

Araştırma Makalesi / Research Article

IMPROVEMENT OF THE FLAME RETARDANT PERFORMANCE OF COTTON FABRICS USING SILANE-PHOSPHATE BASED SOL-GEL SYSTEM

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ABSTRACT: In this study, a hybrid sol-gel formulation based on silane and phosphorus/nitrogen containing components was applied to cotton fabrics to enhance their flame-retardant properties. Prior to the application, a high concentration alkaline pretreatment was performed to induce intramolecular swelling within the cellulose structure, reorganize hydrogen bonding and increase the accessibility of reactive hydroxyl groups. The sol-gel system was developed by integrating flame retardant additives including phytic acid, phosphoric acid, guanidine phosphate and urea into a silanol network formed by TEOS and GPTMS precursors. The prepared formulation was applied onto the fabric surface via padding method followed by thermal curing to form a three-dimensional hybrid structure. FTIR and XPS analyses confirmed the successful formation of a Si-O-Si network on the fabric surface and the incorporation of phosphorus containing components into the system. TGA results demonstrated that the sol-gel coating improved the thermal stability by increasing the degradation temperature. LOI and flame spread tests revealed a significant enhancement in flame retardant performance after coating with LOI values exceeding 52%. However, post-washing FTIR and XPS analyses indicated a noticeable reduction in phosphorus- and nitrogen containing species, which corresponded to a decrease in LOI to approximately 28%. Optical microscopy further confirmed that although a homogeneous coating layer was initially formed on the fiber surface this layer became thinner after washing. The findings indicate that while the silane-based inorganic network forms a relatively stable structural backbone on the fabric surface, the flame-retardant performance is largely governed by phosphorus and nitrogen-containing additives. The partial loss of these components during washing suggests that the interaction between the additives and the substrate is not sufficiently strong. Therefore, this study demonstrates that achieving durable flame retardancy requires not only the deposition of functional additives onto the surface but also their covalent integration with both the cellulose structure and the silane network.

Keywords: Sol-gel network, Cotton fabric, Guanidine phosphate, Phytic acid, Fire retardancy

SİLAN-FOSFAT ESASLI SOL-JEL İLE PAMUKLU KUMAŞLARIN GÜÇ TUTUŞURLUK PERFORMANSININ GELİŞTİRİLMESİ

ÖZ: Bu çalışmada, pamuklu kumaşların alev geciktirici özelliklerinin geliştirilmesi amacıyla silan ve fosfor/azot içeren bileşenlerden oluşan hibrit bir sol-jel reçetesi uygulanmıştır. Uygulama öncesinde kumaş yüzeyine yüksek konsantrasyonda alkali ön işlem yapılarak selüloz yapısında intramissellar şişme sağlanmış, hidrojen bağları yeniden düzenlenmiş ve reaktif hidroksil gruplarının erişilebilirliği artırılmıştır. Sol-jel reçetesi, TEOS ve GPTMS öncülleri ile oluşturulan silanol ağ yapısı üzerine fitik asit, fosforik asit, guanidin fosfat ve üre gibi alev geciktirici katkıların entegre edilmesiyle geliştirilmiştir. Elde edilen kaplama emdirme yöntemi ile kumaş yüzeyine uygulanmış ve ısıtıl işlem ile üç boyutlu hibrit bir yapı oluşturulmuştur. FTIR ve XPS analizleri, kumaş yüzeyinde Si-O-Si ağ yapısının başarıyla oluştuğunu ve fosfor içeren bileşenlerin sisteme dahil edildiğini göstermiştir. TGA sonuçları sol-jel kaplamanın termal stabiliteyi artırarak bozunma sıcaklığını yükselttiğini ortaya koymuştur. LOI ve alev yayılma testleri, kaplama sonrası numunelerde belirgin bir alev geciktirici performans artışı sağlandığını ve LOI değerinin %52'nin üzerine çıktığını göstermiştir. Ancak yıkama sonrası FTIR ve XPS analizlerinde fosfor ve azot içeren katkıların azaldığı buna bağlı olarak LOI değerinin %28'e düştüğü belirlenmiştir. Optik mikroskop görüntüleri de kaplama sonrası lif yüzeyinde homojen bir film tabakası oluşmasına rağmen yıkama ile bu tabakanın incelendiğini doğrulamıştır. Elde edilen sonuçlar, sistemde silan bazlı inorganik ağ yapısının yüzeyde kalıcı bir iskelet oluşturduğunu buna karşın alev geciktirici etkinliğin büyük ölçüde fosfor ve azot içeren katkı maddelerine bağlı olduğunu göstermiştir. Bu katkıların yıkama sırasında uzaklaşması sistemde bağlanmanın yeterince güçlü olmadığını ortaya koymaktadır. Bu çalışma, yüksek alev geciktirici performansın sürdürülebilirliği için katkı maddelerinin yalnızca yüzeye tutundurulmasının yeterli olmadığını, aynı zamanda lif yapısı ve silan ağı ile kovalent olarak bağlanmasının kritik olduğunu göstermektedir.

Anahtar Kelimeler: Sol-jel ağı, Pamuklu kumaş, Guanidin fosfat, Fitik asit, Güç tutuşurluk

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1. INTRODUCTION

Cellulose fiber, which is widely used in the textile industry, is known to be highly flammable by nature. It ignites easily, burns rapidly without self-extinguishing and produces only a minimal amount of char during thermal decomposition [1]. In addition, since these fibers exhibit a low Limiting Oxygen Index (LOI~18-22%) and have a pyrolysis temperature range of 300-400°C. Researchers have focused on the use of flame-retardant (FR) compounds to enhance the flame resistance of this natural fiber [2,3]. These flame retardants primarily consist of halogen and their derivatives as well as nitrogen- and phosphorus-based compounds. The fundamental mechanism of these compounds involves improving flame-retardant performance by reducing levoglucosan production minimizing the release of flammable volatile gases and promoting char formation [4]. For cellulose-based textiles, the negative environmental and human health impacts of traditional flame-retardant strategies such as high smoke and toxicity generation associated with halogenated salts and compounds, including brominated compounds, have led to an increased preference for phosphorus-based flame retardants. Although relatively low in thermal stability phosphorus-based compounds exhibit high flame resistance and release fewer toxic gases during combustion and their effectiveness is enhanced in the presence of nitrogen and silicon [1,5,6]. Phytic acid, on the other hand, acts as a powerful charring agent due to its high phosphate group content and promotes the early dehydration of cellulose [7,8]. Another important group of flame-retardant compounds consists of nitrogen-based flame retardants. Guanidine phosphate, due to its content of both phosphorus and nitrogen, offers a dual-action mechanism, enhancing charring during the solid phase while also creating an intumescent effect in the gas phase. Among these, guanidine phosphate is particularly remarkable due to its low toxicity, environmental compatibility, absence of halogenated acids and without producing toxic smoke during combustion [9,10]. Nitrogen-containing compounds such as urea also exhibit a flame-retardant effect by generating inert gas during decomposition. It has been reported that the phosphorus-nitrogen-silicon synergy both enhances carbonization in the solid phase and contributes to the suppression of flammable species in the gas phase resulting in significant reductions in heat release [10,11,12,13].

