere,[15] there is a correlation between coating thickness and solution density, liquid–vapor surface tension, and especially viscosity. In our case, it was observed that the viscosity of silica sol significantly varies depending on P-based precursor. Due to this reality, viscosity for dip coating is a key factor in controlling film thickness. As is well known, the viscosity is in the numerator since as this variable increase, thicker films are easily obtained. For less viscous solutions, the liquid–vapor surface tension also affects the amount of solvent on the substrate. High surface tension yields a higher volume/surface area ratio, resulting in a thicker liquid film. In our experiments, it is expected to be produced thicker films from P-doped sols and thinner films from silica sol owing to their viscosities.

Film properties

DTA-TGA analysis

Thermal behavior of Si and P-doped Si-based xerogel powders dried at 150°C for 1 h in air is depicted in Figure 3. DTA curve revealed that endothermic and exothermic reactions became at temperatures between 40 and 555°C as shown in Figure 3(a). It was due to the fact that physical water and solvent in the gel evaporated and carbon based materials coming from alkoxide, solvent and chelating agent burnt out. The first thermal phenomenon was the solvent removal at temperature range of ~ 108 and 99°C. The broad endothermic peaks of Si and P-doped Si powders were determined at 108 and 99°C,

respectively. The difference in the endothermic temperature results from P-based precursor. At this temperature, the endothermic reaction is mostly owing to evaporation of the physically absorbed water and alcohol solvent.[16] Generally speaking, the second phenomenon was combustion of OR groups at temperatures between 200 and 400°C. Specifically, it was seen that there was a small exothermic peak at 280°C for P-doped SiO_2 powders because of decomposition of organic substances in P and Si-based precursors. At this stage the combustion likely occurred with the fracture of C—O—Si and C—O—P and formation of Si—O—Si and P—O—P with weak bonding as indicated in Ref. 15. The last stage was the formation of ceramic oxides between 450 and 550°C. For only SiO_2 powders, the oxidation peak was seen at 478°C. The addition of P to SiO_2 structure provided that the oxidation temperature was reduced to lower temperatures.

The TGA curves [Fig. 3(b)] illustrated in the present cases for P-doped and undoped Si-based powders, show a weight losses for temperature range of 25–550°C. In this range of the thermal treatment, the weight decrease is due to evaporation of mainly water and ethanol and combustion of carbon-based materials. As seen from Figure 3(b), P-doped SiO_2 powders have much more weight loss than only
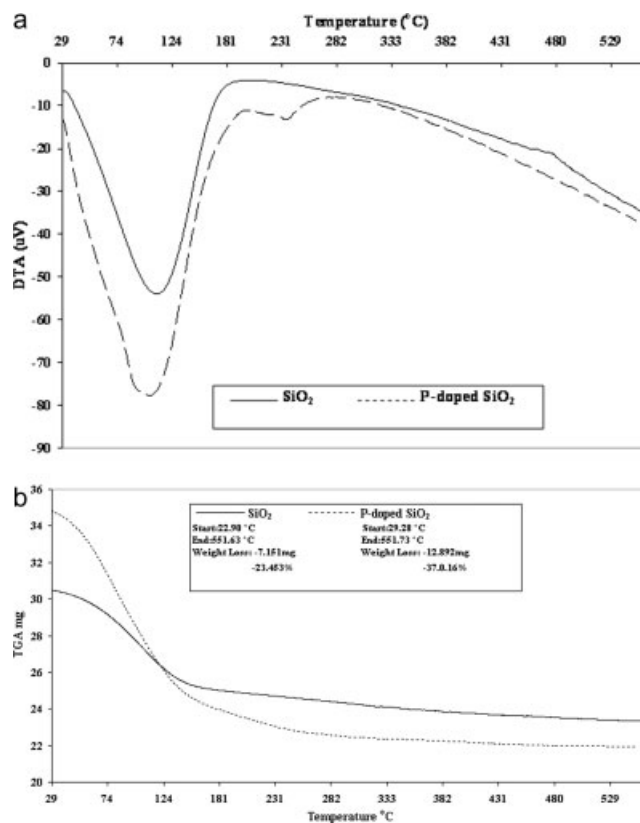

