

## Flame-retardant Cotton Fabrics Based on Sol-gel Technique

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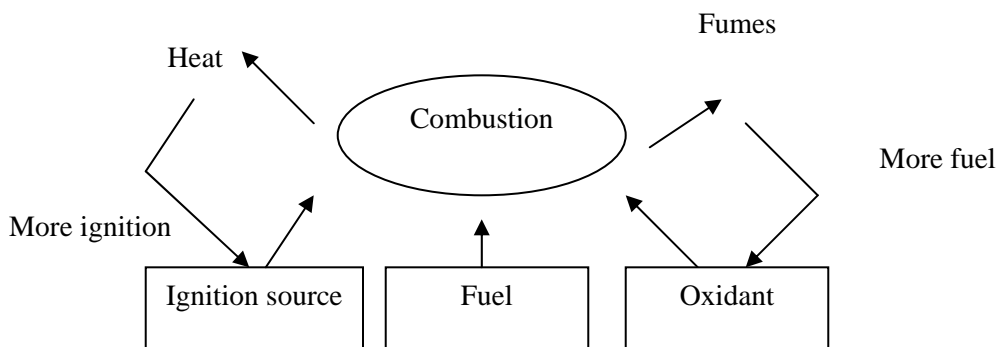
### ABSTRACT

Sol-gel containing silica and phosphorous was examined as a flame-retardant on cotton fabric. To prepare the sol-gels, diethylphosphatoethyltriethoxysilane (DPETS), tetraethoxysilane (TEOS), and 3-glycidoxypolytrimethoxysilane (GPTMS) were mixed at the different ratios and stirred for 24 hr. at room temperature in water-ethanol solvent. The resultant sol-gels were coated on cotton using pad-dry-cure method. TGA (Thermogravimetric Analysis) and flammability test were used to investigate thermal decomposition behavior and char formation of the treated fabrics. Percent of char yield was increased with increasing amounts of DPETS in the sol-gel precursors.

*Keywords*; flame-retardant, cotton fabrics, sol-gel, pad-dry-cure, TGA, char formation

### INTRODUCTION

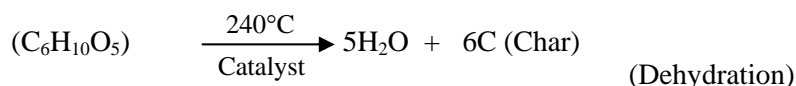
Flame-retardant finishing on textiles has gained significant attentions as a result of enormous loss of life and property in case of fire hazards. In order to reduce the risk of fire accident, it is necessary to understand the principle of the combustion process (Oulton, 1995). Figure 1 shows three fundamental components of the combustion process, that is, fuel, an oxidant (usually air) and ignition source.



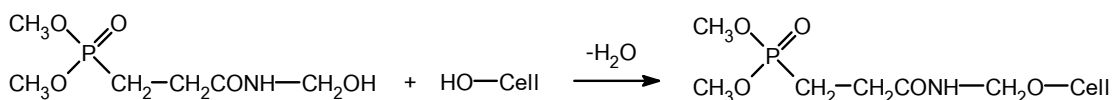
**Figure 1** Thermal combustion process

Cotton is the most important natural cellulosic fibers and has been used widely in textile applications due to its distinct characteristics such as softness, high water absorbancy and comfort (Nevell, 1995). However, the cotton textiles burn

freely, once ignited (Oulton, 1995; Parmar and Chakraborty, 2001). During the thermal degradation, i.e., pyrolysis of cellulose, a large number of low molecular weight aldehydes, ketones and alcohols which are highly volatile and flammable are produced. Less volatile but equally flammable higher molecular weight, tars are also formed. In addition, some materials are turned into solid carbonaceous char. Typically, two main reactions occur during the pyrolysis, i.e., oxidation and dehydration as shown below.