Currently, various technical methods including chemical grafting and surface coating are used to address the flammability problem of cotton fabrics. Among these methods, sol-gel and layer-by-layer (LbL) techniques have gained popularity in recent years due to their simplicity, minimal interference with the fiber and ability to preserve the fiber's natural properties [14]. Among the methods mentioned, sol-gel technology has become a highly preferred method in the textile industry due to its minimal chemical usage, low-temperature requirements, simple application equipment and strong bonding mechanisms [15]. In general, it is known that the sol-gel process is extremely practical for bonding inorganic and organic thin films to textiles due to its ability to withstand irregular

surfaces and harsh environments [16]. In the sol-gel processes, silanes act as precursors and form porous Si-O-Si network structures because of acid-catalysed hydrolysis and condensation reactions [17]. Since these coatings can form covalent bonds with textile surfaces, they are known to have the potential to produce durable and wash-resistant flame-retardant textiles [10]. It has also been noted that silane-based network structures act as a physical barrier, thereby limiting heat and mass transfer [18, 19]. Malucelli, for example, applied coatings containing silane agents such as TEOS and APTES, along with phosphorus-containing compounds, to cotton fabrics using sol-gel and layer-by-layer (LbL) techniques [19]. When the results were compared, it was found that the coatings applied via the sol-gel method were more resistant to washing. It was also pointed out that this durability is based on the covalent bonds formed between the silanes and the hydroxyl groups on the cotton surface.

To enhance the flame-retardant efficacy of textile materials, sol-gel systems modified with phosphate- and nitrogen- compounds have been developed. For example, Fu et al. [20] observed that the LOI value of functional fabrics coated with 3-aminopropyltriethoxysilane (APTES) and 3-hydroxyphenylphosphinylpropanoic acid (CEPPA) reached up to 30.4% and reported that the fabric exhibited self-cleaning properties due to its hydrophobic nature [20]. In a similar study based on DPPA and APTES, Ma et al. [14] found that the flame-retardant coating provided a certain level of hydrophobic performance to the surface of the cotton fabric, thereby reducing its susceptibility to liquid contamination [14]. In addition, it was reported that the LOI value of pure cotton increased from 17.8% to 26.5% among the produced samples. In another study, Sergin and Akşit[21] cotton fabrics were treated with a guanidine phosphate (GF) based sol-gel to improve flame-retardant properties. They reported that the LOI value of the cotton fabric, which was 18.4% in the untreated fabric, increased up to 32.5% in the cationized fabrics [20]. It was observed a decrease of up to 6% in LOI values after dry cleaning process. In another study, LOI values of the cotton fabrics increased to 27.1%, demonstrating good flame-retardant properties and passing the vertical burning test [22]. It was reported that the LOI value dropped to 23.8% and 22% after 5 and 30 wash cycles, respectively, yet the fabric still retained good charring properties.

A study of current research indicates that the application of various chemical modifications and sol-gel based processes to improve flame-retardant performance in cotton fabrics has significantly increased the LOI values, particularly for phosphorus- and silane-based systems. However, it has been determined that a comprehensive approach where the formation of the silanol network, guanidine-based functionalization and the active hydroxyl group density on the cellulose surface are simultaneously optimized is still limited. Furthermore, it was observed that surface functionalization strategies aimed at enhancing sol-gel network-cellulose interactions remain limited and the morphological and functional effects of network structures

formed through mechanical transfer methods have not been detailed. In this study, a sol-gel formulation was applied to form silanol network structures and functionalize the terminal groups with guanidine phosphate, phosphoric acid, urea and phytic acid with the aim of enhancing the flame resistance of cotton fabric. A pretreatment was performed on the cellulose to increase the number of hydroxyl terminal groups on the cotton fabric surface and improve bonding. This study aimed to investigate the integration of guanidine phosphate, phytic acid, urea and phosphoric acid into a silane-based sol-gel network on the pre-treated hydroxyl end groups and to investigate the effect of this on flame-retardant properties before and after washing procedure.

2. MATERIAL AND METHOD

2.1 Material

In this study, a 100% cotton, bleached plain-weave fabric with a weight of 130 g/m² was used. For pre-treatment, the fabric was treated with NaOH. Tetraethyl orthosilicate (TEOS), 3-glycidoxypentyl trimethoxy silane (GPTMS) and trimethylamine (TMA) were used as silane initiators in the sol-gel process. Guanidine phosphate, phosphoric acid, phytic acid and urea were applied as flame-retardant additives. Citric acid and sodium hypophosphite were added to strengthen cross-linking and the network structure. Ethanol and distilled water were used as solvents. In wash resistance tests, 0.5% (by weight) ECE Phosphate-Based Standard Detergent B was used.

2.2 Method

2.2.1 Alkaline pre-treatment of cotton fabric

Cotton fabric samples were subjected to an alkaline pre-treatment using a 20% (w/w) NaOH solution to increase the activity of the hydroxyl groups on the surface and enhance the reactivity of the cellulose chains. This treatment was carried out under boiling conditions at 200 rpm for one hour. During this process, the hydroxyl (-OH) groups in the cellulose macromolecules present in the alkaline environment interact with Na⁺ ions converting into the cellulose alcoholate (Cell-O- Na⁺) form [23, 24]. This reaction

leads to the weakening of hydrogen bonds both between and within cellulose chains, the partial opening of crystalline regions and the swelling of the fiber structure. As a result of treatment with NaOH, a rearrangement occurs in the cellulose I crystal structure, leading to the formation of a more reactive structure. The formation of cellulose alcoholates facilitates the creation of active sites on the fiber surface with higher nucleophilic character (Figure 1). It is expected that silanol groups (Si-OH), epoxy functional groups (GPTMS), and carboxylic acid derivatives (such as citric acid) will react more readily through these active centres, leading to the formation of covalent bonds. This will enable both stronger bonding of silane-based network structures to cellulose and improved stability of flame-retardant additives on the fabric surface. The alkaline pretreatment will also enhance coating uniformity and bonding efficiency by facilitating better diffusion of the sol-gel solution into the fiber due to fiber swelling.

