

Permanent Flame Retardant Finishing of Textiles by the Photochemical Immobilization of Polyphosphazenes

Opwis K.^{1,*}, Mayer-Gall T.^{1,2}, Gutmann J.S.^{1,2}

¹ *Deutsches Textilforschungszentrum Nord-West gGmbH, Adlerstr. 1, Krefeld, Germany*

² *University Duisburg-Essen, Universitätsstr. 5, D-45117 Essen, Germany*

*Corresponding author's email: opwis@dtmw.de

ABSTRACT

UV-based grafting processes are appropriate tools to improve the surface properties of textile materials without changing the bulk. Based on our previous investigations on the photochemical immobilization of vinyl phosphonic acid, here, a new photochemical method for a permanent flame retardant finishing of textiles is described using allyl-modified linear polyphosphazenes and derivatives. Exemplarily, we show results on the flame-retardant finishing of cotton and cotton/PET blends with allyl polyphosphazene. We used the terminal allyl group for the photo-induced coupling of allyl polyphosphazene on textile substrates. Using our UV technology 20 to 40 weight percent of the functionalized polyphosphazenes can be fixed covalently to different textile substrates. We observed a slight decrease of the fixed polyphosphazene amount after the first washing cycle indicating the removal of non-bonded molecules. After this initial washing step the add-on is stable. Even after six laundering cycles the modified material withstands various standardized flammability tests. In summary, photochemical treatments allow the permanent surface modification of natural and synthetic fibers by irradiating with UV light in the presence of reactive media. We have successfully demonstrated that these procedures are appropriate for the fixation of flame retardants as well. Polyphosphazene modified textiles show high levels of flame retardant performance even after several textile laundering cycles.

KEYWORDS: Textiles, cotton, polyester, polyphosphazenes, flame retardant finishing.

INTRODUCTION

Textiles made of natural and synthetic polymers such as cotton (CO), polyester (PET) or polyamide (PA) are omnipresent in our day-to-day life. Besides apparel, typical in-door applications are curtains, carpets, bedding or upholstered furniture. Because of their high flammability, these materials represent a potential hazard for goods and life [1]. To achieve flame retardant textiles, the polymers are usually blended or finished with inorganic salts (e.g. nontoxic aluminum or magnesium hydroxide), organohalogens (e.g. chloroparaffins, bromobiphenylether and bromobisphenols) or formaldehyde-based flame retardants [1-4]. Because of their high toxicity the political pressure is growing steadily to replace halogen- and formaldehyde-based flame retardants [5, 6]. Due to the fact that conventional organohalogen-based flame retardants are getting banned more and more, several halogen-free substitutes have been developed, e.g., polyphosphates, organic phosphates or nitrogen compounds [7]. In this context nitrogen and phosphorus-containing chemicals are especially interesting, because of their P-N synergistic effect in flame retardant applications. However, their low stability with regard to washing and mechanical abrasion is limiting their applicability [8, 9]. Furthermore, an increasing amount of organo-phosphorus derivatives from flame retardants are found in the environment and even in human tissue. Some of these substances have a potential hormone like effect. Thus, alternative products that combine safety, high flame retardant properties and the possibility to fix them permanently to the textile

Proceedings of the Ninth International Seminar on Fire and Explosion Hazards (ISFEH9), pp. 981-990

Edited by Snegirev A., Liu N.A., Tamanini F., Bradley D., Molkov V., and Chaumeix N.

Published by Saint-Petersburg Polytechnic University Press

ISBN: 978-5-7422-6498-9 DOI: 10.18720/spbpu/2/k19-105

matrix are still desirable. One new approach to achieve flame retardant textiles is the use of layer-by-layer coatings, e.g., the combination of cationic polyelectrolytes such as polyallylamine, chitosan or polyethylenimine with anionic nano-clays, polyphosphates or DNA. Other strategies are based on sol-gel chemistry, carbon nanotubes, polycarboxylic acid, casein coating and photo- or plasma-grafting. More information on textile flame retardants are given in different reviews [10, 11] and books [2, 6-8].