Figure 3 (a) DTA and (b) TGA curves of SiO_2 and P-doped SiO_2 xerogels which were dried at 150°C for 1 h in air.
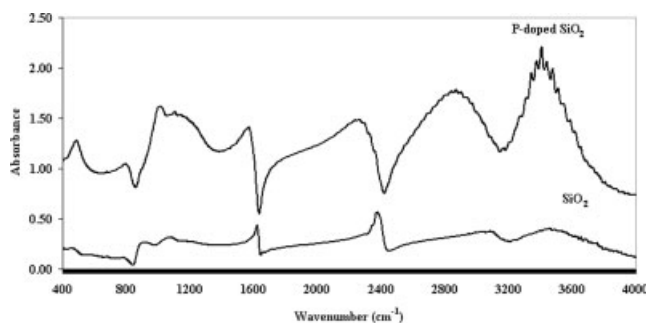
Figure 4 FTIR spectra of P-doped and undoped SiO$_2$ powders dried at 150°C for 1 h in air.

SiO$_2$ powders during heating up the samples in DTA-TGA analyzer. While weight loss percentage of P-doped Si-based powders is found to be 37%, this mass loss value was determined as 23% in Si-based sample. As demonstrated in DTA explanation, TGA curve can be divided into three stages. Similar to the present results, Yu et al.[16] have observed that the largest weight loss is in the temperature range from room temperature to 125°C, which can be attributed to the evaporation of the physically adsorbed water and ethanol. The second stage is from 125 to 380°C. This may be the result of the combustion of a small amount of organic residues. In the third stage from 380 to 550°C, the mass loss is very low. This is assigned to the evaporation of chemisorbed water.[16,17]

FTIR analysis

Figure 4 indicates the FTIR absorbance spectra of P-doped and undoped Si-based powders, which were dried 150°C for 1 h in air. The bands at 3200 and 3600 cm^{-1} are due to O—H stretching in the P-doped and undoped Si-based powders, which were heat treated at 150°C and those at 2200–2600 cm^{-1} is due to C—H stretching frequencies. To illustrate, the presence of CH$_2$ and CH$_3$ organic groups was monitored through their vibrational modes occurring in the 2400–2900 cm^{-1} range. The spectra of both samples were nearly similar. However, the peaks of P-doped Si-based powder shifted towards lower frequencies for the OH band between 1400 and 3600 cm^{-1} frequency as those of the other powder as seen in Figure 4. Upon the addition of phosphorous compound, the frequencies of O—H and C—H bands decreased. The common features that appear in the wavenumber band range of 1000–1110 cm^{-1} corresponds to the contributions of Si—O bonds. Additionally, the bands at 900–600 cm^{-1} in the P-undoped Si-based powder were due to the contributions of Si—O bonds. The peaks of Si—O for P-undoped SiO$_2$ powders were with low absorbance, but for the P-doped SiO$_2$ powders, the peaks of

Si—O were with high absorbance.[18] The peaks of P-doped Si-based powder shifted towards higher frequencies for the Si—O band between 700 and 1400 cm^{-1} frequency as those of the other powder and are very much sharper than those of the other powder as seen in Figure 4. The reason of that could be the bands at 1100–950 cm^{-1} and ~ 1050 cm^{-1} appeared because of P—O—R and P—OH bonds for P-doped Si-based powder, respectively.

Structural analysis

Figure 5 displays XRD diffractograms of the as-deposited pure SiO$_2$ and P-doped SiO$_2$ films on the cotton fabrics after annealing at 110°C. The bulk of the X-ray signal originated from cotton as cotton is the underlying substrate.[19] For comparison among pure SiO$_2$ and P-doped SiO$_2$ films on the cotton fabrics as well as untreated fabric, even though SiO$_2$ phase present in only pure SiO$_2$ coated fabric, SiO$_2$ having high intensity and silicon phosphate (Si$_5$P$_6$O$_{25}$) with very low intensity were found in P-doped SiO$_2$ films on the fabric. The SiO$_2$ peaks can be found at 2θ = 14.6°, 19.9°, 21.5°, 22.5°, 26.1°, 30°, 34°, 38°, 42.3°, 48°, and 59.2°. The Si$_5$P$_6$O$_{25}$ (SiO$_2$) peaks can be seen at 2θ = 25.2° and 40.1°. An enhancement of the cotton associated peak at 14.6°, 22.5°, and 26° was observed. According to the literature,[20] the pure SiO$_2$ xerogel films particularly shows a broad peak centered at about 26°, indicating its amorphous character. The similar behavior can be seen in P-doped SiO$_2$ xerogel films. Their XRD diagrams are similar to that of liquids because there is no crystalline peak of SiO$_2$ on account of the fact that these films were prepared at low temperature. At about 26°, P-doped SiO$_2$ film is different from SiO$_2$ xerogel film, because the peaks are becoming broader and less intense. That is to say, there is decrease in liquid order of the films due to P-doping
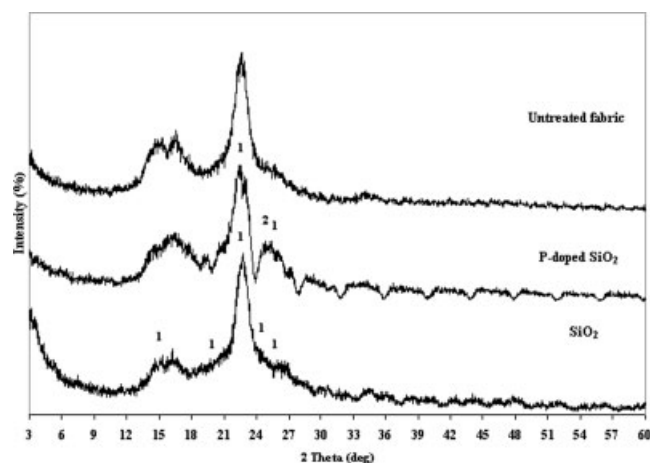

