Multifunctional silk fabrics by means of the plasma induced graft polymerization (PIGP) process

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ABSTRACT

An argon plasma induced graft polymerization (PIGP) process has been used to impart durable flame retardancy to silk fabrics. Phosphate and phosphoramidate monomers are known to be especially effective as flame retardants and have been used in this work for this application. Furthermore, water repellent finishing on silk fabrics could be achieved by means of SF_6 plasma treatment. The grafting and the polymerization processes taking place on the surface of the textile were followed by weighing measurements, IR(ATR) spectroscopy, XPS and SEM. The flammability of the treated fabrics was investigated by thermogravimetric analyses, heat of combustion (THC and HRR) and LOI measurements. The fastness properties have been evaluated as well.

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1. Introduction

Nowadays it is still very challenging to confer to textiles of natural origin wash resistant flame retardant properties [1]. The main issue lies in the fact that only a surface treatment can be applied and this has to be performed without altering the bulk (tensile, tear strengths, abrasion resistance, etc.) and the surface properties (permeability, soft handle, outward appearance, etc.). This implies that the finish should be a thin, homogeneous transparent coating. In case of woven textiles it should allow as well the breathability of the fabric. Moreover, the finish should not exhibit any toxicity before or during burning. All these constraints explain why the researchers are still in search of a flame retardant that can meet all these requirements. In addition, it should be highly effective, i.e. active at low concentrations, and versatile, i.e. usable on diverse textiles.

Flame retardancy of cotton fabrics has already been intensively investigated. However, relatively few papers relate attempts to confer flame resistant property to silk fabrics [2–4]. This is surprising because silk is widely used in interior design, home furnishing, curtains, beddings and clothes (especially pyjamas). Although silk exhibits a low natural flammability (compared to cotton fabrics, its LOI is 5 units higher on the average) due to its high nitrogen content (15–18%) it

still produces fuel for fire [5]. Therefore it is worth investigating new fire retardant finishes for silk fabric in order to render it more difficult to ignite or provide better self-extinguishing properties when removed from a flame.

Most of the treatments applied in order to confer a flame retardant behaviour to silk fabrics involved a pad-dry process of various formulations containing well-known organophosphorus compounds [6–10]. This family of compounds is the most commonly used as flame retardant due to its ability to promote char formation. The char residue acts as barrier to protect the fabric from attack of oxygen and radiant heat of fire and it can also reduce smoke emission [11–15].

Although flame retardation of the fabrics could be improved, these treatments exhibited poor wash-fastness properties. In order to increase their laundering durability, recently, Chaiwong et al. have tried to graft a non-durable phosphorus-based flame retardant agent (Pyrovatim® PBS) by means of an atmospheric Ar-plasma jet [16]. These treated fabrics exhibited a good resistance towards washing which could be attributed to the presence of covalently linked phosphorus compounds. However the SEM micrograph showed a very inhomogeneous stacking of large PBS particles (about 10 μm) mainly localized on the knot of the silk. This might affect dramatically the surface properties of the fabric. Phosphate derivatives such as DEMEP (diethyl 2-(methacryloyloxyethyl) phosphate), DMMEP, the di-methyl analogue were also successfully graft-polymerized onto silk fabrics with potassium persulfate in an acidic media. The treated silk fabric with DMMEP could still pass the flammability test after 30 cycles of laundering. But the yield of the grafting (about 3% of

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weight gain for a DMMEP concentration of 40% on the weight of the fabric) was very poor and is incompatible with industrial and environmental requirements [8,10].

Previously, we have successfully developed and applied in our laboratory the plasma induced graft polymerization (PIGP) process of various phosphorus monomers (phosphate, phosphonate and phosphoramidate derivatives) onto cotton fabrics in order to reduce the flammability of these materials. In these cases, thin homogeneous flame resistant coatings with good fastness properties have been obtained. Among these compounds, the phosphoramidate derivative DEAEPN (diethyl 2-(acryloyloxyethyl) phosphoramidate) gave the best results (i.e. highest LOI, highest grafting rate and best fastness properties) due to the presence of the nitrogen in the structure of the monomer and its "synergistic action" with the phosphorus [4]. Therefore it was interesting for us to investigate to which extent this process using the same monomer can be applied for silk fabrics. The grafting yield and the flame retardant behaviour will be compared with those obtained with the phosphate analogue, the diethyl 2-(acryloyloxyethyl) phosphate (DEAEP).

Furthermore, in order to respond to the customer needs, the textile industry seeks for more multifunctional fabrics combining multiple properties such as flame retardancy with hydrophilicity/hydrophobicity, antibacterial properties, UV-resistance, etc.

We have already demonstrated on cotton fabrics that the PIGP process is an excellent tool for that purpose [17]. Tetrafluoromethane (CF_4) plasma treatment has been applied on flame retarded cotton fabrics with various phosphoramidate monomers and we observed an increase of the Schmerber pressure which is an indication for surface fluorination. The fabrics which were originally absorbent became water-repellent. However, the water droplets did not roll on the surface, indicating a moderate decrease of the surface free energy of the fabrics. Besides CF_4 it is well known that plasmas containing fluorinated compounds such as hexafluoroethane (C_2F_6) [18], hexafluoropropylene (C_3F_6) [19] and sulphur hexafluoride (SF_6)[20,21] also enhance the hydrophobicity of fabrics. Especially, with sulphur hexafluoride (SF_6) as the fluorine source excellent results are obtained while undesired polymerization reactions in the plasma are suppressed. Therefore we applied a post-SF_6 plasma treatment onto the silk fabric in order to confer to the fire retarded samples an additional water repellent character.