Now, we have identified polyphosphazenes (PPZ) as another promising group of halogen-free flame retardant materials for textile applications. Polyphosphazenes can be divided into different polymer types: linear polyphosphazenes and polymers with cyclophosphazene units (back bone or side chain) [12]. These materials exhibit high limiting oxygen indices [13, 14] and improve the flame retardant properties of polymer blends significantly [14]. Technically, polyphosphazenes are used, e.g. in hydrocarbon insoluble O-rings, biomedical applications, as bio-inert or bio-compatible coatings or in fuel cell membranes. A small number of textile finishings based on polyphosphazenes are already described. Shukul and Arya showed that poly(fluorophosphazene) in combination with organo-bromine compounds improve the flame retardant properties of PET, while it is still unclear if the effect depends on the bromine-containing compounds or the polyphosphazene [15]. Other textile application for polyphosphazenes as finishing agents, textile polymer blending or in a polyurea coating are described in patents. Even fully inorganic polyphosphazenes such as (poly)aminophosphazene, phospham, phosphorus oxynitride and cyclophosphazenes have been used as flame retardants. While these examples demonstrating the general usefulness of polyphosphazenes as flame retardants, no commercial textile PPZ-based finishing is available. The main reasons for this are the lack of polyphosphazenes with appropriate anchor groups for the durable fixation on the fiber surface and suitable process technologies. Because of our experience in the field of photo-initiated reactions for the surface functionalization of textile substrates [16-19], our goal was to develop a flame retardant linear polyphosphazene with sufficient side-chain functionalities, that allow photochemical covalent bonding to typical textile materials, e.g. cotton and cotton/polyester blends.

Generally, polyphosphazenes can be synthesized by different synthetic routes [20]. The most common route is the high temperature ring opening polymerization of the cyclic trimer hexachlorophosphazene in a sealed glass tube developed by Allcock et al. A solvent-based synthesis was developed by the group of Magill [21] that produces polymers with up to 15,000 monomer units. The substitution of the chlorine atoms by, e.g., alkoxy, phenoxy, amino, fluoroalkoxy groups or even mixtures of them results in chemically and thermally stable species [13, 20]. Due to the huge variety of possible side-chain functionalities, the properties of polyphosphazene derivatives can be varied easily, e.g., from water-soluble to highly hydrophobic polymers [22].

EXPERIMENTAL

Textiles and chemicals

Table 1 summarizes the used textiles. Hexachlorotriphosphazene was obtained from Eurolabs Limited (United Kingdom) and allyl alcohol ($\geq 99\%$) from Merck (Germany). Sulfamic acid ($\geq 99.3\%$), calcium sulfate ($\text{CaSO}_4 \times 2 \text{H}_2\text{O}$, $\geq 98\%$) and tetrahydrofuran (THF $\geq 99.9\%$) were obtained from Carl Roth (Germany). 1,2,4-trichlorobenzene ($\geq 99\%$), sodium hydride (55-65%, moistened with oil) and acetylacetone ($\geq 99\%$) were obtained from Sigma-Aldrich (USA).

Instrumentation

Table 2 summarizes the used instruments.

Table 1. Textiles used

Textile	Composition [%]	Textile construction	Mass per unit area [g/m ²]	Supplier
CO white	100	twill 3/1	230	CHT R. Beitlich GmbH (Germany)
CO/PET orange	50/50	warp satin 4/1	340	Huntsman Textile Effects GmbH (Germany)
CO/PET camouflage	50/50	twill 2/1 core PET/shell CO	170	Bluecher GmbH (Germany)

Table 2. Instruments used

Instrument	Analytical method/method/remarks	Supplier
DSC Q20	differential scanning calorimetry (DSC), under 50 mL/min N ₂ , heating rate 10 K/min	TA Instruments (USA)
Bruker DMX300	NMR spectroscopy, ¹ H, ¹³ C, ³¹ P	Bruker (USA)
SEM S-3400 N II	Scanning electron microscopy (SEM)	Hitachi High-Technologies Europe
X-Max 50 mm ² SDD Detector	Energy disperse x-ray (EDX)	Oxford Instruments (UK)
HPV-E2, H emitter, Type 100 - 200	Ultraviolet A (UVA) print system lamp with dichroitic reflector for IR reduction, power 200 W/cm	Hoenle UV Technology (Germany)
linitester	Washing test	Atlas Material Testing Technology (Germany)
Nu-Martindale	Abrasion test	James H. Heal & Co. (UK)
Varian 720-ES spectrometer	Inductively coupled plasma optical emission spectra (ICP/OES)	Varian (Germany)
MarsXpress instrument	Microwave digestion	CEM (Germany)