2.2.2 Preparation of the Silane-Based Sol-Gel Solution

In the first stage of preparing the silane-based sol-gel solution, TEOS was hydrolysed by dissolving it homogeneously in a water:ethanol mixture prepared at the specified molar concentration. Phytic acid was then added to the system, and the pH of the solution was adjusted to pH 2 by adding phosphoric acid. The resulting mixture was stirred in a closed container at 60°C and 500 rpm for one hour to ensure the controlled hydrolysis of TEOS. This step was intended to generate the Si-OH groups necessary for the formation of flexible, three-dimensional silane network structures on the fabric surface (Table 1). In the second stage, while the hydrolysed solution obtained in the first step was continuously stirred using a magnetic stirrer, phytic acid, GPTMS, and TMA were sequentially added to the system in a controlled and slow manner. Subsequently, guanidine phosphate, citric acid, and sodium hypophosphite (SHP) were added, and the mixture was stirred for an additional 15 minutes at 60°C and 500 rpm in a closed system. Finally, a homogeneous and transparent sol-gel solution containing flame retardant (FR) additives was obtained upon the addition of urea. The sol-gel recipe adapted from previous study [4].

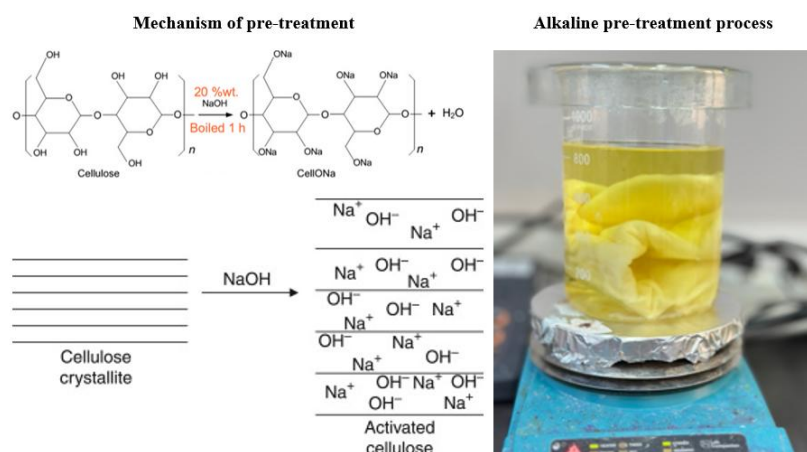


Figure 1: Mechanism and experimental procedure of the alkaline pretreatment applied to cotton fabrics

In this formulation, citric acid, SHP, and GPTMS were used as cross-linking agents to ensure that the flame-retardant additives are covalently bonded to the cellulose chains. The reason for choosing phytic acid is that, in addition to having a polyacid structure containing multiple phosphate groups, it can form strong interactions with both silanol networks and the cellulose surface. Citric acid, on the other hand, exhibits high reactivity due to its multiple carboxylic acid functional groups and supports cross-linking formation through esterification. In the study, guanidine phosphate, phosphoric acid, and urea which are rich in phosphorus and nitrogen were included in the formulation to produce flame-retardant textile surfaces, thereby aiming to support both the intense charring mechanism and the gas-phase flame-suppression effect.

2.2.3 Application of FR-modified sol-gel to cotton fabric

The application process was carried out on cotton fabric samples that had undergone an alkaline pretreatment using a pre-prepared TEOS-based FR-modified sol-gel solution. This process was based on the padding principle. The fabric sample was immersed in the sol-gel bath and then passed through rollers to remove excess solution (ensuring at least 97% sol-gel solution uptake). As a result, silanol groups derived from the hydrolysed TEOS precursor diffused into the fiber surface and internal structure. Following coating, the samples were subjected to a two-stage thermal treatment. In the first stage, drying was performed at 70°C for approximately 20 minutes to remove the solvent phase. In the second stage, a curing process was applied at 120°C for 10 minutes. During this curing process, condensation reactions occurred between the silanol groups, leading to the formation of Si-O-Si network structures. At the same time, the formation of Si-O-C covalent bonds between the silanol groups and the active -OH groups of cellulose were also stimulated. This process aimed to create a three-dimensional, hybrid organic-inorganic silane network on the fabric surface, thereby fixing the flame-retardant additives to the fiber structure. Thermal treatment parameters were carefully selected to ensure both sufficient condensation and the maintenance of the fabric's dimensional stability.

2.2.4. Characterization of Sol-gel coated fabrics

Changes in the chemical structure of the samples and the formation of functional groups were analysed using ATR-FTIR in the wavenumber range of 4000-650 cm⁻¹. Surface elemental composition and chemical bonding states were evaluated using X-ray photoelectron spectroscopy (XPS) using Si2p, P2p, C1s, O1s, and N1s peaks and surface elemental compositions were determined as atomic percentages. The thermal decomposition behaviour of the samples was investigated via thermogravimetric analysis (TGA) under an inert atmosphere, with a heating rate of 10°C/min from room temperature up to approximately 700°C and the maximum decomposition temperature (T_{max}), total mass loss, and residual ash content were calculated. Differential scanning calorimetry (DSC) measurements were performed simultaneously with TGA under a nitrogen atmosphere at a heating rate of 10

°C/min from room temperature to 700 °C. The DSC thermograms were used to evaluate the thermal transition behaviour and heat flow characteristics of the coated fabrics. Fiber surface morphology and coating homogeneity were examined using an optical microscope at 40×, 100× and 400× magnifications, and the structural changes resulting from the coating were visually evaluated.

