Investigation and Optimization of Vacuum Plasma Treatment of PA66 Fabric for Reduced Fire Retardant Consumption

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ABSTRACT: Flame retardant (FR) textiles were obtained by surface treatments of polyamide 66 fabrics with microwave (MW) plasma technology in order to reduce the amount of FR involved in the fabric finishing process. More specifically, MW vacuum plasma was employed for polymer surface activation by using a helium/oxygen (He/O₂) gas mixture, evaluating the effect of different treatment parameters on the affinity toward thiourea impregnation. Surface fabric modification was investigated both in terms of uniformity and increased thiourea absorption by infrared spectroscopy, wicking properties, and gravimetric characterization to define an operative window for plasma treatment conditions. According to the results obtained, the dry add-on content of thiourea improved up to 38%, thanks to the increase of the fabric surface activation. The effectiveness of plasma treatment resulted in an absolute increase up to 2% in limiting oxygen index (LOI) performance with respect to untreated fabric. As a consequence, a drastic reduction of 50% in thiourea concentration was required to achieve a similar fire retardant performance for plasma-treated fabric. On the basis of these preliminary results, a design of experiment (DoE) methodology was applied to the selected parameters to build a suitable response surface, experimentally validated, and to identify optimized treatment conditions. At the end, a final LOI index up to 43% has been reached.

1. INTRODUCTION

The modern textile industry still relies on many traditional chemical finishing processes, such as coating and padding, to impart specific final properties to fabrics such as softening, anti-static behavior, wettability/repellency, and dyeing.¹ These processes are characterized by extensive use of energy and water, production of solid waste and wastewater to be treated, as well as the employment of different types of synthetic chemicals which can have specific health and environmental impacts.²,³ From this point of view, the high level of competition on the international markets and the growing concern of the public opinion toward sustainability are two driving forces that are influencing the development strategies of the textile industry.⁴ Therefore, innovative production techniques are required to improve product performance and address the issues related to the detrimental impacts generated by textile production.

Plasma treatment is a versatile technology capable of providing surface modification without altering the bulk properties of a material.⁵ Its main advantage is related to its environmental friendliness, low treatment times, no use of hazardous chemicals, and absence of solvent for the processing. In the context of the textile products, cold plasma treatments have been mainly investigated by low temperature atmospheric equipment, revealing substantial changes of the material surface properties in terms of adhesion, friction, wettability, morphology, and wicking.⁶⁻¹³ As a consequence, such technology can be potentially integrated into different stages of fabric production as pre-treatment for wet processes such as desizing,¹⁶ dyeing,¹⁷ printing,¹⁸⁻²¹ and finishing,²² with beneficial results in terms cost saving and reduced waste and toxic by-products.²³ Another aspect of great interest is the possibility to impart flame retardant (FR) properties to synthetic fibers which usually are quite prone to combustion, due to the organic nature of their composition. Two alternative strategies are commonly employed to provide flame retardancy to textiles by either provide a physical blending with a suitable FR or by chemical incorporation of the latter into the polymer structure.²⁴⁻²⁶ For synthetic fibers, this approach has been

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proven more difficult to realize due to the low compatibility of these materials with FR additives, which alters the normal fiber spinning process and the final properties of the textile in terms of physical and mechanical properties.\textsuperscript{27} These aspects have been an important obstacle to the development of FR solutions for aliphatic polyamides (PAs) fibers, which are mainly limited to few commercial processes. Among them, a well-established finishing procedure is the treatment of PA textile with a thiourea-formaldehyde resin, crosslinked in the presence of an acid catalyst.\textsuperscript{28} However, a few alternative and promising approaches related to the use of plasma to improve fire response have also been demonstrated in the pertinent scientific literature. Jama et al.\textsuperscript{29} used cold remote nitrogen plasma to produce a thin protective film on polyamide 6 (PA6) and PA6/clay nanocomposite substrate by polymerization of the 1,1,3,3-tetramethyldisiloxane monomer doped with oxygen. The final coating displayed efficient fire retardant properties in terms of increased LOI and lower heat release rate. Schartel et al.\textsuperscript{30} employed a MW plasma treatment to deposit an organosiloxane protective layer on the surface of PA6 showing that, through careful control of the thickness, valuable fire retardant effects can be obtained. Errifi et al.\textsuperscript{31} improved PA6 fire behavior by graft polymerization of a fluorinated acrylate monomer by MW vacuum plasma treatment. The functionalized PA6 showed consistent improvement with a 50\% reduction in the heat release rate in comparison to virgin PA6. In a similar work,\textsuperscript{32} the same authors used low pressure argon (Ar) plasma-induced graft polymerization of methacrylate phosphate to provide higher thermo-oxidative stability to PA6. Few authors have also reported the employment of plasma treatment to improve fire behavior or reduce the amount of FR necessary to obtain a specific polymer fabric fire response performance, but mainly related to the specific case of polyester fibers.\textsuperscript{33–35}

In the present work, we analyzed the effect of cold plasma treatments for the surface modification of a polyamide 66 (PA66) fabric to optimize its FR properties with a minimal amount of chemicals involved in the finishing process. The aim of the study was to improve the fabric surface absorption of FR in order to provide the same level of reaction to fire with the use of a lower amount of additive. Once identified the relevant process parameters, a subsequent part of the study has been devoted to the optimization of the plasma setting to provide a consistent surface activation and optimized fire performance.