Figure 5 XRD patterns of P-doped and undoped SiO$_2$ films on cotton fabrics by sol–gel technique.
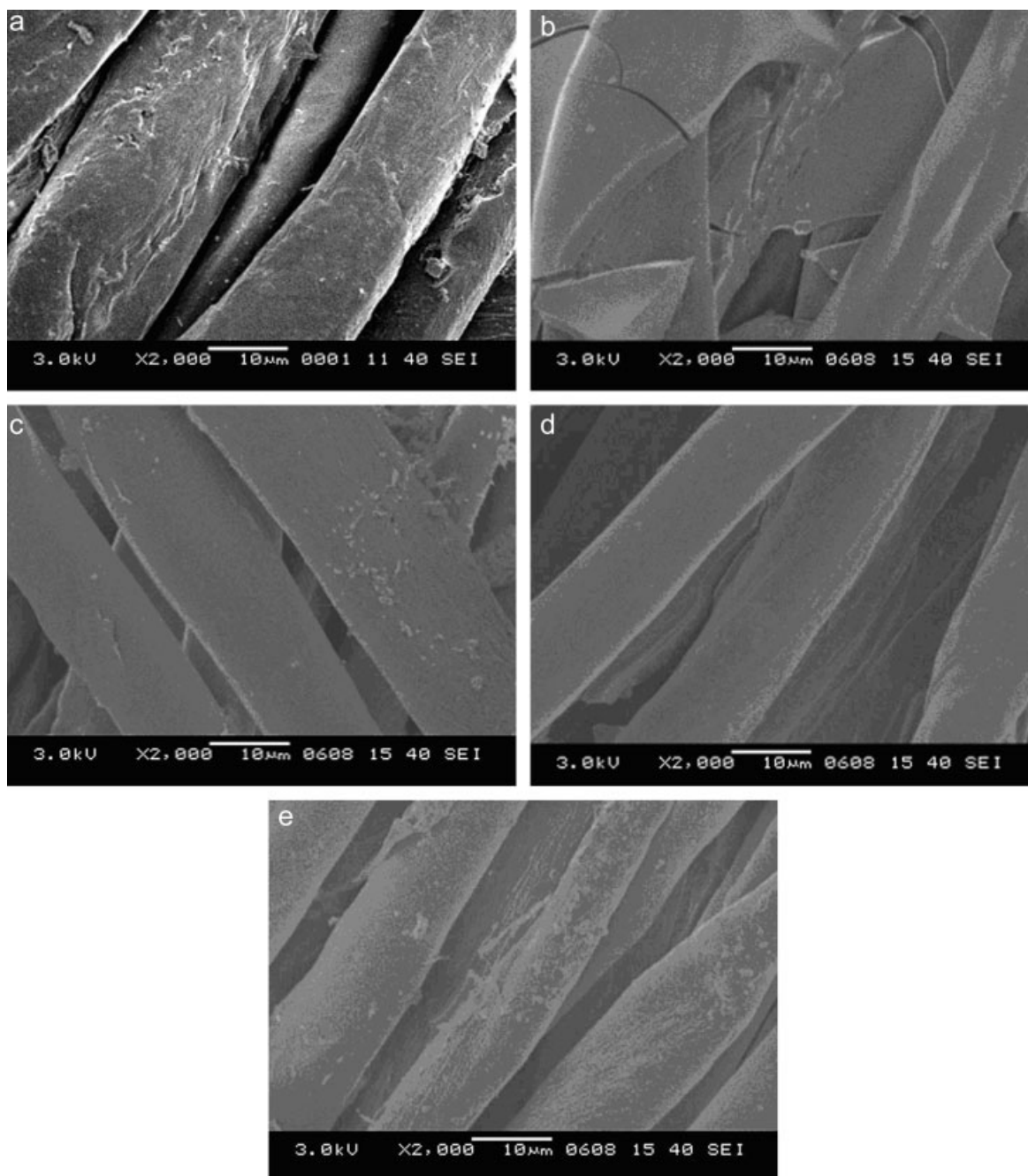
Figure 6 SEM micrographs of (a) untreated cotton fabric, (b) the treated fabric with Si-based solution before washing, (c) the treated fabric with Si-based solution after washing 10 times, (d) the treated fabric with P-doped Si-based solution before washing, and (e) the treated fabric with P-doped Si-based solution after washing 10 times. The scale bars are 10 μm.

