

The Influence of Precursor Ratios on the Properties of Cotton Coated with a Sol-gel Flame Retardant

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Cotton's many desirable characteristics include its hygroscopic nature, making it a popular material for use in garments that keep the wearer cool. It has a natural softness and an inherent strength that increases when wet. These properties, together with its stability in water and alkaline solutions, contribute to cotton's durability, resulting in its use in a wide range of applications from sleepwear, workwear, and bedding to curtaining.¹ Cotton, however, is a flammable material that is easily ignited and rapidly consumed. With the implementation of worldwide flammability standards, there is a need for improvements in flame-retardant cotton.^{2,3}

A wide range of non-durable, semi-durable, and durable treatments are available for producing flame-retardant cotton. Water-soluble phosphate salts that are easily applied by normal textile processes have been used for more than a century as non-durable or semi-durable flame retardants. Phosphorous compounds are almost unique in their ability to prevent afterglow and their effectiveness as flame retardants is improved by the addition of a nitrogen-based compound, such as urea.^{3,4}

Sol-gel coating of textiles is a relatively new process. It is used to produce oleophobic, hydrophobic, hydrophilic, anti-static, UV-stable, and abrasion-resistant properties on fabrics.^{5,6} The coating can be applied by common finishing techniques such as padding, spraying, or dip coating. The sol-gel process is also used for enhancing the washfastness of direct dyes on cotton,⁷ as an inorganic-organic finish for nylon carpeting⁸ and, in the current study, for the application of a phosphate-urea flame

retardant onto cotton.⁹

In the textile sol-gel process, the precursors are typically alkoxysilanes having the general structure $(RO)_4Si$, where R is typically $-CH_3$ or $-C_2H_5$. The alkoxysilanes are mixed with water in a mutual solvent, such as ethanol, and undergo hydrolysis and condensation reactions with the aid of an acid or base catalyst. The sol-gel coating can be easily modified chemically or physically to introduce different functionality. Physical modification can be effected by doping the nanosol with additives that are homogeneously incorporated and immobilised within the silicon oxide network. Chemical modification can be achieved by the use of different metal alkoxides or organo-functional silanes of the type $A-X-Si(OR)_3$. A is an organo-functional group (e.g., an epoxy group). X is an inert spacer, usually $-(CH_2)_n-$ ($n = 2, 3$) and R is $-CH_3$ or $-C_2H_5$.^{6,10,11}

As with any coating process, the flexibility and hand of the coated fabric is a function of both the precursors used and the thickness of the coating. In the sol-gel coating process, higher flexibility can be obtained by increasing the proportion of organo-functional silanes in the precursors and by controlling the coating parameters (e.g., padding speed and padding pressure).¹²

Properties such as percent add-on, bending rigidity (fabric stiffness), and vertical flammability can give an indication of the properties and effectiveness of a sol-gel flame retardant coating. It is also useful to examine the evenness of the coating on the fibers and the distribution of the "active" (i.e., the phosphate flame retardant) on the fibers. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) are useful tools for examining the fiber surface coating.¹³⁻¹⁵

ABSTRACT

Cotton has many desirable properties, but is flammable. The flame retardant treatment of cotton is an important textile process. To study the effect of a sol-gel phosphate-based flame-retardant coating on fabric properties (flammability, stiffness, and strength), coatings were applied to cotton fabrics using different ratios of sol-gel precursors. The results showed that the ratio of sol-gel precursors influenced fabric stiffness and strength but not flammability. The distribution of the sol-gel flame retardant was examined using scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDAX) elemental mapping. SEM images showed the formation of a thin coating and different features on the surface of the fibers. EDAX scan analysis revealed different distribution patterns of silicon and phosphorus on the fiber surfaces.

Key Terms

Cotton
Flame Retardant
Phosphate
Sol-gel

EXPERIMENTAL

Materials

Bleached 100% cotton drill fabric (234 g/m²) was used for the treatments. The following analytical grade reagents were used: tetraethyl orthosilicate (TEOS) (99%, Merck), 3-glycidoxypropyltrimethoxysilane (GPTS) (98%, Sigma-Aldrich), ethanol (100%, Merck), orthophosphoric acid (85%, Merck), diammonium hydrogen phosphate (DAP) (Merck), urea (Minema Lab supplies), and deionized water with a conductivity of $< 2 \mu S$.

Treatment Preparation

The sol-gels were prepared using GPTS, an organo-functional silane, and TEOS with ethanol as a solvent and orthophosphoric acid as a catalyst. GPTS and TEOS were mixed in different

ratios, as shown in Table I, a portion of the ethanol was added, and the solution stirred. The remainder of the ethanol, deionized water, and a catalyst were then added and stirring continued for 45 min. DAP/urea dissolved in deionized water was then added to the sol-gels.