In this paper we describe a two step protocol in order to produce multifunctional silk fabrics. In the first step we applied the PIGP process of two phosphorus containing monomers the diethylacryloyloxyethyl-phosphate (DEAEP) and -phosphoramidate (DEAEPN) onto the fabrics (Scheme 1). The surfaces of the untreated and most of the treated fabrics are rather hydrophilic. However, depending on their applications, fabrics with hydrophobic and flame retarded surfaces could be useful. Therefore, the fabrics with a flame retardant finish were exposed to a SF_6 plasma in a second step. The grafting and the polymerization processes taking place on the surface of the textile were followed by weighing measurements, IR (ATR) spectroscopy, XPS and SEM. Heat release rate (HRR) and LOI measurements allowed us to evaluate the flammability of the treated fabrics. The thermal decomposition behaviour was investigated by thermogravimetric

analyses. The water repellent properties were evaluated by measuring their Schmerber pressures (P_{Sch}). Moreover, because the durability of the treatment as well as the preservation of the bulk properties of the fabric was the main concern in this study, the fastness properties were measured as well.

2. Experimental

2.1. Materials and reagents

Degummed and bleached silk fabric (plain weave, 75.4 g/m²) was supplied by EMPA Test Materials Company, Zurich, Switzerland. The synthesis of the flame retardant monomers used in this study diethyl 2-(acryloyloxyethyl)phosphate DEAEP and diethyl 2-(acryloyloxyethyl) phosphoramidate DEAEPN has been previously described [4,22]. The cross linking agent EGDA (ethyleneglycoldimethacrylate) was purchased from Aldrich and used as received. The photoinitiator phenyl-bis(acyl)phosphanoxide (IRGACURE 819) was kindly supplied by BASF Swiss (former CIBA Specialty Chemicals, Switzerland). Solvents were obtained from the usual suppliers (FLUKA, BAKER and MERCK) and were purified prior to use, if necessary, by standard methods. Argon and SF_6 were provided by PANGAS. Argon was further purified with an MBraun 100HP gas purification system.

2.2. Low pressure plasma process

The microwave plasma was generated by an Europlasma DC 300PC system composed of three parts: (i) a microwave generator (2.46 GHz) with a tunable power ranging from 0 to 600 W, generating the argon glow discharge, (ii) the vacuum chamber (27 l) (aluminium based container) in which the process takes place and (iii) a pumping system composed of a primary pump (E2M28 PFPE, Edwards). The gas flow was regulated by unit mass flow controllers.

2.3. Graft-polymerization induced by Ar-plasma (step 1) and SF_6 plasma treatment (step 2)

Pieces (50 mm × 100 mm) of silk fabric were cut in the warp direction and kept under the standard conditions (humidity 65%, 20 ± 2 °C) for 24 h before the experiments.
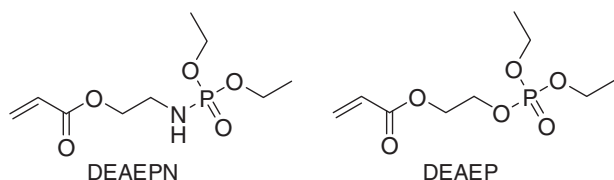
Step 1: The samples were weighed and then impregnated at room temperature with 0.7 ml of an ethanol solution containing 10 to 30% by weight of fabric (w.o.f.) of monomer, 10% by weight of monomer (w.o.m.) of cross-linking agent (EGDA) and 5% w.o.m. of Irgacure 819 as photoinitiator. They were padded with a glass roller in order to get a homogeneous spreading. After drying in air the fabrics were placed on a glass plate and exposed to a MW argon plasma treatment ($F_{Ar} = 125$ sccm; $P = 100$ W; $p = 500$ mT; $t = 20$ min). Then the samples were washed using a Soxhlet apparatus with ethanol (4 times) and water (1 time) and dried at room temperature. The dried samples were stored under standard conditions with a relative humidity of 65% and a temperature 20 ± 2 °C for at least 24 h before measurements.

Step 2: The flame retarded (FR) silk fabrics were then submitted under SF_6 plasma exposure ($F_{SF6} = 25$ sccm; $P = 100$ W; $p = 500$ mT; $t = 5$ min).

2.4. Analytical techniques and evaluation of the flame retardant effect and the water repellency of the fabrics

The degree of grafting was determined as follows:

Scheme 1. Diethyl 2-(acryloyloxyethyl) phosphoramidate (DEAEPN) and diethyl 2-(acryloyloxyethyl) phosphate (DEAEP).

$$\text{Degree of grafting } (\%) = \left(W_g - W_0 \right) / W_0 \times 100$$

where, W_0 and W_g are the weights of the fabric samples before and after grafting, respectively.

The phosphorus content of the treated fabrics was determined by UV-spectroscopy with the vanadomolybdophosphoric acid colorimetric method using an Uvikon 810. After perchloric acid–sulphuric acid digestion, carbon, hydrogen and nitrogen contents were determined using a LECO CHN-900.

Amino acid analysis was performed by using the UPLC Amino Acid Solution (Waters Corp., Milford, MA, USA). A small piece of approximately the same size for each sample was hydrolyzed in 6 N HCl at 110 °C for 24 h under argon. The dried hydrolysate was dissolved in 70 µl derivatisation buffer and 20 µl was derivatised (Accq-Tag Ultra, Waters Corp., Milford, MA, USA) according to the manufacturer's instructions. The relative amino acid content was calculated for each sample. Each experiment was performed twice and the results were averaged.

The attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) spectra were recorded on Nicolet 6700 FT-IR spectrometer in range 4000–400 cm^{-1}, the ATR technique was applied.

The chemical composition of the silk surface has been investigated using X-ray photoelectron spectroscopy (XPS). Measurements were carried out on an ADES 400 photoelectron spectrometer using Mg K$_\alpha$ radiation (1253.6 eV) and equipped with hemispherical electron energy analyzer.

The flammability of the untreated and treated fabrics was assessed by the Limiting Oxygen Index (LOI) method according to ASTM Standard Method D2863-76, using an oxygen index test apparatus from Fire Instrumentation Research Equipment LTD with a digital readout of oxygen concentration to ± 0.1%. The LOI value corresponds to the minimum concentration of oxygen in an oxygen/nitrogen mixture necessary to burn the sample during 3 min over a length of 80 mm. Thermogravimetric analysis (TGA) and derivative thermal gravimetry (DTG) were performed on a NETZSCH STA 409C instrument by using continuous nitrogen flow 10 °C/min and a heating flow rate 10 °C/min at the temperature from 30 to 700 °C. The sample weights were about 2–3 mg.