Synthesis and characterization of allyl-oxy-polyphosphazene (PPZ)

Freshly sublimated hexachlorotriphosphazene (40 g), sulfamic acid (170 mg) and CaSO₄ x 2 H₂O (150 mg) were dissolved in 32 mL 1,2,4-trichlorobenzene under a nitrogen atmosphere and heated to 210 °C for 45-60 min. At the end of the reaction, a strong increase of the viscosity can be observed. The chloropolyphosphazene was precipitated by the addition of dry petroleum ether and the solids were washed twice with petroleum ether. The obtained polymer was dissolved in 100 mL THF. The concentration of the solution was determined by evaporating an aliquot and weighting of the residue. Afterwards, a freshly prepared sodium allyl alcoholate solution (4 eq. allyl alcohol with 1.25 eq. NaH in 50 ml THF) was added. The reaction mixture was rigorously stirred for 4 h at room temperature (RT), then refluxed for 6 h. The PPZ was precipitated by the addition of water. ¹H NMR (300 MHz, THF-d₈): δ 5.93 (ddt, J = 17.2, 10.4, 5.1 Hz, 1H), 5.29 (dd, J = 17.2, 1.8 Hz, 1H), 5.05 (dd, J = 10.4, 1.7 Hz, 1H), 4.48 (d, J = 5.5 Hz, 2H). ¹³C{¹H} NMR (75 MHz, THF-d₈) δ 135.8, 116.0, 30.7. ³¹P NMR (122 MHz, THF-d₈): δ -7.71. IR (ATR): 802 (P-O-C), 864, 923, 991, 1024 (P-N-backbone), 1101 (P-O-R), 1232 (P=N-backbone), 1423 (P-O-C), 1458 and 1647 (C=C), 2854 (C-H, sp³), 2924 (C-H, sp³), 3016 (C-H, sp²), 3076 (C-H, sp²) cm⁻¹. DSC (10 K/min, N₂ (50 mL/min)): T_G 180 °C, T_{Decomp} 282 °C.

Fabric UV treatment and characterization of the fixed PPZ

PPZ was dissolved in acetylacetone (25 wt%). The fabrics were wetted with 1 mL/g textile of the PPZ solution. The fabrics were irradiated single-sided for 10 min under an argon atmosphere. The distance between the light source and the sample was 20 cm. Subsequently, each sample was washed once in a textile linitester to remove non-bonded PPZ, afterwards dried at RT and weighed. In order to determine the phosphor content of the textiles quantitatively, 0.4 g were digested with 8.0 mL HNO₃ (65%) in a microwave digester at 180 °C. After digestion, the samples were diluted to 25 mL with water and measured by ICP-OES. The error of the phosphorus determination is less than 5%.

Washing resistance and abrasion test

In order to evaluate the washing fastness of the modified textiles, the materials were washed up to six times in a linitester according to EN ISO 105-C06 (liquor volume 150 ml, liquor ratio 1:80, ECE detergent 4.0 g/l, 30 min, 40 °C). The samples were then dried at room temperature and weighed. To investigate the fastness against mechanical stress, the modified textiles were subjected to 5,000, 10,000 or 50,000 abrasion cycles with a pressure of 9 kPa in a Martindale apparatus (abrasion test). Afterwards the samples were weighted. For the test an inverted Martindale setup has been used to get samples of at least 5 cm × 10 cm for a flammability test. The sample size was 140 mm diameter and the abrasive cloth (Martindale SM 25 (ISO 12947-1)) 40 mm diameter, with an abrasive exposed area of 110 mm diameter.

Evaluation of the flame retarding properties

All flame retardant and LOI measurements were carried out after at least one washing cycle. The flame retardant properties were measured according to DIN EN ISO 15025 (protective clothing - protection against heat and flame - method of test for limited flame spread), with a reduced sample size of 5 cm × 10 cm and a Proxxon lighter (combustion gas butane). In addition, selected samples were tested externally by Staatliches Pruefamt fuer das Textilgewerbe - University of Applied Science Hof (Germany) according to DIN EN ISO 4589-2 (limiting oxygen index, LOI, 0.5% steps), DIN 75200, DIN EN ISO 15025 and EN ISO 11925-2.