Fabric Treatments

Fabric samples were coated with the sols by a pad-hang-dry-cure process. The fabrics were padded using a Roaches BVHP laboratory padder set to run at a speed of 1.0 m/min and a nip pressure of 1.5 bar. Each sample was passed twice through the nip rollers to ensure a more even treatment. The wet pickup was between 75% and 80%, varying slightly with the different sols. Fabrics were hung on a line for a period of 45 min at room temperature prior to being dried at 70°C for 1 min, and then cured at 160°C. Drying and curing of samples was done in a Roaches TFO/S laboratory oven/steamer.

Rinsed samples were obtained by soaking the treated samples in clean water at a liquor ratio of 30:1 for 20 min, squeezing, and then tumble drying for 30 min.

Analysis of Treatments

SEM analysis of fabric samples was performed on a JEOL JSM-6380 scanning electron microscope. EDAX elemental mapping scans of specific elements (carbon, silicon, and phosphorous) on selected areas were also performed. All samples were gold-coated to increase the surface conductivity of the fabric for better image resolution.

Fabric Stiffness

As a measure of fabric stiffness, the bending rigidity of samples was determined using the CSIRO FAST (Fabric Assessment by Simple Testing) system. The bending rigidity (B) in $\mu\text{N}\cdot\text{m}$ is calculated according to Eq. 1.

$$B = W \times C^3 \times (9.81 \times 10^{-6}) \quad \text{Eq. 1}$$

W is the fabric mass per unit area (g/m^2) and C is the bending length (mm).

Flammability Testing

Flammability testing was conducted according to ASTM D6413-99, "Standard Test Method for Flame Resistance to Textiles (Vertical Test)" with the following deviations: the sample size and specimen holder were reduced to 160 x 65 mm, with the burnable area of the fabric being 150 x 51 mm instead of 300 x 51 mm, the flame source was provided by a small butane burner, and samples were only tested in the warp direction. The weight used for determining the char length had a mass of 200 g. All samples were conditioned in a standard atmosphere prior to flammability testing.

In addition to the after-flame time, afterglow time, and char length, the percent combustion was also calculated using Eq. 2.

$$\text{Percent combustion} = \frac{[M_1 - (M_1 \times 0.264)] - [M_2 - (M_1 \times 0.264)]}{[M_1 - (M_1 \times 0.264)]} \times 100 \quad \text{Eq. 2}$$

TABLE I.

Sol-gel Compositions^a

Sol-gel	GPTS (mL)	TEOS (mL)	EtOH (mL)	Water (mL)	DAP (g)	Urea (g)	Water (mL)
7	20	10	75	45	25.00	27.39	150
9	15	15	75	45	25.00	27.39	150
8	10	20	75	45	25.00	27.39	150

^aContained 0.03 mL orthophosphoric acid catalyst.

TABLE II.

Effect of Sol-gel Coating on Fabric Stiffness and Strength

Sample Numbers	GPTS/TEOS	Curing Time (min)	Bending Rigidity Warp ($\mu\text{N}\cdot\text{m}$)	Tensile Strength Warp (N)
7.1	1.33/0.67	5	416.0	660.4
7.2	1.33/0.67	0.5	427.0	752.0
9.1	1/1	2	42.3	825.8
8.2	0.67/1.33	0.5	33.3	1010.2
Untreated	—	—	22.4	938.6

M_1 and M_2 are the masses of the fabric test sample in grams before and after testing respectively. The factor (0.264) represents the percent of the fabric test sample that is not available for combustion during the test because it is clamped in the specimen holder.

RESULTS AND DISCUSSION

Physical Properties

The fabric samples were coated with approximately 1.5% (mass of fiber) phosphorous and 1.0% (mass of fiber) silicon, with some variation due to the percent wet pickup. A summary of test results are given in Tables II-IV.

Bending Rigidity

The results for bending rigidity (fabric stiffness) showed an increase in fabric stiffness for all coated samples when compared with the untreated control sample. Samples treated with sol-gel 7, which had the lowest proportion of TEOS (and a highest proportion of GPTS), were significantly stiffer than samples treated with the sol-gels having a higher proportion of TEOS. This was somewhat in contrast to the findings of Min, et al.,⁷ who found that the use of TEOS in the sol-gel resulted in a stiffer fabric.