Pyrolysis Combustion Flow Calorimetry (PCFC) measurements were performed on a PCFC instrument (Fire Testing Technology Instrument). PCFC is able to measure the following flammability parameters for textile using milligram sample sizes: Heat release capacity (HRC), heat release rate (HRR), temperature at peak heat release rate (PHRR), total heat release (THR) and char yield. The silk fabrics (~5 mg) were heated from ambient temperature to 750 °C in nitrogen flowing at 80 cm^3/min at a linear heating rate of 1 °C/min. The gaseous pyrolysate mixture exiting the pyrolyser was mixed with a 20 cm^3/min stream of oxygen prior combustion in a furnace at 900 °C during 10 s. Each step was performed at least twice.

The surface morphology of the silk fabrics before and after grafting with monomer was observed by Scanning Electron Microscope (SEM), using a model JEOL JSM-6400. Silk fabrics were observed at 15 keV acceleration voltages. Photographs were taken with a TOSHIBA 3CCD COLOR CAMERA "IK-TU48P" fitted with a Leica microscope MZ6.

Owing to the roughness and irregularity of the textile surfaces, the commonly used contact angle measurements were not reliable for the investigation of the wettability of the treated fabrics. Therefore, it was evaluated by Schmerber tests, according to DIN 53886, using a Textest FX 3000 Water Impermeability II apparatus. The Schmerber value (P_{Sch}) recorded at the end of the test corresponds to the water pressure (mb) reached when water has penetrated through the fabric at three different places.

2.5. Fastness properties

The wash-fastness was tested according to the accelerated laundering method proposed by McSherry et al. [23]. The treated

samples were boiled for 4 h in a solution of 0.5% Na$_3$PO$_4$, 12 H$_2$O and 0.1% Triton X-100 at a liquor-to-goods-ratio of 40:1 and then dried at room temperature.

The tensile strength including elongation at break was measured by a Lloyd's tensile tester (Lloyd LR 5K) on standardized samples (5 × 15 cm^2; 25 ± 2 °C; 65% humidity). Three measurements were taken in warp direction and averaged afterwards.

The degree of whiteness was evaluated with the grey scale for the assessment of staining (BS 1006A03) (DIN 54001). It is measured by a comparison to a scale of five pairs of grey and white coloured plates in which each pair of plate indicates a different degree of contrast. The contrast intensity between the untreated and treated fabric is related to one of the standard pairs to yield the grey scale rating. On these scales, 5 indicate no yellowing and 1 a heavy colour change.

3. Results and discussion

3.1. Evidence of the grafting of polyDEAEPN and polyDEAEP onto silk fabrics by the PIGP process

The weight gain and the phosphorus content of the DEAEPN and DEAEP treated silk fabrics, at different monomer concentrations, after washing in solvents in which the monomer and the polymer are well soluble are listed in Table 1.

First of all, regardless the nature of the monomer, the grafting yield is over 50% in each experiment and increases almost linearly with the initial concentration of the monomer. This result can be compared with other pad-dry-cure processes described in the literature using analogous monomers. For instance, in the experiment reported by Guan and Chen [10], less than 5% of weight gain was obtained with an initial concentration of 40% (w.o.f.) of DMMEP. This result demonstrates the efficiency of the PIGP process which allows to reduce significantly the amount of chemicals. This is even more appreciable in the experiments with the phosphoramidate monomer. We explain this observation with the higher affinity of this monomer for the polar silk protein surface due to the interaction with the N–H bonds. We have already observed this behaviour with cotton fabrics where we could reduce considerably the amount of cross-linking agent [4].

The grafting of a phosphorus containing polymer by the PIGP process was evidenced by several techniques. Among them, the evaluation of the phosphorus content indicates a non-negligible amount of remaining phosphorus containing polymer, up to 2% by weight of the fabric, after washing (Table 1). XPS surveys exhibit the P$_{2s}$ and P$_{2p}$ components respectively at 189.0 and 130.6 eV (Fig. 6). Finally, the FT-IR spectra of the polyDEAEPN (curve a), the control silk fabric (curve b), and the treated silk fabrics with 20% (w.o.f.) of DEAEPN (curve c) and 20% (w.o.f.) of DEAEP (curve d) are presented in Fig. 1. The treated fabrics, after washing, show the characteristic absorption bands at 1250, 1150, 1024–1078 and 985 cm^{-1} corresponding to the P O, P–O–C and P–O stretching vibrations also seen in polyDEAEPN. FT-IR spectra have been recorded for treated

Table 1
Weight gain, measured phosphorus content before and after burning, LOI and char yield of the silk fabrics treated with DEAEPN and DEAEP at different monomer concentrations.

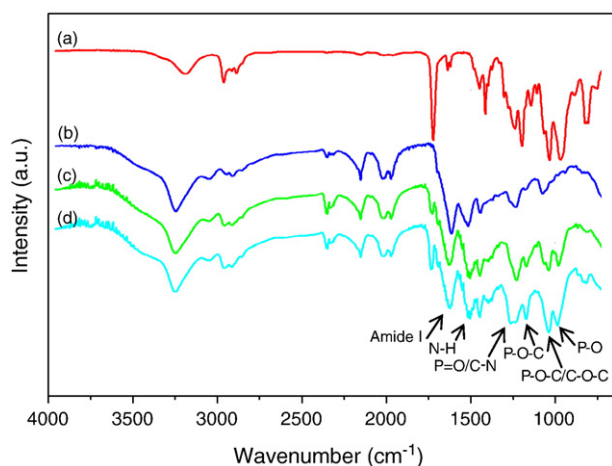| Sample	FR monomer % w.o.f.	Weight gain [%]	% P [%]	LOI [% ± 0.1]	Char yield [%]	%P of char [%]
Untreated silk	–	–	–	25.0	9.38	–
DEAEPN treated silk fabric	10	6.62	0.66	29.0	18.95	4.56
	20	11.22	1.38	30.5	29.98	5.21
	30	16.68	2.10	31.0	32.50	6.69
DEAEP treated silk fabric	10	5.37	0.63	28.0	16.10	2.47
	20	10.12	1.34	29.0	25.98	3.38
	30	13.47	1.69	30.0	31.74	6.54
	40	20.10	2.18	30.5	32.70	6.23

Fig. 1. The IR-ATR spectra: (a) polyDEAEPN; (b) untreated silk; (c) DEAEPN (20% w.o.f.) treated silk; and (d) DEAEP (20% w.o.f.) treated silk.

fabrics with 10% and 30% (w.o.f.) of the monomer and they show a similar pattern of the absorption bands as in the polymers. As expected, the intensities increase with increasing concentrations. Furthermore in all spectra of the treated samples, the most intense absorption bands of the silk fabric are still visible, notably the strong N–H vibration at 1506 cm^{-1} characteristic for the peptide bond of the silk protein. This indicates that the thickness of the deposited polymer is smaller than the thickness analysable either by XPS or FT-IR.