Normally, the role of flame-retardant system is to alter the course of decomposition so that a lower percent of flammable volatiles is produced and a corresponding larger char is formed (Hsiue *et al.*, 2000). The char behaves as a thermal barrier to fire by limiting access to air (Guan and Chen, 2006). One example of commercial fire-retardant for cotton is Pyrovatex CP, which is N-methylol dialkyl phosphonopropionamide (Oulton, 1995). This compound forms stable covalent bonds with cellulose (Cell-OH) to give good washfastness property.



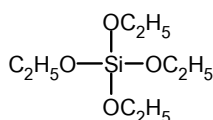
Sol-gel method is widely used in glass or ceramic applications where hydrolysis and condensation of inorganic or organo-metallic such as metal alkoxides take place (Perkins *et al.*, 1966). This leads to the formation of three dimensional networks on the surface of coated material. Recently, some works has been carried out to employ sol-gel technique in textile application. For example, Mahltig *et al.* (2004) embedded three triarylmethane dyes into sol-gel layers of TEOS and 3-glycidyloxypropyltriethoxy silane (GLYEO) and then coated on the surface of polyester, polyamide and cotton fabrics. Daoud *et al.* (2004) prepared transparent and durable super-hydrophobic silica coating films based on TEOS, GPTMS, and hexadecyltrimethoxysilane (HDTMS) on cotton. Min *et al.* (2003) treated the direct dyed cotton fabrics with a series of sol-gels of TEOS and GPTMS, to enhance the washfastness of the dyed fabrics. Xin *et al.* (2004) developed a UV-blocking property on cotton using a thin film nanosol of titanium tetraisopropoxide.

The objective of this article is to study cotton flame retardancy through the introduction of sol-gel process. The sol-gels containing silica and phosphorous were prepared from TEOS, DPETS, and GPTMS and applied to cotton fabrics using pad-dry-cure process. The results on thermal decomposition behaviors of the treated fabrics evaluated by TGA and flammability test were also reported.

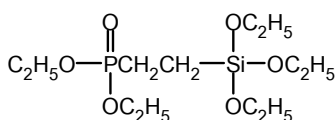
## EXPERIMENTAL DETAILS

**Fabric:** Commercially desized, scoured and bleached plain weave cotton fabric (weighing 209 g/m<sup>2</sup>) was used.

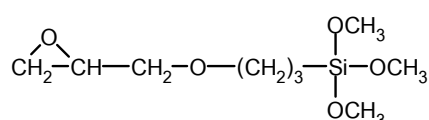
**Sol-gel precursors:** Tetraethoxysilane (TEOS), diethylphosphatoethyltriethoxysilane (DPETS), and 3-glycidoxypropyltrimethoxysilane (GPTMS) were purchased from Gelest, Inc., USA.



TEOS



DPET



GPTMS

**Chemical reagents:** Pyrovatex<sup>®</sup> CP New and Lyofix<sup>®</sup> CHN (a cellulose crosslinking agent) were supplied by Huntman (Thailand). Hydrofluoric acid (HF) and 85% Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) were obtained from Merck KGaA, Germany. Ethanol (EtOH) was purchased from Labscan Asia Co.,Ltd. All chemicals were used as received without further purification.

**Preparation of sol-gels:** Three sol-gel precursors, i.e., TEOS, DPETS, GPTMS were mixed at different molar ratios (100:0:0, 90:10:0, 70:30:0 and 45:10:45, Table 1) in ethanol by stirring for 5 min (Cardenas *et al.*, 1996). An aqueous solution of HF was added slowly to the above mixture. The resultant mixture was stirred for 24 h at room temperature. Also, the molar ratio of HF:sol-gel precursors was 2.2x10<sup>-3</sup>, whereas that of ethanol : water : sol-gel precursors was 35 : 50 : 15.