2.2.5. LOI and Flame Spread Tests

The LOI (Limiting Oxygen Index) test was conducted in accordance with the ASTM D2863-77 standard. Prior to testing, the samples were conditioned under standard atmospheric conditions for at least 24 hours. The test specimens were cut to dimensions of 54x140 mm and the test was conducted with the N₂ concentration set to 68% for non-flammable specimens and 74% for flammable specimens. LOI values were calculated using the formula given in Equation 1. The determined LOI value was tested at least three times to verify the result.

$$\% \text{ LOI} = (100 \times \text{O}_2) / (\text{O}_2 + \text{N}_2) \quad (1)$$

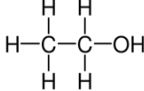
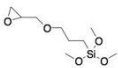
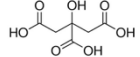
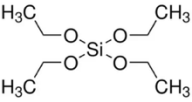
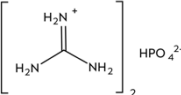
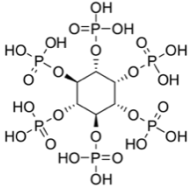
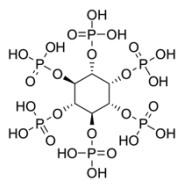
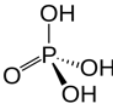
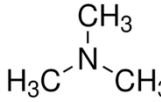
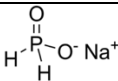
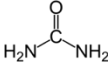
Where, “O₂” represents the measured oxygen concentration (cm³/s), and “N₂” represents the nitrogen concentration (cm³/s).

Additionally, a flame resistance test was conducted in accordance with ISO 15025:2017 to evaluate the flame behaviour of FR-modified sol-gel samples. Similar to the previous procedure, samples prepared in 200x160 mm dimensions were conditioned under standard atmospheric conditions for at least 24 hours. Subsequently, the test was conducted by securing the samples to the test apparatus and exposing the lower edge of the fabric to a burner flame from a specific distance, ensuring the flame contacted the surface for 10 seconds. After the flame was removed, the following results were recorded the duration of the after flame, the duration of afterglow, the length of the damage, and the type of damage (melting, dripping, perforation, or preservation of structural integrity).

2.2.6. Washing Procedure

A brief washing procedure was conducted to evaluate the wash durability of the cellulose layer coated onto the cotton fabric surface and the flame-retardant silane network formed via the sol-gel process. The washing conditions were established by adapting the washing parameters (detergent composition, liquor ratio, temperature, treatment time, and rinsing procedure) specified in the ISO 6330 standard to controlled laboratory conditions. The washing solution was prepared using ECE Phosphate Standard Detergent B at a concentration of 0.5 wt.%. The solution was stirred at 400 rpm until the temperature reached 40 °C. Coated and GPTMS-crosslinked fabric samples (20 × 20 cm) were washed at 40 °C for 15 min, followed by rinsing with distilled water and drying at room temperature prior to further characterization.

Table 1: Composition of the FR Sol-Gel solution and the materials used (modified from [4]).

Material	Molar concentration	Structural formula	Material	Molar concentration	Structural formula
First stage			Second stage		
Ethanol	5.28 M		GPTMS	0.204 M	
Distilled water	17.09 M		Citric acid	0.267 M	
TEOS	0.920 M		Guanidine Phosphate	0.542 M	
Phytic acid (50wt.% aqueous solution)	0.078 M		Phytic acid (%50 aqueous solution)	0.120 M	
Phosphoric Acid	0.450 M		TMA	0.329 M	
			SHP	0.291 M	
			Urea	0.513 M	

3. RESULTS AND DISCUSSION

The FTIR spectra revealed significantly chemical changes. It is clearly evident that significant chemical changes occurred on the fabric surface following the alkali pretreatment (PT) and sol-gel coating. In particular, the change in the broad -OH band in the 3300-3400 cm^{-1} range indicates that the hydrogen bonds between cellulose chains were rearranged because of the NaOH pretreatment, leading to the emergence of more reactive hydroxyl groups (Figure 2) [25]. Furthermore, high concentration alkali pretreatment has been shown to induce an intramolecular effect, leading to partial opening of the cellulose crystalline structure and reorganization of hydrogen bonds [12,25]. This facilitates more effective reaction of silanol and carboxylic acid groups with cellulose. The peak observed at approximately 1719 cm^{-1} in the pre-treated sol-gel sample corresponds to the C=O stretching vibration and confirms the presence of citric acid and phytic acid, as well as cross-link formation via esterification (Figure 2). It also indicates the formation of cross-links resulting from the esterification reaction between carboxylic acid groups and cellulose -OH groups. In other words, it demonstrates that citric acid ester bonds form covalent cross-links with cellulose. It has been reported that this method enhances wash durability by providing permanent bonding [9,11]. Thanks to its multiple

phosphate groups, phytic acid facilitates both hydrogen bonding and partial covalent interactions. It has also been reported that phytic acid strengthens the network structure through both hydrogen bonds and partial covalent interactions due to its multiple phosphate groups [11, 27, 28]. The slight decrease observed in this carbonyl band after washing indicates that some of the ester bonds may have hydrolysed but have not completely disappeared. The peak around 1269 cm^{-1} corresponds to the P=O stretching vibration, confirming that guanidine phosphate and phytic acid have been successfully incorporated into the system (Figure 2). It has been reported in the literature that phosphorus containing hybrid silica coatings exhibit flame-retardant effects on cotton surfaces and that similar P=O bands are observed [29, 30, 31]. The decrease in the intensity of this peak after washing suggests that a portion of the phosphorus-containing additives is bound via physical adsorption or weak interactions and is partially removed after washing. This is consistent with the decrease in the LOI value. The Si-O-Si band, clearly observed in the region around 1135 cm^{-1} , confirms the formation of a three-dimensional silane network structure as a result of the hydrolysis and condensation reactions of TEOS and GPTMS (Figure 2). It has been reported that the Si-O-Si network structure in silane-based sol-gel systems adheres to the textile surface through both physical and chemical bonding mechanisms [32, 33, 34, 35]. The

fact that this band is largely preserved after washing indicates that the silica network remains on the surface and that the system's fundamental structural framework is largely preserved. The P-O-C vibrational band around 1053 cm^{-1} suggests that phosphorus-containing compounds form ester-like bonds with cellulose chains (Figure 2). It is known that P-O-C bridges form in phosphorus-silica hybrid systems and contribute to flame-retardant performance [29, 30]. When these results are evaluated together,

it is understood that both silane-based covalent Si-O-Cell bonds and phosphorus-containing cross-linking structures form in the system, the flame-retardant efficacy, however, decreases due to the partial removal of phosphorus-containing salt-like compounds particularly after washing. Conversely, the persistence of the Si-O-Si network confirms that the sol-gel-based structural network remains stable on the surface and that the system acquires a hybrid inorganic-organic structure.