at about 26°. The small peaks associated with silica suggest that the film is predominantly amorphous with a small content of silica. Furthermore, the thin film containing especially phosphate contributed that the fabric acquired the flame retardancy property.

Surface morphologies

Figure 6 demonstrates SEM micrographs of untreated cotton fabric, the treated fabric with Si-based transparent solutions before washing, the treated fabric with Si-based transparent solution after washing with 10 times, the treated fabric with P-doped Si-based solution before washing and the treated fabric with P-doped Si-based solution after washing with 10 times. It is clear from Figure 6 that the surface morphology of treated cotton fabric with the P-doped and undoped Si-based solution was smoother than that of the untreated cotton fabric. It was deduced that the thin film layers were formed

TABLE II
The Tensile (in Warp Direction), Surface Properties, and Flame Spread (in Warp Direction)
Times of Treated and Untreated Fabrics

	Time of flame spread (s)	Tensile properties		Contact angle
		Load (kgf)	Extension (mm)	
Untreated	5[a]	27.25	28.98	39°
SiO$_2$	15.64[a]	26.19	29.04	ND[b]
P-doped SiO$_2$ with phosphoric acid	Not flammable[c] 8[a,d]	20.5	43.81	ND
P-doped SiO$_2$ with ethyldichloro phosphate	20.19[a]	20.59	43.42	ND
P-doped SiO$_2$ with phosphoric acid→PU[e]	Not flammable[c]	24.81	35.28	92°

[a] After exposing to flame for 5 s.
[b] Not-detectable.
[c] After exposing to flame for 15 s.
[d] After washing 10 times.
[e] The samples were treated with polyurethane [Tubicoat PU 80 (CHT)] after the treatment with P-doped SiO$_2$ with phosphoric acid.

on the surface of the treated fabrics. The thickness of the P-doped and undoped SiO$_2$ film on the surface of cotton fiber was about order of nanometer. In Figure 6, the thin film layers were maintained on the surface of treated fabrics with P-doped and undoped Si-based solutions after they were washed 10 times. However cracks on the surface of the treated fabric with Si-based solution were removed after washings and a thin film layer remained on the surface.

Cracks generally form inside the coating prepared from highly viscous sols, however, film layers were not flaken off from surface of fabrics in our case owing to the solutions with optimum viscosity. It can be stressed that not only solution viscosity but also coating thickness influence film structures.

Textile features

Add-on values of the fabrics

On account of the fact that materials with a high density and thus a high degree of coverage generally have a high flame retardancy, the add-on values of the fabrics will gain importance with this regard. Since both the cotton and silica absorb moisture, untreated and coated fabrics were also dried under the same conditions with treated fabrics. In add-on value calculation, moisture absorbing properties of coated and uncoated fabrics were taken into consideration during weighing. The treated and untreated fabrics were conditioned at standard atmosphere of $(20 \pm 2)°C$ and $(65 \pm 2)\%$ relative humidity before weighing. The add-on values of treated cotton fabrics with P-doped and undoped Si-based solutions were listed in Table I. The add-on-values of the treated cotton fabrics with P-doped with phosphoric acid and with ethyldichloro phosphate and P-undoped Si-based solutions were 24.5, 20.6, and 30.6%, respectively. Of these values, add-on-value of the treated cotton fabric with only Si-based solutions

was the highest because of the film formation on the fabrics. Si-based solutions on the fabrics have fast gelation property at 80°C. Thus fast gelation of Si-based solutions on the fabric caused higher add-on-value of the treated fabric.