Tensile Strength

The results for tensile strength showed that there was a slight increase in the warp tensile strength of the sample treated with the lowest proportion of GPTS (Sample 8.2). The other samples showed a decrease in warp tensile strength as the proportion of GPTS in the sol-gel was increased. The curing time influenced the warp tensile strength slightly (Sample 7.1 and 7.2).

Polysilanol, formed after the hydrolysis and condensation of the sol-gel precursors, may react with the hydroxyl groups

TABLE III.

Effect of Sol-gel Coating on Fabric Flammability

Sample	GPTS/TEOS	After-flame (sec)	Afterglow (sec)	Char Length (mm)	Combustion (%)
7.1	1.33/0.67	10	0	>150	43.6
7.2	1.33/0.67	0	0	87	8.6
9.1	1/1	0	0	97	9.9
8.2	0.67/1.33	0	0	88	8.8
Untreated	—	18	23.8	>150	86.5

TABLE IV.

Effect of Sol-gel on Fabric Flammability—Rinsed Samples

Sample	GPTS/TEOS	After-flame (sec)	Afterglow (sec)	Char Length (mm)	Combustion (%)
7.1	1.33/0.67	10	0.5	>150	59.8
7.2	1.33/0.67	12.4	0.6	>150	72.4
9.1	1/1	9.4	0	>150	63.0
8.2	0.67/1.33	13	1	>150	72.6
Untreated	—	18	23.8	>150	86.5

of cellulose in cotton to form linkages between the cellulose and the sol-gel.¹⁵ Nevell,¹⁶ and Gardon and Steele,¹⁷ reported that low levels of cellulose crosslinking can result in increased tensile strength because crosslinking inhibits cellulose chain slippage when stress is applied. At a certain point, however, increasing the number of crosslinks decreases the tensile strength because the relative movement of chains becomes restricted to such an extent that the proportion of chains available to resist the applied stress decreases. The variation in tensile strength could, therefore, be a function of the crosslinking of cotton and sol-gel. The lower tensile strength of sample 7.1 could also be the result of the flame retardant reacting with the fiber (phosphorylation) which may have resulted in fiber damage.

Flammability

The results for fabric flammability before rinsing (Table III) showed that samples 7.2, 9.1, and 8.2 had an excellent level of flame resistance, especially when compared to the untreated control. The ratio of GPTS/TEOS did not appear to have any influence on the flammability results. Sample 7.1, which was cured for a longer period of time, showed a lower level of flame resistance.

A loss in flame resistance was observed after rinsing the treated samples. The treated samples, however, showed a lower level of after-flame, afterglow, and percent combustion when compared with the untreated fabric (Table IV). The samples that were cured for longer periods of time (Sample 7.1 and 9.1) showed a lower percent combustion compared to the samples that were cured for only 30 sec. The reduced percent combustion is related to the shorter after-flame and afterglow times for the cured samples.

Instrumental Analysis

SEM images revealed a number of different features on the fiber surface after coating. These included crystals, globules, inter-fiber bonding, and film-like layers (Fig. 1).

The surface of the fibers appeared to have been coated with a smooth, somewhat irregular layer. The EDAX analysis results for the fiber surface coating (film-like structures) showed the presence of both phosphorous and silicon. Phosphorous was present in proportions of less than 0.5 times, and silicon in proportions of less than 0.2 times, that of the amount of carbon detected. The presence of small quantities of both phosphorous and silicon on the fiber surface suggested a thin coating of the sol-gel on the fibers. Examination of the film-like layers indicated that the thickness of the sol-gel layer was ~0.6-1 mm.

Globular structures were observed on samples (9.1 and 8.2) that were coated with lower levels of GPTS sol-gels. The globules on sample 8.2 were ~1-2 mm in diameter and were clustered together on the fiber surface (Fig. 2). The globules were not evident on the samples (7.1 and 7.2) coated with the sol-gel containing the high level of GPTS. The images suggested a link between the quantity of GPTS and TEOS present in the sol-gel and the formation of globules. Globule formation appeared to decrease as higher levels of GPTS were used, possibly because of increased organic crosslinking in the sol-gel. The EDAX results for the globules showed that the globules had a high proportion of silicon in relation to the amount of carbon detected. Phosphorous was also present in the globules in proportions ~0.5-2 times that of