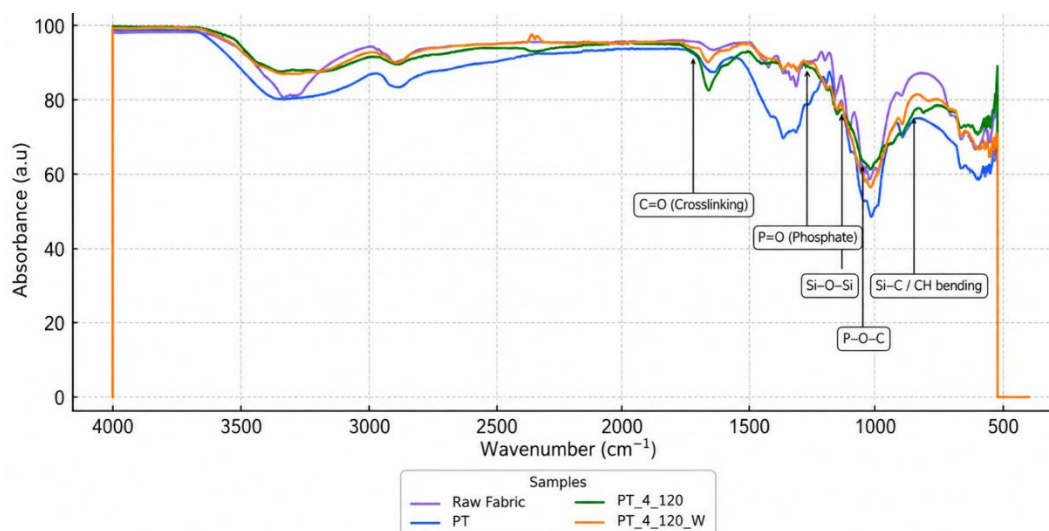


Figure 1: FTIR spectra of raw fabric, PT, PT-4-120, and PT-4-120W samples, showing the characteristic absorption bands associated with C=O crosslinking, P=O phosphate groups, Si-O-Si network formation, Si-C/CH bending, and P-O-C bonding

The XPS survey analysis together with the characteristic binding energies further confirmed the chemical states of the surface elements. The Si2p peak observed at approximately 102.9 eV is characteristic of siloxane (Si-O-Si) and Si-O-C bonds formed through the hydrolysis and condensation reactions of TEOS and GPTMS, confirming the successful formation of the hybrid silane network. The P2p peak located at approximately 133.5 eV corresponds to phosphate species (P-O and PO_4^{3-} groups), indicating the incorporation of phosphorus-containing flame-retardant additives such as phytic acid, phosphoric acid and guanidine phosphate into the coating. The C1s peak at approximately 284.6 eV is attributed mainly to C-C/C-H, C-O and O-C=O bonds originating from the cellulose backbone together with GPTMS derived organic groups. The O1s peak centred at approximately 532.3 eV is associated with Si-O, P-O and C-O bonds within the hybrid inorganic-organic network, while the N1s peak located at approximately 399.9 eV confirms the presence of nitrogen-containing species originating from guanidine phosphate and urea.

The XPS analysis results clearly demonstrate the changes in surface chemistry following sol-gel coating and the effect of the washing process. In agreement with the characteristic Si2p binding energy at approximately 102.9 eV, the significantly higher Si2p atomic percentage observed in the sol-gel-coated sample confirms the successful formation of the TEOS/GPTMS-derived

silane network on the fabric surface (Figure 3). The increase in the Si2p ratio after washing suggests that the silica network has become relatively more dominant accompanied by the partial removal of organic and phosphorus containing impurities from the surface. It has been clearly stated in the literature that the increase in the Si percentage after washing in silane-based sol-gel coatings indicates that the inorganic Si-O-Si network structure is persistent on the surface [11, 25]. This finding is consistent with the preservation of the Si-O-Si bands observed in FTIR after washing. The significant decrease in the P2p signal after washing indicates that a portion of the phosphorus containing compounds (guanidine phosphate and to a lesser extent phytic acid) have dissolved and removed from the surface (Figure 3). It has been noted that in phosphorus-containing salt-type flame retardants, when the covalent bonding is not sufficiently strong, these compounds may be removed from the surface during washing [13, 28, 39]. This finding can be directly linked to the decrease in the LOI value because phosphorus components are the primary active agents that promote charring during the condensation phase. The decrease in the P2p signal indicates that a portion of the phosphorus in the system is removed via physical adsorption or weak ionic interactions. The absence of a significant change in the C1s ratio also indicates that the coating and washing processes did not significantly alter the organic carbon content (Figure 3). This confirms that the fundamental carbon structure of the silane network and the cellulose skeleton remains unchanged. Likewise,

it has been found that the C1s signal remains relatively stable in hybrid sol-gel coatings [9, 13, 25, 28]. The increase in the O1s signal after washing can be attributed to the relative increase in hydroxyl groups (-OH) and oxygen containing inorganic structures that become re-released on the surface. The removal of phosphorus and amine-based additives relatively increases the oxygen content on the surface (Figure 3). Additionally, the oxygen-rich nature of the silica network structure supports the O1s

ratio. It has been reported that the high O1s contribution in silica-based coatings originates from Si-O-Si structures [25]. The decrease in the N1s signal after washing confirms that nitrogen-containing additives such as guanidine phosphate and urea were partially removed from the surface, which is consistent with the simultaneous reduction in the P2p signal and the observed deterioration in flame-retardant performance (Figure 3).