RESULTS AND DISCUSSION

Synthesis of allyl-oxy-polyphosphazene (PPZ)

PPZ was successfully synthesized by ring-opening polymerization of cyclic hexachlorotriphosphazene and subsequent nucleophilic substitution of the chlorine atoms by allyl alcoholate as shown in Fig. 1. The material is well soluble in acetylacetone.

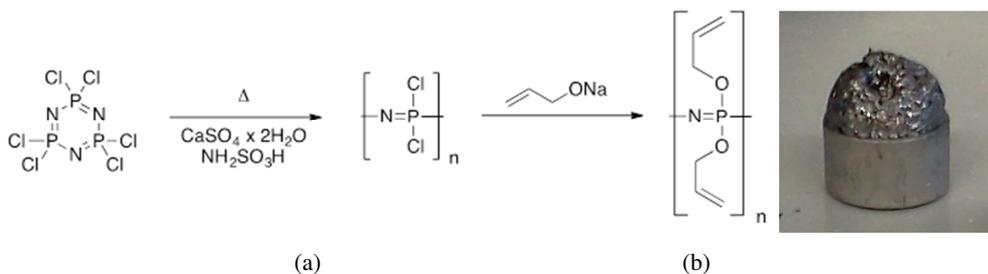


Fig. 1. Allyl-oxy-polyphosphazene. (a) Synthesis, (b) after heating to 600 °C.

The ^{31}P NMR spectrum exhibits one singlet at -7.61 ppm, which indicates the presence of a non-crosslinked polymer with a typical chemical shift for a polyphosphazene. In addition, the ^1H NMR spectrum exhibits the typical signals for an allyl group. This correlates with the IR bands at 1232 cm^{-1} (P=N band) and at 1024 cm^{-1} (P-N band), which are characteristic bands for the polymeric backbone. The band at 1101 cm^{-1} represents the signal for the P-O-C ether. To achieve flame retardant properties, the flame retardant should have a decomposition temperature lower than the textile. Using DSC, we found a sharp exothermic degradation peak at $282\text{ }^\circ\text{C}$. When heating PPZ up to $600\text{ }^\circ\text{C}$ the polymeric material shows an intumescent behavior. The foam-formation is shown in Fig. 1. In the case of fire the foam layer can act as a heat barrier.

Photochemical bonding of PPZ to textile materials

For our studies, we chose three different kinds of fabrics, one cotton fabric and two CO/PET blends (both 50/50 mixtures) used in common textile applications (e.g., clothing incl. protective clothing, car interior and furniture), where an improvement of the flame retardant properties is highly desired. The CO/PET blends differ in their fabric construction. The orange fabric is a warp satin woven material with one CO and one PET side. The second fabric (camouflage) consists of a PET core yarn with CO in the shell.

Beside phosphorus and nitrogen, which are responsible for the flame retardant properties of polyphosphazenes, our PPZ contains allyl groups, which are suitable for photo-induced grafting and cross-linking/homopolymerization. After wetting the textiles with a PPZ solution the materials were irradiated by a broadband-UV lamp under an argon atmosphere. Before characterization, the materials were washed once to remove non-bonded compounds. The PPZ-modified textiles were characterized by gravimetric measurements and SEM in combination with EDX for surface morphology and composition. Total phosphorus content was measured by ICP-OES after digestion. Table 3 summarizes the results. After the first washing step a high add-on of PPZ between 20 and 40 wt% was determined by gravimetry. An average weight loss after one washing step in the range of only 2–3% proves the general efficiency of our photo-induced immobilization method. The phosphorus content found by ICP-OES is close to the calculated P content obtained by gravimetry. The surface P determined by EDX is between 18.5 and 22.5 wt%, which correlates with the mass fraction of P in the PPZ. Therefore, the layer thickness of immobilized PPZ must be higher than the information depth of the used EDX technology - thus at least $1.0\text{ }\mu\text{m}$. The measured phosphorus contents (about 4 wt%) are higher than the recommended value for flame retardant properties ($> 1.5\text{ wt}\%$).