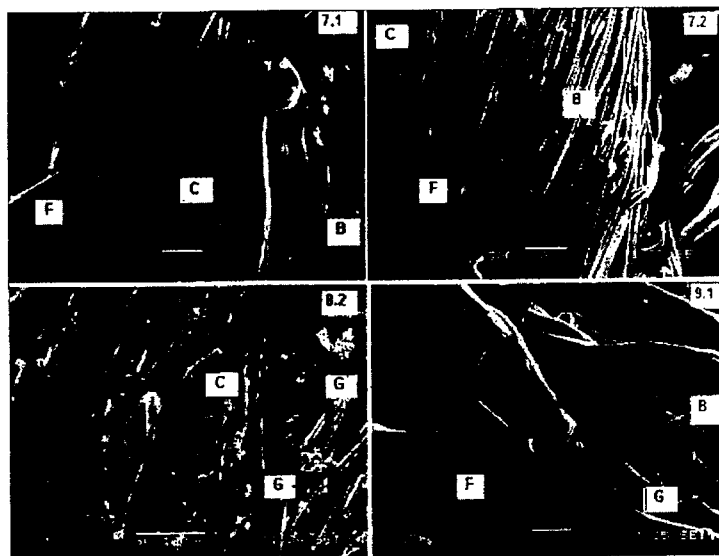


Fig. 1. SEM images showing structures on sol-gel coated samples: (B) inter-fiber bonding, (C) crystals, (F) film-like structures, and (G) globules. Top (left to right): samples 7.1 and 7.2, Bottom: (left to right) samples 8.2 and 9.1.



Fig. 2. Clustered globules on sample 8.2.

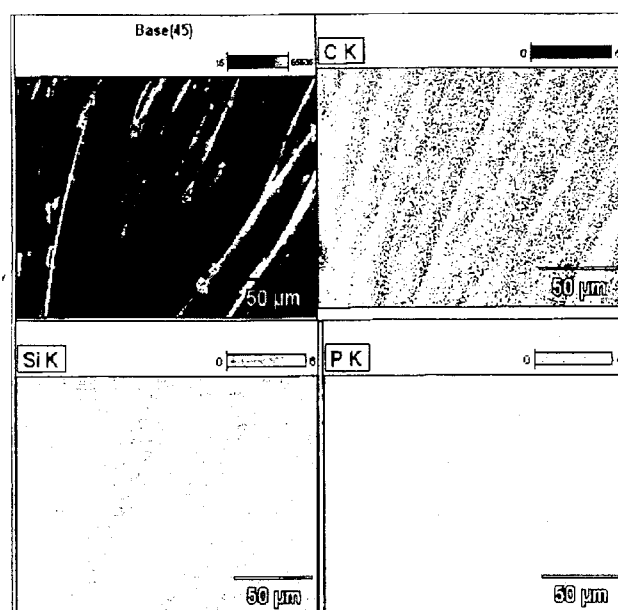


Fig. 4. Elemental mapping of sample 9.1: C K-carbon; Si K-silicon; P K-phosphorous.

the amount of carbon detected. This suggested the incorporation of phosphorous into the sol-gel structure.

Small crystals that were hexagonal or irregular in shape were evident on samples 7.1, 7.2, and 8.2, but appeared to be absent from sample 9.1. The EDAX point analysis results for the crystals showed that they had a high proportion of phosphorous in relation to the amount of carbon detected. The presence of phosphorous crystals on the surface of the fibers suggested that the crystals formed after coating. Silicon, in a similar proportion to carbon, was also detected in the crystals.

Inter-fiber bonding was evident on all samples, but appeared to be more extensive in samples 7.1 and 7.2, which contained more GPTS than the other samples. The coating from the inter-fiber bonding region showed a higher proportion of silicon in relation to phosphorous. The presence of more extensive inter-fiber bonding in samples 7.1 and 7.2 suggested that this

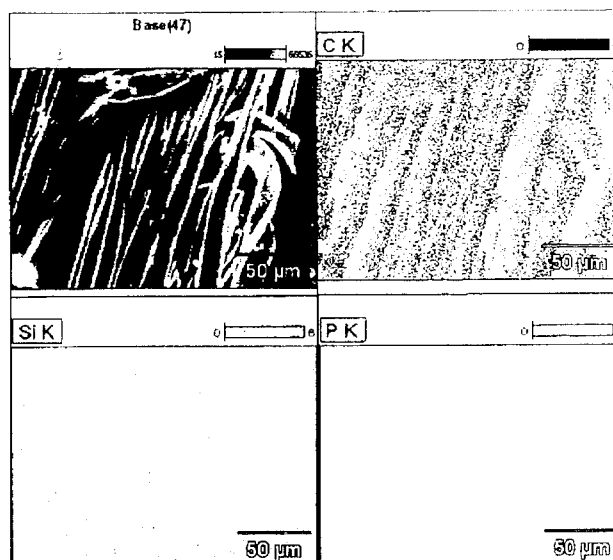


Fig. 3. Elemental mapping of sample 7.1 (high GPTS): C K-carbon; Si K-silicon; P K-phosphorous.