In order to determine whether the grafting of the polymer on the silk fabric occurred via reactions with some amino acid (AA), Amino Acid Analyses were performed on the treated silk fabrics (DEAEPN, 20% w.o.f) and compared to the untreated one. The results are shown in Table 2. As observed by other authors [8], the content of some amino acid decreases after the treatment which indicates their contribution in the grafting process. In our case, only the relative content of glycine which together with alanine constitutes more than 70% of the AA of this silk fabric decreases slightly (by about 2%). This observation indicates that a covalent grafting in the plasma process may occur via a radical reaction involving the activated glycine CH$_2$-groups. On the contrary, Guan and Chen [8] observed that DEMEP has been graft-polymerized using potassium persulfate as initiator in an acidic media, whereby mainly the AA containing polar side chains or –CH$_2$S–SCH$_2$-bonds (cystine) were affected.

Table 2
The contents of amino acid of untreated silk and DEAEPN (20% w.o.f.) treated silk fabric.

Amino acids	Untreated silk fabric [%]	DEAEPN treated silk fabric (20% w.o.f.) [%]
Histidine	0.29 ± 0.01	0.32 ± 0.01
Threonine	0.78 ± 0.01	0.90 ± 0.01
Serine	9.48 ± 0.06	10.22 ± 0.1
Glutamic acid	0.31 ± 0.0	0.32 ± 0.0
Glycine	53.71 ± 0.36	51.76 ± 0.07
Alanine	16.31 ± 0.31	15.48 ± 0.48
Valine	1.94 ± 0.01	1.92 ± 0.04
Methionine	0.12 ± 0.01	0.13 ± 0.01
Isoleucine	0.65 ± 0.0	0.65 ± 0.02
Leucine	0.53 ± 0.0	0.52 ± 0.01
Tyrosine	12.77 ± 0.50	14.34 ± 0.31
Phenylalanine	2.25 ± 0.10	2.62 ± 0.06
Lysine	0.03 ± 0.01	0.03 ± 0.01
Aspartic acid	0.37 ± 0.0	0.36 ± 0.02
Arginine	0.00	0.00
Proline	0.46 ± 0.01	0.43 ± 0.01

3.2. Flammability of the silk fabric samples

3.2.1. LOI of silk finished fabrics at different concentrations of monomers

The flammability of the samples has been investigated by taking LOI measurements which is a straightforward and reliable analysis to compare the behaviour of different polymers. The LOI, the amount of residual char and the phosphorus content before and after burning of the DEAEPN and DEAEP treated silk fabrics at different concentrations of the monomers (w.o.f.) are listed in Table 1. As can be seen, the indices measured for the untreated silk fabric (25) increase up to 6 units in the fabrics which were treated either by the phosphate or the phosphoramidate monomers. The flame retardant finished silk fabrics became easily self-extinguished materials with only 5% of grafted polymer (LOI >28). Interestingly, for an equal content of grafted phosphorus atom on the fabric, the oxygen indices measured for polyDEAEPN finished fabrics are higher (1 unit) than the values obtained with polyDEAEP. We attribute this result to the presence of the nitrogen in the phosphoramidate which contributes to reduce the flammability of the fabric. Furthermore, the amount of the residual char, rich in phosphorus, increases quite rapidly with the amount of grafted polymers.

The remaining char presents interesting features that can be seen in the SEM pictures displayed in Fig. 2. In each case unburned and burned fabrics are presented. Fig. 2b shows that an untreated silk fabric melts while burning and the structure of filaments of the unburned fabric (Fig. 2a) is completely lost. The SEM photographs of both treated silk fabrics either with 20% (w.o.f.) of DEAEPN (Fig. 2c) or DEAEP (Fig. 2e) exhibit no stacking of polymer between the fibres but a smooth entangling polymer film on the surfaces of the filaments. After burning, the structure of the treated fabrics can still be seen, but holes and channels are formed in place of fibroin filaments. Moreover, these pictures reveal two very different burning behaviours for the polymers. While the first one (Fig. 2d) coated with polyDEAEPN produces an intumescent-like layer above the molten silk, of which the thickness increases with the amount of grafted polymer (pictures not presented), the second one (Fig. 2f) presents a thin brittle covering.

All these results suggest the formation of a protective layer which insulates the fabric from the effect of the heat as major reason for decreasing the flammability of the fabric. From the characteristics of the remaining chars, DEAEPN seems to provide a more efficient insulating coating than DEAEP. The remaining char is composed by degraded silk and flame retardant polymer, as confirmed by its high content of phosphorus (% P/g fabric) which was determined by elemental analyses (Table 1).

3.2.2. Pyrolysis Combustion Flow Calorimetry (PCFC) analyses

Pyrolysis Combustion Flow Calorimetry (PCFC) analysis is frequently applied nowadays in order to assess the flammability of polymeric materials and it is now recognized to be an effective bench scale method [24,25]. The heat release rate has been found very effective to evaluate fire hazards. The heat release rate versus temperature for untreated (curve a) and DEAEPN (20% w.o.f.) and DEAEP (20% w.o.f.) treated silk fabrics, respectively (curve b) and (curve c) is presented in Fig. 3. The total heat release (THR) and the peak heat release rate (PHRR) obtained from Fig. 3 are listed in Table 3.