Table 3. Summary of calculated and measured values for the P content of PPZ modified textiles

Textile	Add-on [wt%]	P calculated from add-on [wt%]	P measured ^a [wt%]	P surface ^b [wt%]
CO white	40.8	5.7	4.9	18.8
CO/PET orange	22.3	3.6	3.1	18.5
CO/PET camouflage	32.8	4.8	4.2	22.7

^a Measured quantitatively by ICP-OES.

^b Measured qualitatively by EDX.

Accordingly, flame retardant properties for the PPZ finished textiles can be expected. SEM micrographs (Fig. 2) show a film deposition of PPZ on the textile's surface. As a consequence the corresponding ATR-FT-IR spectra of the textiles (Fig. 3) changes completely to the IR signals of pure PPZ; only the strong substrate signals like the carbonyl band of the PET part of the blends or the OH-signal of CO are weakly left. Taking the high add-on and the corresponding thickness of the

PPZ layer into account we assume that the PPZ is mainly bound by photo-induced homopolymerization between PPZ polymer chains yielding a stable film surrounding the fiber.

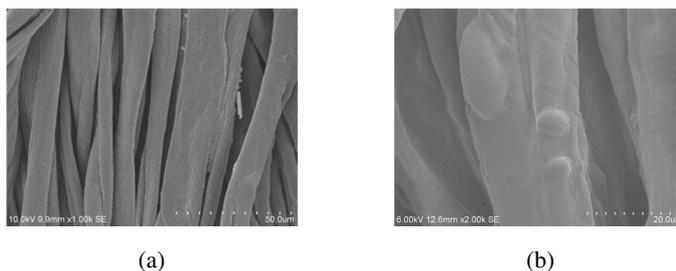


Fig. 2. SEM micrographs of cotton fibers before (a) and after PPZ finishing (b).

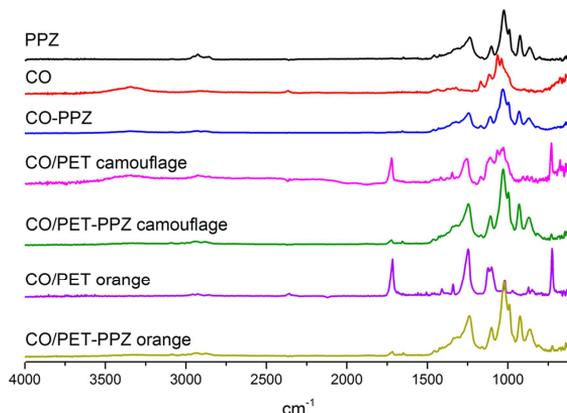


Fig. 3. ATR-IR-spectra of cotton/polyester blends and cotton fabrics before and after PPZ finishing in comparison to pure PPZ.

Flame retardant properties

In order to evaluate the flame retardant properties of the textiles, various methods were used. By measuring the limiting oxygen index (LOI) the minimum amount of oxygen in a mixture of oxygen and nitrogen is determined that is required to keep an ignited polymer burning. Normally, an increased LOI is accompanied by a lower ignitability and, therefore, improved flame retardant properties. For different textile applications different flammability testing standards exist. Here, we choose three methods. In the first test, the burning speed of a horizontal sample is measured, this test is described in DIN 75200 and is essential for textiles used in car interiors. DIN EN ISO 15025 represents a test for protective clothing. In addition, the test EN ISO 11925-2 was carried out to achieve the classification „normal flammability” according to DIN 4102-1 class B2 or EN ISO 13501-1 class E for building materials. Because of the vertical edge ignition applied in this test, the conditions are highly ambitious for textiles.

Table 4 summarizes the results of the various burning tests and the corresponding LOI measurements. Compared to the untreated materials, the LOI of the PPZ-finished textiles increases by 5-8%, which provides a first indication for a reduced flammability. During the horizontal burning test (DIN 75200), the untreated fabrics burn completely down with burn rates of 60-120 mm/min. In contrast, both modified CO/PET blends are self-extinguishing after the removal of the flame. In the case of modified CO, an acceleration of the burning was observed, however, the char yield is raised due to a significant carbonization of the material. By changing to a vertical flame test (DIN EN 15025), with a 10 s flame contact at the surface, the untreated materials burn down again

completely. In contrast, the PPZ-modified cotton and the CO/PET orange blend do not keep burning after the removal of the flame and no afterglowing was observed.