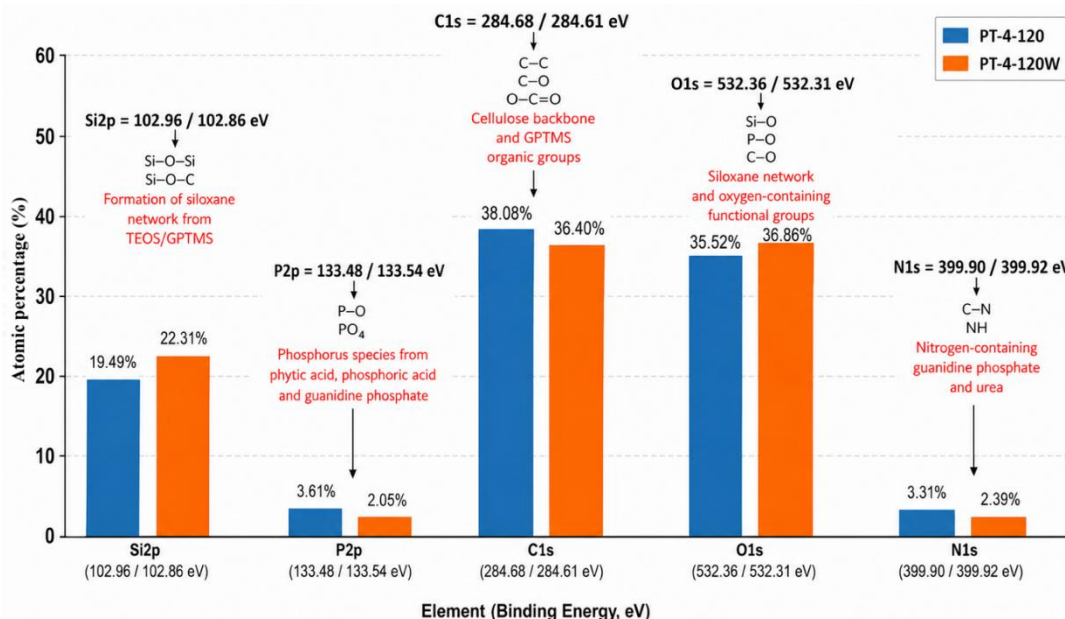


Figure 2: XPS surface elemental composition of PT-4-120 and PT-4-120W samples showing the atomic percentages together with the characteristic binding energies and chemical state assignments of Si2p, P2p, C1s, O1s and N1s peaks before and after washing.

The TGA and DSC results clearly demonstrate the effect of the sol-gel coating and the washing process on thermal behaviour. While the maximum decomposition temperature (T_{max}) was determined to be 265.7°C for the pre-treated fabric, this value increased to 298.8°C after sol-gel coating. This increase indicates that the silane-based inorganic network structure creates a thermal barrier effect and shifts decomposition to higher temperatures (Figure 4a). The fact that silica-based sol-gel coatings slow down heat transfer on the textile surface and increase the T_{max} value is consistent with the literature [18, 19, 25]. The increase in T_{max} to 319.9°C after washing suggests that the residual silica network on the surface has a more significant influence on thermal behaviour. This finding is also confirmed by the increase in the Si2p ratio observed in the XPS analysis (4b). When examining the main mass loss, a loss of 59.5% was observed in the pre-treated fabric, whereas this ratio decreased to 44.8% after sol-gel coating. This reduction indicates that phosphorus-containing compounds promote carbonization during the condensation phase, thereby limiting the formation of volatile combustible products. It is known that phosphorus containing systems accelerate the dehydration mechanism, leading to the formation of a charcoal layer earlier and more intensely [18, 36]. However, the increase in main mass loss to 62.3% after washing and the decrease in residual content from 8.9% to 5.7% suggest that phosphorus and nitrogen containing additives have partially moved

away from the surface. The fact that the residue amount in the sol-gel coated sample is lower than that in the pre-treated sample suggests that both condensation phase and gas phase mechanisms are operating simultaneously in the system. Nitrogen containing additives such as guanidine phosphate and urea exhibit a flame-retardant effect in the gas phase, while phytic acid and phosphoric acid promote charring in the condensation phase. However, the removal of some of these additives during washing has reduced the effectiveness of both mechanisms. The literature indicates that such a two-step mechanism is observed in phosphorus silica hybrid systems [11, 19]. Upon examining the DSC curves, it is observed that endothermic events in the sol-gel coated sample are distributed over a wider temperature range and occur in a more controlled manner (Figure 4a). This indicates that the silica network structure absorbs heat, thereby reducing the decomposition rate. The fact that the curve after washing approaches that of the pre-treated fabric again supports the findings that the removal of additives reduces thermal stability. In conclusion, the TGA-DSC results show that the sol-gel coating increases thermal stability and shifts decomposition to higher temperatures. However, it was demonstrated that additives containing phosphorus and nitrogen are removed by washing reducing carbonization efficiency and residue content. This is consistent with the decrease in the LOI value.

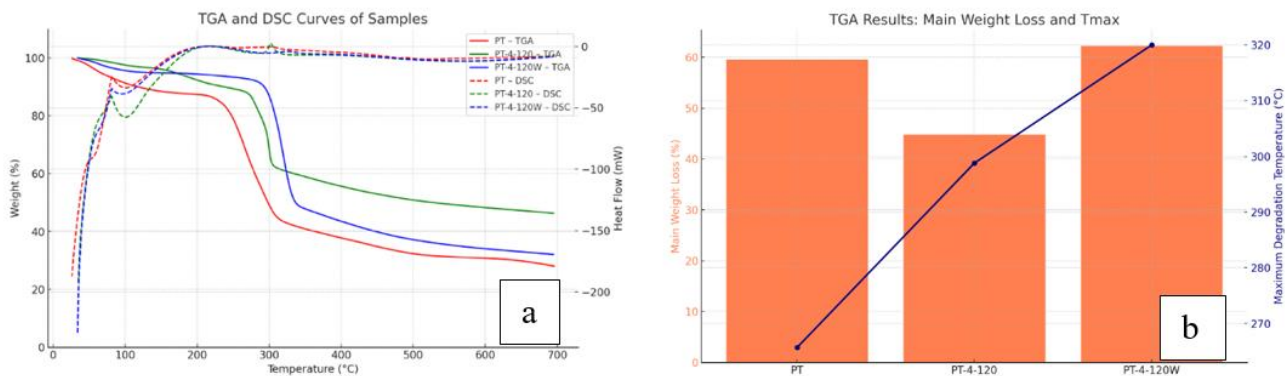


Figure 3: Thermal analysis of PT, PT-4-120 and PT-4-120W samples a) TGA and DSC curves b) main weight loss and maximum degradation temperature (Tmax) values.

The LOI results enabled an evaluation of the effect of the sol-gel coating on flame-retardant performance and the role of the washing process on system stability. The LOI value of the pretreated fabric was calculated as 32%, indicating that the cotton fabric exhibited relatively limited but improved flame-retardant behaviour (Figure 5a). It is known that cellulose-based fabrics typically have LOI values in the range of 18-21% and phosphorus additives are commonly used as a chemical to increase this value [36]. This LOI value of 32% indicates that the surface reactivity of the cotton fabric was enhanced through the NaOH pretreatment and that partial chemical modification improved the combustion behaviour to some extent.