**Table 1** Composition of the prepared sol-gels 1 - 4

Sol-gel	Molar ratio TEOS:DPETS: GPTMS	Mol (weight, g)		
		TEOS	DPETS	GPTMS
1	100:0:0	0.5 (104)	0	0
2	90:10:0	0.45 (93.6)	0.05 (16.4)	0
3	70:30:0	0.35 (72.8)	0.15 (49.2)	0
4	45:10:45	0.225 (46.8)	0.05 (16.4)	0.225 (53.1)

**Application of sol-gels on fabric:** Cotton fabric was first immersed in the prepared sol-gel for 5 min, padded at 80%wpu on a laboratory padding mangles (Mingscape International Co.,Ltd.). The padded fabric was then dried at 100°C for 5 min and cured at 150°C for 5 min in a laboratory mini-dryer (Mingscape International Co.,Ltd.). The obtained fabric was rinsed with water at 50°C for 20 min, rinsed with water at room temperature for 10 min and finally dried at 100°C for 5 min.

**Application of a commercial fire-retardant on fabric:** Cotton fabric was immersed in the solution of Pyrovatex CP New (350 g/L), Lyofix CHN (45 g/L), and phosphoric acid (21.5 g/L) for 5 min, padded at 80%wpu on a laboratory padding mangles, dried at 120°C for 3 min and cured at 150°C for 5 min. The fabric was washed with Na<sub>2</sub>CO<sub>3</sub> (30 g/L) at 50°C for 30 min, rinsed with water at room temperature for 10 min and then dried at 100°C for 5 min.

**TGA (Thermogravimetric analysis):** TGA was performed with a Perkin Elmer TGA-7, at a heating rate of 10°C/min under air atmosphere.

**Burning behavior:** ASTM D1230-94 standard test method was used as a guide to study the burning behavior of the fabrics in terms of their flame-spread rates. The dry specimen (size 50 cm x 150 cm) was held in a flammability tester, Atlas 45 Automatic Flammability Tester as shown in figure 2 at an angle of 45 degree. A standardized flame is applied to the surface of the specimen near the lower end for 5 sec and the time required for the flame to proceed up the fabric for 12.5 cm was recorded.



**Figure 2** Atlas 45 Automatic Flammability Testers

## RESULTS AND DISCUSSION

As illustrated in figure 3, TGA showed that there were three distinct stages during thermal decomposition of cotton. Below 140°C, there was a slight weight loss due to the desorption of absorbed water and some volatile matters. The major weight loss caused by thermal degradation of cellulose chain occurred at 145-400°C. After 400°C, less weight loss was noticed due to char formation. From TGA data, the % Residue and % Char (Table 2) were calculated according to

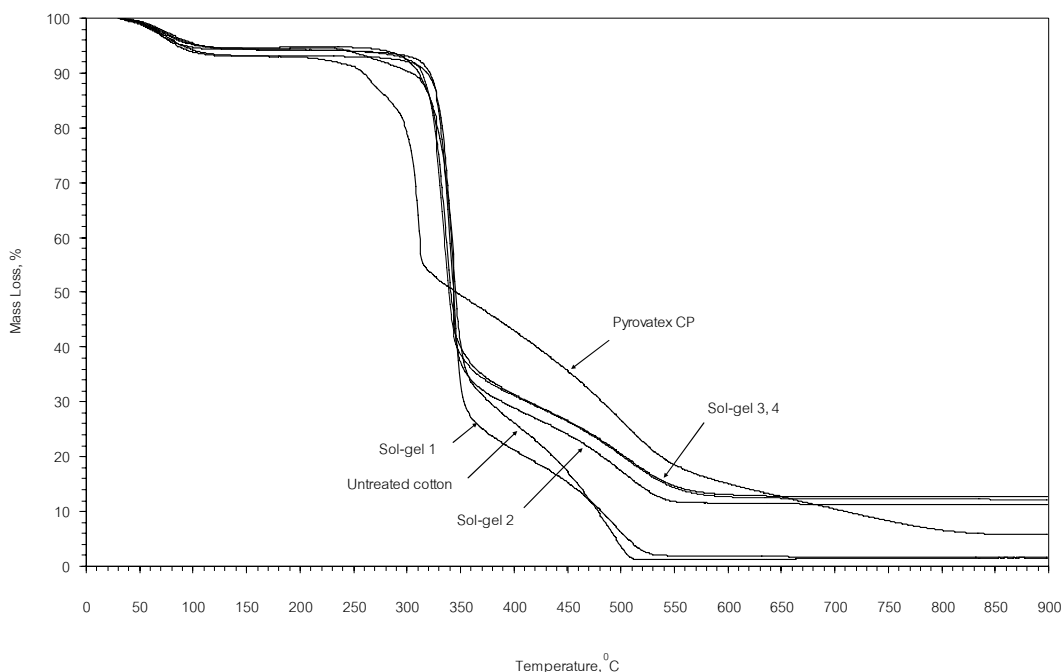
$$\% \text{ Residue} = (W_1 / W_0) \times 100$$