The tensile strength of the fabrics

Microfracture behaviors in coated and uncoated fabrics were considered to be decided by the following parameters; one is the geometry of textile fabric, coating type and deposition system. Table II shows the tensile properties (in warp direction), such as tensile strength and extension for the treated and untreated fabrics. A slightly decrease on tensile strength of fabric treated with P-doped SiO$_2$ solutions could be observed from 27.25 to 20.5 kgf because of the lower pH values (1.25) of P-doped SiO$_2$ solutions than the SiO$_2$ solutions (2.8). By coating with polyurethane after treatment with P-doped SiO$_2$ sols, the lost strength was compensated and the strength increased from 20.5 to 24.81 kgf.

Wettability and hydrophobic properties of the fabrics

To evaluate the wettability and hydrophobic properties of such coatings, the contact angle measurements were performed on the coated cotton fabric substrates. Table II shows the contact angles of the treated and untreated cotton fabrics. The water drop sink into the treated cotton fabrics with P-doped Si-based solutions in short time less than 20 s, thus in this case the contact angle was not detectable. After treatment with P-doped Si-based solutions, the contact angles of cotton fabrics coated with polyurethane increased from 39° to 92°. Figure 7 shows the image of contact of water on polyurethane coated cotton fabric after treated with P-doped Si-based solutions.
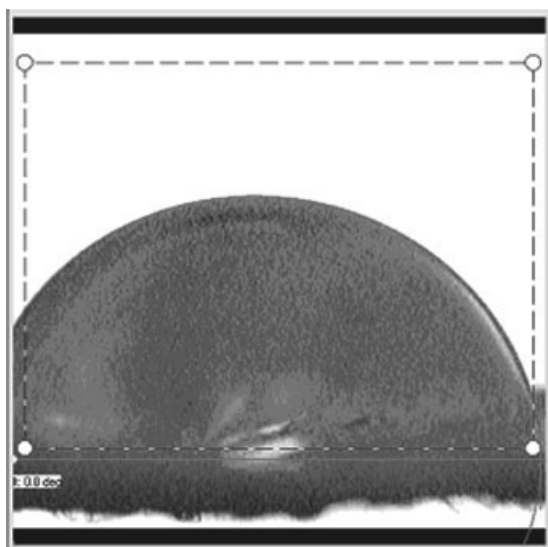
Figure 7 The contact image of water on polyurethane coated cotton fabric after treatment with P-doped Si-based solution.

While the cotton fabrics, which treated with P-doped Si-based solutions, have got hydrophilic property, the cotton fabrics, which treated with P-doped Si-based solutions and then coated with polyurethane at second step, have got hydrophobic property.

The flame retardancy properties of the fabrics

Table II shows flame spread (in warp direction) times of the treated and untreated fabrics. The treatment of the cotton fabrics with P-doped Si-based solutions with phosphoric acid provide the production of nonflammable cotton fabrics. The cotton fabrics which were coated with polyurethane still were not flammable. Nonetheless the times of flame spread of the treated cotton fabrics with P-doped Si-based solutions with ethyldichloro phosphate were longer than that of the untreated cotton fabric. After washing as 10 times, the flame spread times of the treated cotton fabrics with P-doped Si-based solutions were still longer (8 s) than that of untreated cotton fabric (5 s). Therefore, it was observed that the flame retardancy properties of the samples after even washing for 10 times were not completely lost. Thus it could not found a serious failure on fabrics untreated and treated with sols after washing for 10 times. With coating with polyurethane after treatment with P-doped Si-based solutions, the lost strength could be compensated. The slightly decrease on tensile strength of fabrics treated with P-doped Si-based solutions could be observed owing to the lower pH values with 1.25 of P-doped Si-based solutions than the Si-based solutions having 2.8 of pH value.