The fact that the LOI value exceeded 52% after sol-gel coating indicates that a strong flame-retardant mechanism has been activated in the system (Figure 5b). LOI values above 50% indicate that the material cannot sustain combustion at atmospheric oxygen concentrations and point to high-performance flame-retardant systems. Since these values represent dangerous upper limits, the test could not be continued further. This LOI value can be explained by the fact that phosphorus-containing compounds promote charring during the condensation phase, while the silica network structure creates a physical barrier effect. It has been detailed in the literature that phosphorus silica hybrid systems limit oxygen and heat transfer by forming an intumescent like carbon layer on the textile surface [35]. Additionally, nitrogen containing compounds such as guanidine phosphate and urea can suppress flame spread by diluting flammable radicals in the gas phase [9, 11, 13]. Visually, it is observed that the surface of the sol-gel-coated sample largely retains its integrity and forms a homogeneous carbonization layer. In contrast, the drop in the LOI value to 28% after washing indicates that a significant portion of the flame-retardant additives has been removed from the system (Figure 5c). The 28% LOI value demonstrated even lower performance compared to the pretreated value (LOI: 32%). This can be explained by the dissolution and removal of salt like compounds containing phosphorus and nitrogen (guanidine phosphate and urea) during washing. The decrease in P2p and N1s signals in XPS analysis and the reduction

in the intensity of the P=O band in FTIR also support this result. Although the silica network structure remains on the surface after washing, it is understood that the Si-O-Si network alone cannot provide a strong chemical flame-retardant mechanism and that the primary effect stems from the phosphorus and nitrogen components. In conclusion, the LOI results indicate that the system exhibits a two-step mechanism. Firstly, the presence of phosphorus induced charring during the condensation phase and second the silica network providing a barrier effect. However, the insufficient formation of covalent bonds for the additives limits the washing performance. Therefore, the next study will focus on binding phosphorus and nitrogen containing compounds to the silane network or fiber structure through stronger covalent bonds.

The results of the flame spread test provided insight into the flame spread behaviour of the sol-gel coating. In the pre-treated PT sample, an after-flame duration of 11 seconds and a burn length of 6 cm were observed and perforation occurred (Figure 6). This indicates that the material continues to burn for a period after the flame source is removed and fails to form a sufficient protective carbon layer during the condensation phase. It has been reported that phosphorus-free systems in cellulose-based textiles generally exhibit this type of burning behaviour [13, 36]. In the sol-gel coated PT-4-120 sample, however, the flame was extinguished immediately upon removal, resulting in an after-flame duration of 0 seconds. The damage length of 4 cm and the preservation of structural stability indicate that an effective char formation mechanism was activated in the system. Liu et al. [35] and Alongi and Malucelli [37] reported that phosphorus-containing treatments accelerate charring, forming a protective carbon barrier on the surface and limiting flame propagation. Additionally, Grancaric et al. [18] reported that the silica network structure creates a physical barrier effect that limits heat transfer. Visually, the formation of a homogeneous and compact char layer in the PT-4-120 sample supports this mechanism. The upper measurement limit of the instrument was reached; therefore, the exact LOI value could not be determined.

After washing, the after-flame duration of the PT-4-120W sample was recorded as 61 seconds and the burn length increased to 14

cm. This confirms that the flame-retardant effectiveness has significantly diminished. Although the after-glow duration remaining at zero suggests that the gas phase mechanism continues to some extent, the long after-flame duration has served as significant evidence indicating that the active additives containing phosphorus and nitrogen have been largely removed. As previously stated, this finding was confirmed by the decrease in P2p and N1s signals in XPS analysis and the weakening of the P=O band in FTIR. Consequently, consistent with the literature, it was concluded that the stability of the salt-like phosphorus-

containing additives could not be maintained after washing [13, 19, 28, 39]. In particular, the increase in damage length despite the preservation of structural stability in the PT-4-120W sample indicates that the silica network remains physically intact in the system, but the chemical flame-retardant efficacy has weakened. As a result, it was observed that the sol-gel coating provided a high-performance, self-extinguishing structure prior to washing but possessed limited wash durability and performance due to insufficient covalent bonding of the additives.

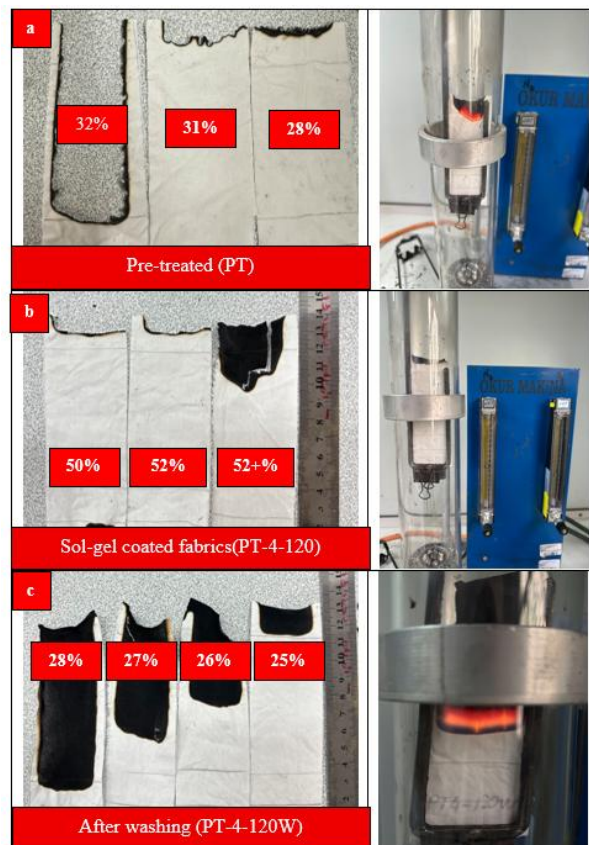


Figure 4: According to ISO 15025 limited flame spread test results of cotton fabrics a) NaOH pretreated cotton fabric b) nitrogen-phosphorus-silica hybrid sol-gel-coated fabric before washing and c) nitrogen phosphorus silica hybrid sol-gel coated fabric after washing.