Table 4. Results of the LOI measurements and the standardized burning tests on PPZ-modified textiles

Textile	CO white	CO/PET orange	CO/PET camouflage
LOI			
Untreated	17.5 - 18.0	18.5 - 19.0	16.5 - 17.0
PPZ	23.0 - 23.5	26.5 - 27.0	24.0 - 24.5
DIN 75200			
Burning rate [mm/min]	142	0	0
Comment	carbonization	-	-
Test passed	no	yes	yes
Burning behavior of untreated material	burns down, 98 mm/min	burns down, 59 mm/min	burns down, 119 mm/min
DIN EN ISO 15025			
Flame reaches upper or lateral edge	no	no	yes
Afterflame time [s]	0	0	20
Afterglow beyond flame area	no	no	no
Afterglow [s]	0	0	0
Appearance of particles	no	no	no
Burning particles	no	no	no
Hole formation	yes	no	no
Comment	-	-	extinguishes almost
Test passed	yes	yes	no
Burning behavior of untreated material	burns down within 8 s	burns down within 22 s	burns down within 11 s
EN ISO 11925-2			
Reaching the test mark	7 s	5 s	4 s
Max. flame height	> 25 cm	> 25 cm	> 25 cm
Moment of max. flame height	12 s	12 s	10 s
Self-extinguished	0 s	0 s	5 s
Dripping	no	no	no
Test passed	no	no	no
burning behavior of untreated material	burns down, test mark 5 s	burns down, test mark 6 s	burns down, test mark 4 s

Finally, the three textile materials were subjected to a fire test with a 15 s vertical edge flame impingement test. All PPZ-modified textiles do not pass the test requirements, because the flame

reaches the upper test mark during impingement. However, a significant flame retardant behavior was observed. In contrast to the untreated materials, all PPZ-modified samples are self-extinguishing after the removal of the flame. Figure 4 illustrates the strong improvement of the flame retardant properties of PPZ-finished textiles compared to the blank substrates.

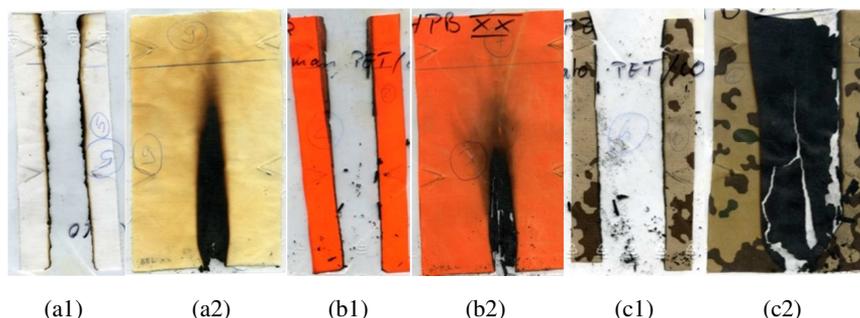


Fig. 4. Blank (1) and PPZ-finished (2) textiles after the 15 s vertical flame test (EN ISO 11925-2). The test mark of 150 mm is visible as blue line on the fabric. (a) CO white, (b) CO/PET orange, (c) CO/PET camouflage.

Investigations on the permanence of the polyphosphazene finishing towards washing and abrasion

To evaluate the stability (fastness) of the PPZ modification, samples were subjected to several washing cycles and rigorous abrasive tests. Afterwards, the flame retarding properties were investigated according to the modified DIN EN ISO 15025 conditions. Figure 5 summarizes the add-on of the PPZ-layer on the orange CO/PET textile after different washing cycles. After the first washing cycle, non-covalently bonded PPZ was removed, which leads to a significant weight loss of nearly 3%. After the following washing cycles, no further weight loss was observed. Moreover, in all flame retardant tests, the specimens are self-extinguishing accompanied by a formation of a carbonized layer. Although the flame reaches the upper edge after six laundering cycles, a strong permanence of the flame retardant effect against washing can be assigned.