Immediately, it can be seen from Fig. 3 and Table 3 that PHRRs – which are the maximum speed at which the fire of the fabric can generate heat – of the treated silk fabrics are considerably lower than for the control fabric. Indeed, they reached 90 and 95 W/g for the DEAEPN and DEAEP treated fabrics respectively compared to 147 W/g for the untreated one. The same trend is reflected in the total heat release (THR) where a decrease of about 1.2 to 1.5 kJ/g is observed. The heat release capacity follows the same pattern. The char yield increases significantly for the treated samples with a neat advantage for polyDEAPN. All these data correlate with the LOI measurements
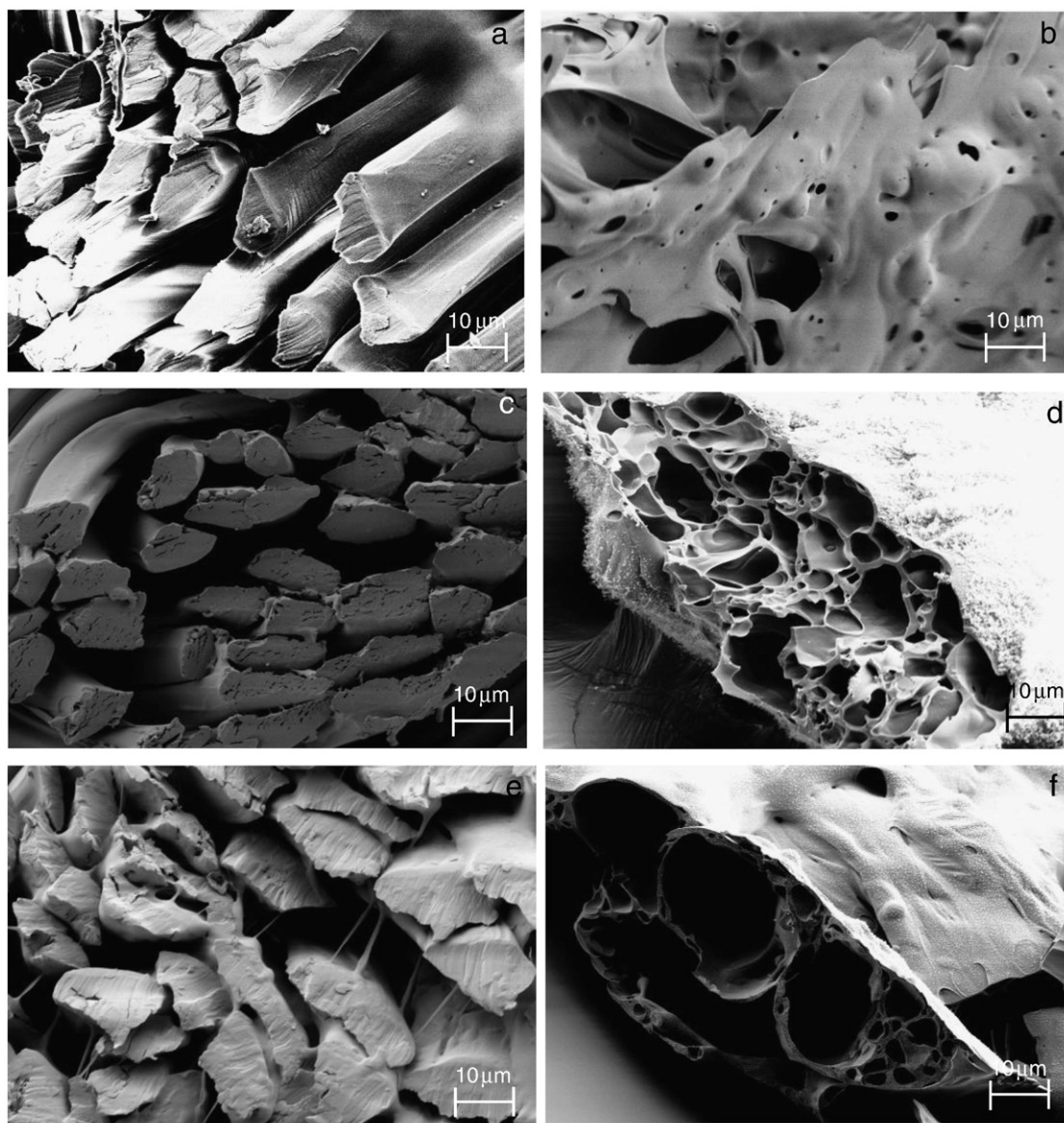
Fig. 2. SEM micrograph of: untreated silk unburned (a) and burned (b); DEAEPN (20% w.o.f.) treated silk (c) unburned and (d) burned; DEAEP (20% w.o.f.) treated silk (e) unburned and (f) burned.

and suggest as well a condensed-phase mechanism leading to the production of char rather than flammable products.

3.3. Thermal analysis

In order to have more insights into the flame resistance mechanism, thermogravimetric (TG) and derivative thermal gravimetry (DTG) analyses have been performed on the untreated and the treated silk fabrics with various concentrations (w.o.f.) of DEAEPN or DEAEP. The TG and DTG curves for treated fabrics with 20% (w.o.f.) of the monomers are presented in Fig. 4.

Although the pyrolysis mechanism of the silk fibre is still unknown, several authors have reported the decomposition behaviour of degummed silk fabrics of different origins. Our results are similar to those described in the literature [8].

Three main mass loss stages can be identified. The first one (4.1%, 30–214 °C), is attributed to desorption of the adsorbed moisture of the silk fabric. In the second stage (48.2%, 214–372 °C) the silk fabric decomposes into CO_2, H_2O and flammable substances. The last stage (20.1%, 372–700 °C) is assigned to the decomposition of the char of the silk fabric.