The lightness and whiteness features of the fabrics

Figure 8 shows the photographs of unwashed and washed fabrics that were untreated or treated with silica or P-doped silica sols. At conventional treatments containing phosphate, the color of cotton fabrics turns yellow. In this study, the color of cotton fabrics, which are treated with P-doped Si-based solutions, also turns yellow. After washing of the cotton fabrics as 10 times, the color of yellow of the fabrics becomes pale. Before and after washing, the color of the fabric which the treated P-undoped Si-based solutions did not change as to that of untreated fabric. Table III shows the lightness values, yellowness index values and whiteness values according to Stensby (D65-10°) of fabric samples. Considerable variation between photometric data and results of the corresponding coated and uncoated fabrics was observed. Notably, notwithstanding the fact that whiteness and lightness index values of the treated fabric with P-doped SiO_2 solution with phosphoric acid before washing was changed considerably, a normal variation was obtained in the treated fabric with SiO_2 solution before washing. It was determined that lightness and whiteness values of the fabrics decreased after coating process, while yellowness index values of the fabrics were increasing. The lightness and whiteness values of treated fabrics
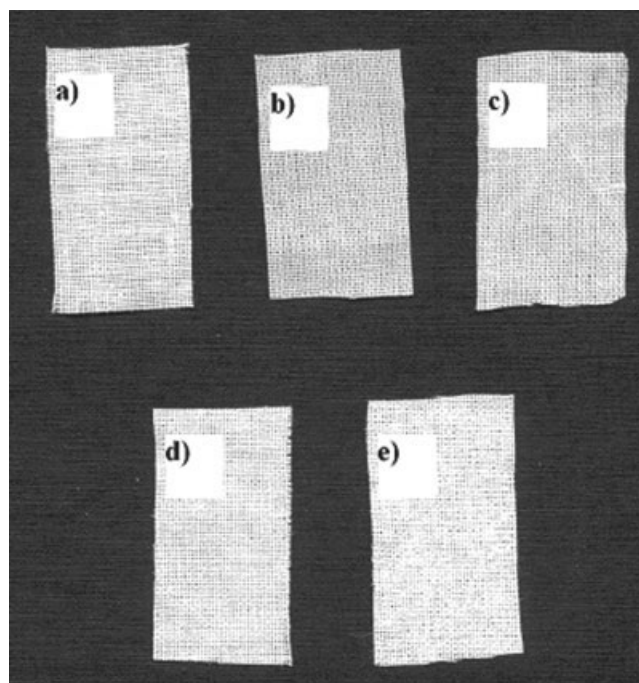

Figure 8 The photographs of fabrics (a) untreated, (b) treated with P-doped Si-based solution with phosphoric acid before washing, (c) treated with P-doped Si-based solution with phosphoric acid after washing 10 times, (d) treated with Si-based solution before washing, and (e) treated with Si-based solution after washing 10 times.

Fabric samples	Whiteness (stensby)	Lightness (L*)	Yellowness index	
			ASTM D 1925	ASTM E 313
Untreated	117.241	89.284	−15.025	−13.108
Treated with P-doped Si based solution with phosphoric acid before washing	62.891	78.94	18.716	13.755
Treated with P doped Si based solution with phosphoric acid after washing 10 times	72.987	85.94	11.488	8.927
Treated with Si based solution before washing	108.008	88.416	−10.827	−9.365
Treated with Si based solution after washing 10 times	110.595	90.696	−9.706	−8.544

slightly increased after washing. Hence it was pointed out that untreated fabric changed from white to yellow after coating process.

CONCLUSIONS

In summary, new halogen-free P-doped SiO_2 thin films were developed on fabrics for flame retardancy application. We found that the treated cotton fabrics with P-doped Si-based solutions by sol–gel process acquired nonflammable property. To decrease the disadvantages of conventional flame retardant finishing process, sol–gel processing with P-doped Si-based solutions to cotton fabrics was applied. It was observed that the property of flame retardancy of the samples by means of this sol–gel process after washing as 10 times was were not completely lost. Thus the application of sol–gel processing presents alternative process based on the new halogen-free flame retardancy finishing process with durability of washing for cotton fabric without requiring combination or after treatment with formaldehyde–urea resin. Furthermore it was concluded that the coating of cotton fabrics with polyurethane after the treatment with P-doped Si-based solutions provides to increase the tensile strength of treated cotton fabrics with P-doped Si-based solutions, while protecting the flame retardancy property of the cotton fabric.

Using phosphoric acid as a flame retardant agent is advantageous since it is cheap and abundant. Moreover concentration of flame retardant of 83 g/L at new flame retardant finishing process based on sol–gel process was much less than the concentration of flame retardant of 300–500 g/L at conventional flame retardant finishing process. As the result of that, the saving of amount of flame retardants would be provided and the environmental loading could be reduced. In our future study, we intended that the durability of the flame retardancy efficiency on the fabric against multiwashing increase by means of the optimization of the treatment and solution preparation conditions.

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