$$\% \text{ Char} = (W_2 / W_0) \times 100$$

where  $W_0$ ,  $W_1$  and  $W_2$  are the weights after the loss of physically bound water, at the end of thermal degradation and after carbonization of the residue, respectively. Increasing the amounts of DPETS in the sol-gels 1-4 yielded higher %char (2.2,

12.3, 13.2, and 13.4, respectively). For the untreated cotton, %char was 1.3, whereas that of the Pyrovatex finished cotton was 6.3.

Except for cotton treated with sol-gel 1, thermal degradation (pyrolysis) started at relatively lower temperature than that of the untreated sample. This is because phosphorous component in the sol-gel acted as a catalyst, thus reducing the activation energy (Tian *et al.*, 1999). In addition to its relatively gradual thermal decomposition, Pyrovatex finished cotton exhibited an oxidation of the char at temperature higher than 550°C. On the other hand, remaining char of cotton treated with sol-gels 2-4 was relatively thermally stable owing to the presence of silica component (Hsiue *et al.*, 2000).

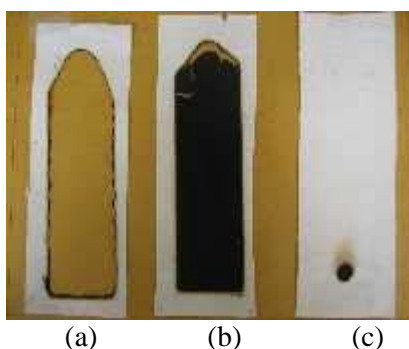


**Figure 3** TGA curves of untreated, sol-gel treated, and Pyrovatex finished cotton fabrics

**Table 2** % Residue and % Char of untreated, sol-gel treated, and Pyrovatex finished cotton fabrics

Cotton fabric	Pyrolysis region (°C)	% Residue	Carbonization region (°C)	% Char
Untreated	240-395	28.4	395-520	1.3
Sol-gel 1 treated	240-400	22.8	400-535	2.2
Sol-gel 2 treated	185-400	30.7	400-575	12.3
Sol-gel 3 treated	145-400	32.9	400-625	13.2
Sol-gel 4 treated	230-400	33.2	400-700	13.4
Pyrovatex finished	195-345	53.9	345-870	6.3

In view of flammability testing, untreated cotton burned freely after ignited with a flame-spread time of 0.24 cm/sec and had little amount of remaining char (figure 4). Cotton treated with sol-gels 1 and 4 burned more quickly than the untreated with flame-spread time of 0.55 and 0.42 cm/sec, respectively. Nevertheless, only cotton treated with sol-gel 4 showed noticeable residual char. Of all, cotton treated with sol-gels 2 and 3 possessed slowest flame-spread times (0.21 and 0.20 cm/sec, respectively) along with significant residual amount of char. In contrast, Pyrovatex finished cotton; the sample was self-extinguishing in 12.3 sec after ignition.



**Figure 4** Cotton fabrics after flammability test: (a) Untreated (b) Sol-gel treated (c) Pyrovatex finished

## CONCLUSION

Cotton treated with sol-gels exhibited improved flame retardancy compared to the untreated by promoting char formation. Phosphorous and silicon components in the sol-gel played critical roles in flame retardancy. The former functioned as a catalyst in thermal decomposition of cotton to increase char yield while the latter provided thermal stability of the produced char. Future works is needed for washfastness and some physical properties testing such as tensile strength and stiffness to determine if this sol-gel technique may cause any negative effects.

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