The decomposition of the finished silk fabrics with the flame retardant polymers follows the same pattern with almost the same onset of decomposition temperatures, with an additional mass loss stage (10.1%, 212–290 °C for finished silk fabrics with DEAEPN 20% w.o.f., 11.4%, 212–289 for finished silk fabrics with DEAEP, 20% w.o.f.), which corresponds to the degradation of the polymer. This is best visible in Fig. 4b which exhibits for the treated fabrics two peaks in the DTG curve while only one is seen for the untreated fabric. These observations can be explained by the fact that the grafted polymers, like the pure polymers, decompose at lower temperatures than the silk fabric. Their decomposition into a stable phosphorus containing residue is almost complete before the silk starts to decompose. This will provide an insulating layer which will delay the decomposition of the silk, as indicated by the slightly higher decomposition temperature found in the treated samples.
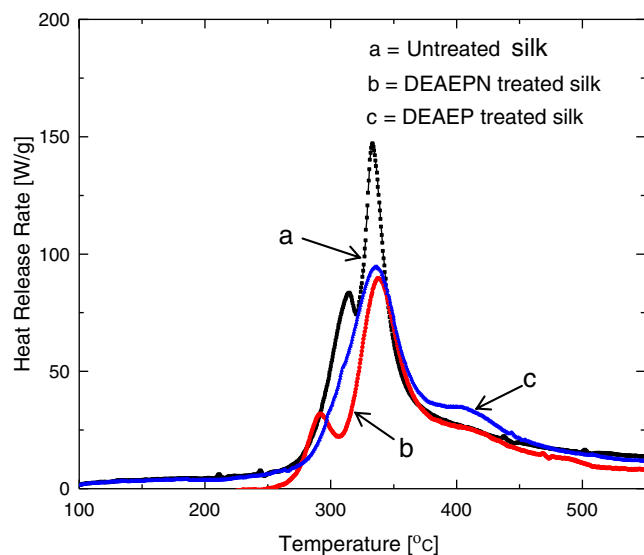
Fig. 3. Heat release rate of (a) untreated, (b) DEAEPN (20% w.o.f.) treated silk; and (c) DEAEP (20% w.o.f.) treated silk.

3.4. Multifunctional properties

Fire retarded silk fabrics could be used for various purposes which require different surface energies. Finished with polyDEAEPN or polyDEAEP, the fabrics obtained in step 1 are hydrophilic. In order to obtain hydrophobic ones, the flame retarded (FR) silk fabrics were submitted in a second step (step 2) to a SF_6 plasma treatment ($F_{SF6} = 25$ sccm; $P = 100$ W; $p = 500$ mT; $t = 5$ min). The protocol is given in Fig. 5 and the results are displayed in Fig. 6.

Fig. 6 shows the XPS survey spectrum of the untreated silk and the FR silk fabrics – with 20% (w.o.f.) of DEAEPN or DEAEP – exposed to a SF_6 plasma. Apart from the P_{2s} and P_{2p} components due to the FR finishing, one can clearly detect the F_{1s} peak indicating a significant fluorination of the surface. Consequently, the wettability of the fabric will be affected. In order to evaluate the extent of this modification, the Schmerber pressures were measured according to Norm DIN 53886. Before and after the plasma treatment, the Schmerber pressures P_{Sch1} and P_{Sch2} were measured respectively. The results obtained are given in Table 4. Before the SF_6 plasma treatment, the FR silk fabrics are completely absorbent ($P_{Sch1} = 0$ mbar). After the SF_6 plasma treatment, the Schmerber values, P_{Sch2} increase significantly from 0 up to 23.5 mbar.

This high value corresponds to an apparent contact angle with water of 134°. The droplets of water roll on the surface which emphasises the low surface energy achieved by this treatment. Interestingly, the LOI is not affected by this treatment; it even slightly increases for the FR samples. Moreover, after several weeks of outdoor exposure, only a slight drop of the Schmerber pressure was noticed (by about 1 unit). The initial pressure P_{Sch2} could be recovered after one hour of heating at 100 °C.

Table 3
Thermal data calculated from Fig. 3.

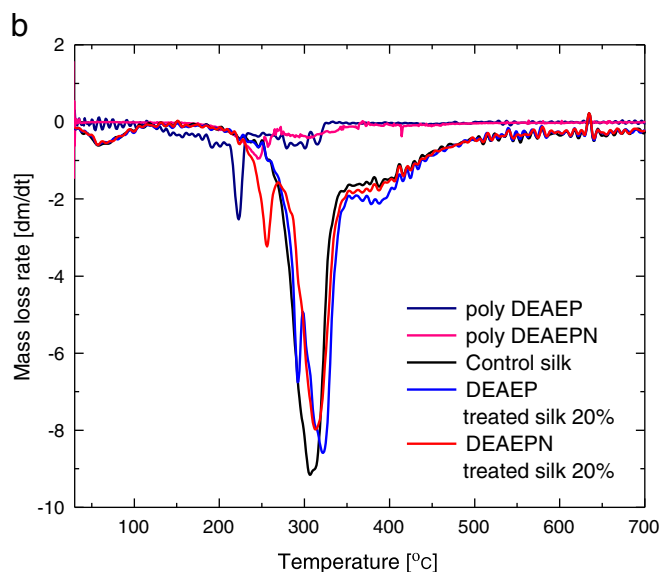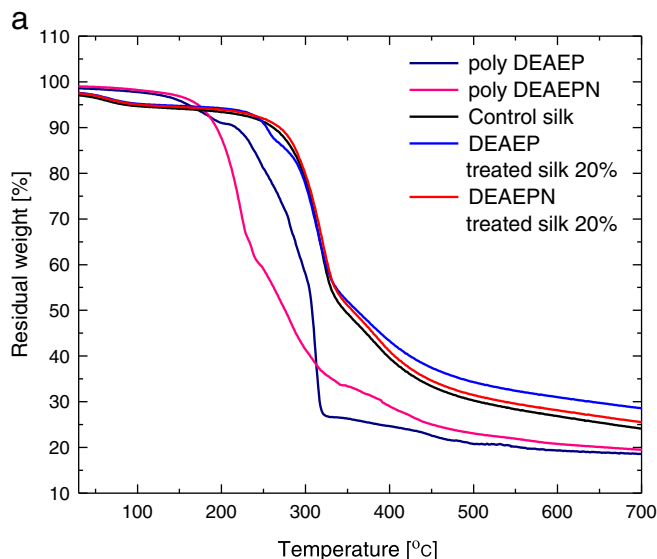| Sample	PHRR (W/g)	THR (kJ/g)	HRC (J/g K)
Untreated	84	7.7	149
	147		
DEAEPN 20% (w.o.f.)	32	6.2	91
	90		
DEAEP 20% (w.o.f.)	36 (shoulder)	6.5	97
	95		

Fig. 4. The TG (a) and DTG (b) curves in nitrogen of the polyDEAEPN, polyDEAEP, untreated silk, DEAEPN (20% w.o.f.) treated silk; DEAEP (20% w.o.f.) treated silk.