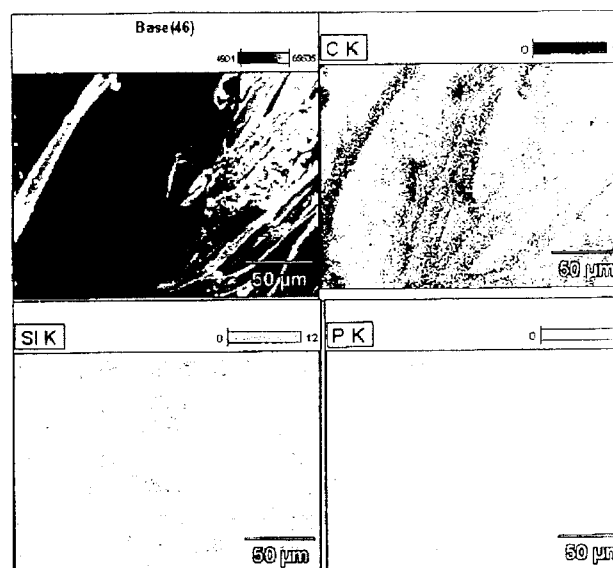


Fig. 5. Elemental mapping of sample 8.2 (low GPTS): C K-carbon; Si K-silicon; P K-phosphorous.

might have had some influence on the bending rigidity of the coated samples.

Compared to the other samples, the level of phosphorous detected in the EDAX scans appeared to be lower in sample 7.1, which was cured for 5 min—the reason for this was not determined. This sample had lower flammability results before rinsing (Table III). It is possible that the extended curing time also resulted in a greater loss of nitrogen (in the form of ammonia) that reduced the phosphorous-nitrogen synergistic flame retardancy effect.

The EDAX results for the rinsed samples of 7.1 and 7.2 showed a relative loss of phosphorous when compared with the unrinsed samples. This indicated the loss of unbound

flame retardant during rinsing. This conclusion was supported by the relative loss of flame resistance for the rinsed samples when compared with the unrinsed samples (Tables III and IV respectively). The loss of flame resistance was less for sample 7.1 than for sample 7.2, highlighting the importance of the curing process in binding some of the phosphorous flame retardant on the fabric, either in the sol-gel matrix or as cellulose phosphate esters.

Elemental mapping of the sample surface was performed on samples 7.1, 8.2, and 9.1 to examine the distribution of phosphorous and silicon on the fibers (Figs. 3-5).

The scans for sample 7.1 (Fig. 3) showed a relatively even distribution of phosphorous on the fibers. Silicon was relatively evenly distributed, with a few high concentration areas associated with rougher or thicker areas of sol-gel coating on the fiber surface.

The scans for sample 9.1 (Fig. 4) showed that the phosphorous was evenly distributed over the fiber surface with no apparent high concentration areas. The silicon was distributed all over the fibers, but with a number of high concentration areas. These areas were associated with uneven areas of coating, inter-fiber bonding, and globules on the fiber surface.

The distribution of phosphorous on the fibers of sample 8.2 (Fig. 5) was relatively uneven, with a few areas of local concentration that appeared to be associated with crystals on the fiber surface. The silicon was distributed over all fiber surfaces, but was relatively uneven with concentrations occurring in several areas, and usually associated with globule clusters.

CONCLUSION

The GPTS/TEOS ratio in the sol-gel had an influence on a number of fabric properties. A high level of GPTS resulted in a stiffer and weaker fabric, possibly as a result of crosslinking and inter-fiber bonding. Use of a higher GPTS/TEOS ratio resulted in a more even coating and, generally, a more even distribution of silicon and phosphorous on the fiber surface. The GPTS/TEOS ratio and the evenness of the coating, however, did not appear to influence the level of flame retardancy achieved, either before or after rinsing of the samples—the curing time appeared to be the overriding factor. The retention of afterglow prevention, however, was retained in the rinsed samples. This was possibly due to the sol-gel coating retaining sufficient phosphorous to prevent the afterglow reaction and also forming a physical barrier, thereby preventing heat and oxygen access to the fibers. The different sol-gels produced a number of different features on the surface of the fibers, including crystals, globules, and inter-fiber bonding. The globules appeared to be associated with higher concentrations of TEOS and inter-fiber bonding with higher concentrations of GPTS. The proportion of phosphorous and silicon varied in each of the features, with

the crystals having a higher proportion of phosphorous, and the globules and areas of inter-fiber bonding a higher proportion of silicon.

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