Sample	After flame (s)	After glow (s)	Damage Length (cm)	Damage Type
PT	11	0	6	Charring Perforation
PT-4-120	0	0	4	Charring Structural stability
PT4-120W	61	0	14	Charring Shrinking Structural stability

Figure 5: Flame spread behaviour and results of sol-gel-coated fabric a) Cotton fabric pretreated with NaOH (PT) b) Fabric coated with a nitrogen-phosphorus-silica hybrid sol-gel before washing (PT4-120-W) c) Fabric coated with a nitrogen-phosphorus-silica hybrid sol-gel after washing (PT-4-120W)

To demonstrate the effect of the sol-gel coating on fiber surface morphology, optical microscope images are presented in Figure 7 (40x, 100x and 400x). It was observed that the fiber surfaces of the pretreated fabric (PT) had a relatively smooth and distinct cotton fiber structure. The alkaline pre-treatment caused swelling in the cellulose fibers and made the microfibrils on the surface more prominent [13,38]. This indicates that the NaOH treatment activated the fiber surface, making hydroxyl groups accessible and increasing surface roughness. A distinct and continuous coating layer was clearly observed on the fiber surfaces after sol-gel coating (PT-4-120). Furthermore, at 400x magnification, it was clearly seen that the fiber surfaces were coated with a thicker and more homogeneous layer and a film-like structure had formed on the surface when compared to the pre-treated sample. This indicates that the Si-O-Si network structure formed because of the TEOS and GPTMS hydrolysis-condensation reactions successfully adhered to the fiber surface. This result is consistent with the literature indicating that sol-gel-based silica coatings form a thin yet continuous inorganic film on textile fibers [18, 25].

Furthermore, this result supports the increase in T_{max} observed in the TGA results and the zero after-flame duration in the flame spread test. Comparison of the images obtained after washing (PT-4-120W) showed that it is observed that the amount of coating on the fiber surface has decreased and the surface has partially become smoother again. At 400x magnification, it is notable that the coating continuity is disrupted and in some areas, the coating thins out, creating an appearance similar to the pre-treated sample. This confirms that a portion of the phosphorus and nitrogen containing additives was removed during washing leaving only the more durable silica network structure on the surface. These images also support the other test results. When evaluated comprehensively the results indicate that the sol-gel system forms a homogeneous coating on the fiber surface, however, due to insufficient covalent bonding of the additives the wash resistance is limited. The optical microscopy observations are also consistent with the XPS results, which showed the persistence of the siloxane network together with the partial loss of phosphorus- and nitrogen-containing species after washing.

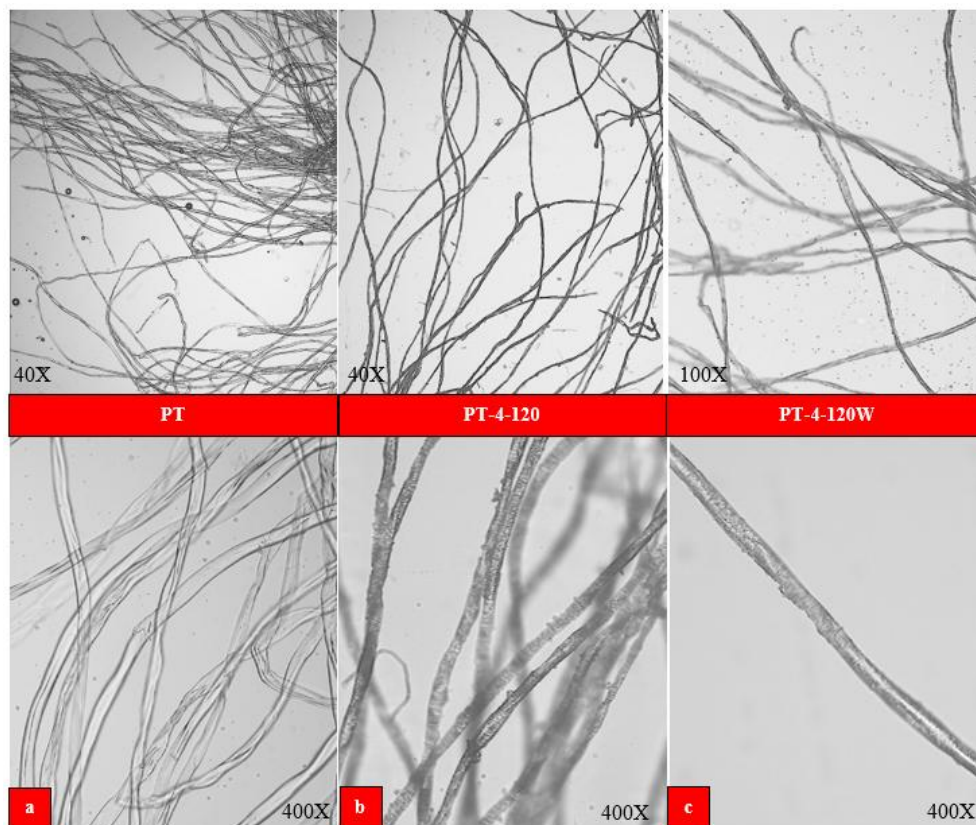


Figure 6: Surface images of the fabric samples and optical microscope images of the fibers a) Cotton fabric pre-treated with NaOH (PT) b) Fabric coated with a nitrogen phosphorus silica hybrid sol-gel before washing (PT-4-120) c) Fabric coated with a nitrogen-phosphorus-silica hybrid sol-gel after washing (PT-4-120W)

4. CONCLUSION

In this study, a silane-phosphorus-nitrogen based hybrid sol-gel system was successfully applied to alkali-pretreated cotton fabrics to improve their flame-retardant performance. FTIR and XPS analyses confirmed the formation of a stable three-dimensional Si-

O-Si network that remained on the fiber surface after washing, demonstrating the durable attachment of the silane-based structure. In contrast, the phosphorus- and nitrogen-containing flame-retardant components decreased markedly after washing, indicating that these additives were mainly retained through weak

physical or non-covalent interactions. Thermal analyses and flammability tests demonstrated that the sol-gel treatment significantly improved the thermal stability and flame-retardant performance of cotton fabrics before washing. However, the considerable reduction in flame-retardant performance after washing revealed that the long-term effectiveness of the system depends primarily on the permanent fixation of the phosphorus- and nitrogen-containing additives rather than on the siloxane network alone. The results demonstrate that the silane network provides a durable structural framework, whereas the flame-retardant performance is governed by the retention of phosphorus- and nitrogen-containing species. Therefore, the main contribution of this study is the demonstration that durable flame-retardant performance requires both an effective Si-P-N formulation and the covalent integration of the active flame-retardant components into the hybrid sol-gel network and the cellulose structure. Future studies will focus on developing reactive silane systems and multifunctional crosslinking strategies to improve the wash durability of phosphorus- and nitrogen-based flame-retardant additives.

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