3.5. Fastness properties

To investigate the effect of the argon plasma induced graft polymerization of DEAEPN and DEAEP before (step 1) and after (step 2) a SF_6 plasma treatment on the mechanical properties of silk fabrics, the tensile strength and the elongation at break were measured and the results are presented in Tables 5 and 6. The mechanical analyses revealed that an Ar-plasma treatment during 20 min on the untreated fabric does not alter the tensile strength of the fabric (<1%). The original value decreased slightly (<2.5%) after the application of the PIGP process with 20% (w.o.f.) of each monomer. On the other hand, these finished textiles treated with a SF_6 plasma are subjected to almost similar alteration of the mechanical properties after 5 min of treatment. However a SF_6 plasma treatment on the fabrics of more than 5 min has a detrimental effect and more than 20% of the tensile strength is lost after the treatment.

This behaviour is reflected as well in the elongation at break measurements. The FR finishing by embedding the fibres provides some elasticity to the fabric (the averaged values increase from 19.2 to 21.2 and 20.6 for silk treated DEAEPN and DEAEP respectively)
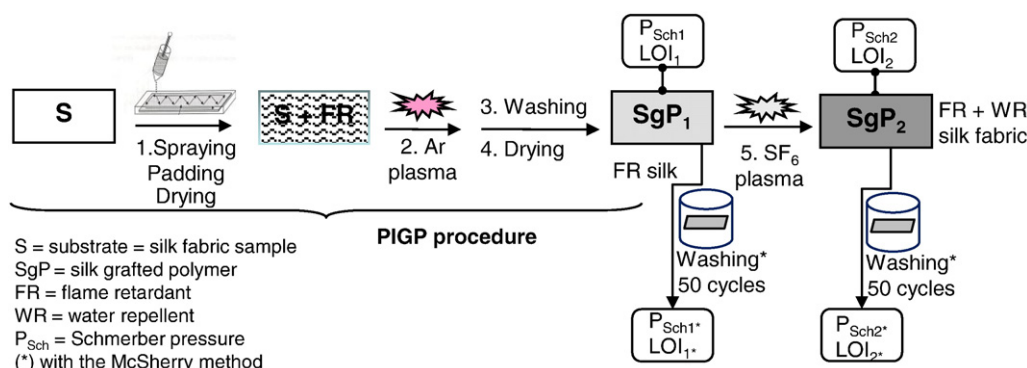
Fig. 5. Procedure of the two-step treatment. Step 1: PIGP process of FR monomers onto silk fabrics. Step 2: SF$_6$ plasma on the FR fabrics.

whereas a post-SF$_6$ plasma treatment led to the opposite effect. After 5 min of treatment a slight decrease of the elongation at break value is observed for all samples, finished or not. Interestingly though this decrease of the textile strength is more remarkable for the untreated silk fabrics than for the FR finished ones. The flame retardant coating provides a protective layer towards the abrasive action of the SF$_6$ plasma treatment [26]. Evidently, the same trend is observed for longer exposure time where cross-linking might occur as well.

With the aim to examine the effect of the PIGP process using phosphorus containing monomers followed up by a SF$_6$ plasma treatment on the colour change of the fabrics, the degree of whiteness has been evaluated according to the grey scale colour testing. The results obtained by comparing our silk fabric samples treated with increasing amounts of DEAEPN to a set of five pairs of grey/white coloured plates with different degrees of contrast are given in Table 7. A value of 4.5 on the scale ranging from 1 to 5 has been estimated for

almost all silk fabrics finished with various amounts of the monomer. The fabric treated with an initial solution concentration of 30% (w.o.f.) corresponding to 16% of grafted polymer exhibits the lowest value of 4 which indicates a slight change in colour. By comparing these results with the untreated silk fabric which is at 5, one can say that the PIGP process with this monomer impacts only slightly the colour properties of the fabric. It is interesting to notice that a post-SF$_6$ plasma treatment of the FR silk fabrics does not affect their colour at all, the same degrees of whiteness as before the SF$_6$ treatment were obtained.

The wash-fastness property of the coating has been evaluated by using the accelerated laundering protocol proposed by McSherry. In this procedure the samples are boiled for over 4 h in a basic medium. This method is set up to mimic 50 cycles of laundering and has been applied on the treated samples with 20% (w.o.f.) of the two monomers after the first step (PIGP process) and after the second step (SF$_6$ plasma treatment). LOIs and Schmerber pressures have been taken after each step and the results obtained are listed in Table 8.

For each flame retardant and water repellent finished fabric the LOI is only slightly altered by the washing process. The decrease of the oxygen index is less than 1.5% even after the fabrics have been subjected twice to the washing process. In contrast the water repellent character is not resistant towards this washing. The fabrics became again absorbent.
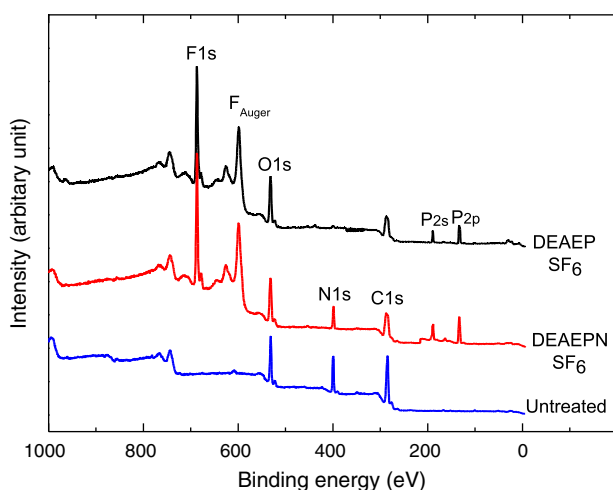

Fig. 6. XPS survey spectra for untreated silk and SF$_6$ plasma treated flame retarded silk fabrics with DEAEPN and DEAEP.