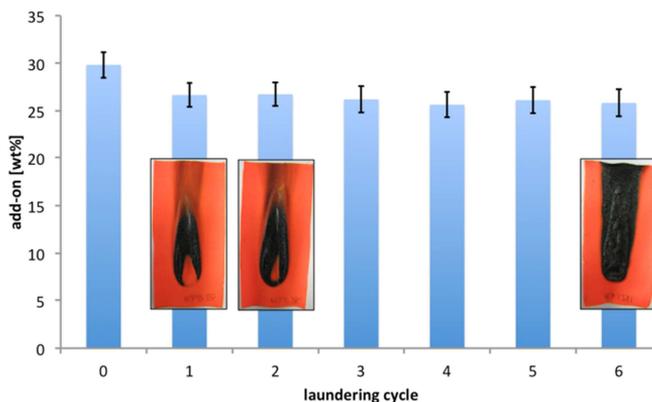


Fig. 5. Washing fastness of PPZ-modified CO/PET blend (PPZ-add-on and flammability behavior after six washing cycles).

In addition, the abrasion fastness of the PPZ-modified CO/PET (camouflage) blend was tested. After subjecting the textiles to 5,000, 10,000 or 50,000 abrasion cycles in a Martindale tester, the

flame retardant properties of the materials did not change significantly. All samples are self-extinguishing after the removal of the flame.

CONCLUSIONS

Polyphosphazenes belong to the class of inorganic polymers. Due to their phosphorus and nitrogen backbone, they exhibit excellent flame retardant properties. However, their industrial application in textile finishing was as yet limited by the lack of durable fixation strategies for a permanent flame retardant effect during the product's lifetime. We succeeded in bonding a non-combustible and strongly foam-forming polyphosphazene derivative by an UV-induced grafting process to cotton and cotton/polyester blends in high add-ons up to 40 wt%. SEM imaging proves the successful immobilization, and a total phosphorus content between 3-5 wt% was found. The polyphosphazene finishing leads to textiles with higher LOI. The textiles exhibit improved flame retardant properties and pass several standardized flammability tests such as standards for protective clothing and automotive textiles. The charred layer acts as a thermal isolating barrier layer and protects the underlying material. The permanence of the finishing was proven by washing and abrasion tests. The most essential results of PPZ-modified cotton and cotton/polyester blends are summarized in Table 5.

Table 5. Results of the LOI measurements and the standardized burning tests on PPZ-modified textiles (- = failed/no improvement, (+) = failed, but significant flame retardant effect, + = passed/strong improvement)

Test	CO white ^a	CO/PET orange ^a	CO/PET camouflage ^a
LOI ^b	+	+	+
DIN 75200	-	+	+
DIN EN ISO 15025	+	+	(+)
EN ISO 11925-2	(+)	(+)	(+)
Washing fastness ^c	+	+	+
Abrasion fastness ^c	+	+	+

^a - = failed/no improvement, (+) = failed, but significant flame retardant effect, + = passed/strong improvement.

^b after one laundering cycle

^c modified DIN EN ISO 15025 procedure.

In consideration of these excellent results, we state that functional polyphosphazenes could be a new class of permanent and halogen-free flame retardant agents for textile applications in the near future. However, competitive and commercial products for the textile industry have to be water-based (water-soluble or at least water-dispersible). Therefore, a future focus will be the synthesis of innovative polyphosphazenes, which combine functional side groups for a permanent attachment and hydrophilic side groups for an improved solubility in aqueous systems.

ACKNOWLEDGEMENT

The authors wish to acknowledge financial support by the Forschungskuratorium Textil e.V. for the project IGF 16780 N. The support was granted within the program Industrielle Gemeinschaftsforschung (IGF) from resources of the Bundesministerium für Wirtschaft und Energie (BMWi) via a supplementary contribution by the Arbeitsgemeinschaft Industrieller

Forschungsvereinigungen e.V. (AiF). We thank the Staatliches Pruefamt fuer das Textilgewerbe - Hof University of Applied Science (Muenchberg, Germany) for LOI and standardized flammability tests and DTNW Oeffentliche Pruefstelle GmbH for the ICP measurements.

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