Table 4
LOI and Schmerber pressures (P_{Sch}) measured for the FR silk fabrics with DEAEPN and DEAEP before (step 1) and after (step 2) SF$_6$ plasma treatment.

Sample	After step 1		After step 2	
	LOI$_1$ [%$\pm$0.1]	P$_{Sch1}$ [mbar]	LOI$_2$ [%$\pm$0.1]	P$_{Sch2}$ [mbar]
Untreated	25.0	0	25.0	23.5
DEAEPN 20% (w.o.f.)	30.5	0	31.0	23.5
DEAEP 20% (w.o.f.)	29.0	0	30.0	23.0

Table 5
Tensile strengths measured for untreated and FR silk fabrics with DEAEPN and DEAEP before (step 1) and after (step 2) SF$_6$ plasma treatment.

Sample	Tensile strength (N)		
	Step 1	Step 2: plasma SF$_6$	
		5 min	10 min
Untreated: 551 ($\pm$10) N	546 ($\pm$9)	535 ($\pm$8)	432 ($\pm$8)
DEAEPN 20% (w.o.f.)	542 ($\pm$6)	533 ($\pm$7)	429 ($\pm$8)
DEAEP 20% (w.o.f.)	538 ($\pm$7)	531 ($\pm$8)	427 ($\pm$8)

Table 6
Elongation at break measured for untreated and FR silk fabrics with DEAEPN and DEAEP before (step 1) and after (step 2) SF$_6$ plasma treatment.

Sample	Elongation at break (mm) and (% elongation)		
	Step 1	Step 2: plasma SF$_6$	
		5 min	10 min
Untreated: 19.2 ($\pm$11); 100%	19.0$\pm$9.7; (98.9)	18.1$\pm$8.2; (94.3)	17.7$\pm$8.6; (92.2)
DEAEPN 20% (w.o.f.)	21.2$\pm$7.6; (110.4)	19.4$\pm$6.7; (101.0)	18.3$\pm$7.3; (95.3)
DEAEP 20% (w.o.f.)	20.6$\pm$7.7; (107.3)	19.2$\pm$7.9; (100.0)	18.0$\pm$7.5; (93.7)

Table 7
Colour-fastness properties of the treated silk fabrics by the PIGP process with various amounts of DEAEPN monomer.

Sample		Grey scale	
		Step 1	Step 2
Untreated silk		5	5
DEAEPN treated silk	6.62	4/5	4/5
	11.22	4/5	4/5
	16.68	4	4

Table 8
Wash-fastness properties of the FR silk fabrics with DEAEPN and DEAEP before (step 1) and after (step 2) SF$_6$ plasma treatment.

Monomer (w.o.f.)	Before washing[a]		After washing[a] — step 1			After washing[a] — step 2		
	% G_1	LOI_1	% G_1[a]	LOI_1[a]	P_{Sch1}[a]	% G_2[a]	LOI_2[a]	P_{Sch2}[a]
Untreated	0	25.0	0	25.0	0	0	25.0	0
DEAEPN (20%)	11.22	30.5	9.45	29.2	0	8.95	29.0	0
DEAEP (20%)	10.16	29.0	8.99	28.0	0	7.61	27.5	0

[a] Washing by the accelerated laundering method of McSherry.

In order to understand this phenomenon which we did not observe previously when we applied a similar CF$_4$ plasma treatment on cotton fabrics [17], the weight of the fabrics at each step has been taken and the weight loss calculated. It appears clearly that after step 1 more than 10% of the grafted polymer is removed. This effect is repeated after step 2 where an additional 5 to 15% weight loss of matter occurs. While this affects poorly the LOI, it has dramatic consequences on the water repellent properties. Likely, while fluorination of the surface occurs during the SF$_6$ plasma treatment, a concomitant surface degradation (etching) takes place leading to a weakening of the polymer which loses readily its thin external fluorinated layer.

4. Conclusion

By means of a two steps process, i.e. argon induced graft polymerization of phosphorus containing monomers followed by a SF$_6$ plasma treatment, a thin colourless flame retardant and water repellent polymer has been grafted on the surface of silk fabrics. Diethyl 2-(acryloyloxyethyl)phosphate (DEAEP) and diethyl 2-(acryloyloxyethyl)phosphoramidate (DEAEPN) have been used for this purpose. The LOI of the treated fabrics reaches 29 and 30.5 for DEAEP and DEAEPN, respectively, with a reasonable amount of loading (ca. 11%). It can be noted that the first step occurred with a grafting yield above 50%. It is clearly shown that the phosphoramidate monomer decreases more the flammability of the silk fabrics than the phosphate analogue, which is consistent with a P–N synergistic effect. Furthermore, SEM analyses of the residual char reveal two different morphologies. While textiles finished with polyDEAEPN exhibit an intumescent like protective layer, those with DEAEP present a thin one. This suggests two different behaviours during the burning process although they both operate in the solid phase as confirmed by the decrease of the heat of combustion and the increase of the residual char of the treated fabrics compared to the non-treated one. In a second step, the flame retarded fabrics have been exposed to SF$_6$ plasma. After 5 min of treatment, the fabrics which were originally absorbent became water repellent and exhibited an apparent contact angle of 134°. This property remains even after several weeks of air exposure. This multifunctional silk fabric retains the original characteristics of the untreated fabric. Indeed, only a slight variation of the tensile strength and the colour fastness has been noticed. However, although a good flame retardant behaviour remains after 50 cycles of laundering (McSherry method), the water repellent properties disappeared under these conditions. Our future research efforts will concentrate on the improvement of this second step in order to provide wash-resistant multifunctional silk fabrics.

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