2. EXPERIMENT AND METHOD

2.1. Materials. PA 66 was kindly provided by Aquafil Ltd. (Trento, Italy) in the form of a fabric with an area density of 149.6 g/m\textsuperscript{2}. Reagent grade thiourea, employed as a fire retardant additive, and Triton X-100, used as detergent, were purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Washing Treatment. A laboratory washing procedure of the textiles, similar to those described elsewhere\textsuperscript{36,37} has always been carried out before any plasma and FR treatment. The fabric samples were placed in a 1\% w/w Triton X-100 detergent solution at 90 °C for 1 h, rinsed with distilled water, and subsequently dried in an oven at 70–80 °C for 2 h.

2.3. Plasma Equipment and Functionalization Procedure. The treatment of the fabric has been carried out with a microwave vacuum plasma apparatus in a custom-made stainless steel reaction chamber (~6 L of volume) equipped with an electron cyclotron resonance coaxial plasma source (Aura-Wave, SAIREM SAS, Décines-Charpieu, France). The system was powered by a microwave solid state generator (MiniFlow 200SS, SAIREM SAS, Décines-Charpieu, France) capable of providing a robust control over the frequency (from 2.4 to 2.5 GHz with steps of 0.1 MHz) and the level of microwave power (from 0 to 200 W with steps of 1 W). The low pressure required for plasma generation (10\textsuperscript{−4}–a few 10\textsuperscript{−5} mbar pressure range) was achieved by connecting the system to a diaphragm pump (MVP 040-2, Pfeiffer Vacuum, Asslar, Germany) to obtain a primary vacuum and subsequently to a turbopump (HiSpace 80, Pfeiffer Vacuum, Asslar, Germany) for high vacuum. The use of vacuum plasma technology with a static source required the setting of different parameters, especially in terms of chamber pressure and treatment time. The complete list of the specific conditions employed is reported in Table 1.

| plasma process parameter | value |
|--------------------------|-------|
| chamber pressure [mbar]   | 0.06  |
| fabric-to-plasma nozzle distance [mm] | 30 |
| treatment time [min]      | 2, 5, 10 |
| power [W]                 | 40–200 W |
| He/O\textsubscript{2} gas mixture composition [vol ratio] | 1:1, 5:1, 10:1 |

Chamber pressure and fabric-to-plasma nozzle distance were selected according to the findings of a previous study on carbon-based fillers,\textsuperscript{38} while the treatment time was varied from 2 to 10 min following the conditions reported in other experiments of vacuum plasma functionalization involving PA fabric.\textsuperscript{39} Plasma power generation was varied in the low to high limit range with a 40 W step, since it directly influences the plasma density, momentum, and energy which in turn affect the final efficiency of the functionalization process. All the experiments were carried out with the employment of a He/O\textsubscript{2} mixture with variable volumetric ratios between the two gases. The use of an inert gas such as He, as a carrier, is due to the evidence\textsuperscript{40} that the relative plasma produced is capable of extracting hydrogen atoms from the polymer chains, generating free radicals, and cleaning the substrate surface by removing low molecular weight species. From this perspective, He is more preferable over Ar due to its high energy metastable state and high heat conductivity.\textsuperscript{41} However, He does not provide surface functionalization while pure O\textsubscript{2} produces polar species, but only with temporary stability. On the other hand, their mixture is capable of increasing the surface energy of the treated substrate and improve the stability of the treatment,\textsuperscript{38} which are essential prerequisites to promote a higher adhesion of FR during finishing processes.

2.4. Impregnation Procedure. Impregnation with thiourea was carried out to provide FR property to the fabric by using solutions with 5–15\% weight concentrations of thiourea in distilled water in order to obtain an 80–100\% wet add on. The untreated or plasma-treated fabric was dipped into the solution for 15 min, followed by two pad procedures with a padding mangle and subsequent drying in an oven at 70 °C. Although it is known that plasma treatment can be employed to alleviate a conventional pad-dry procedure by using FR solution spraying, such a procedure was not followed in the present study in order to have more intimate contact of the selected FR with the fabric surface and more reproducible results due to the better control over the impregnation.
procedure. The amount of thiourea absorbed by the fabric was estimated by thermogravimetric analysis and by a direct gravimetric method by calculating the % dry add on with a Mettler AE 240 analytical balance using the following relation:

\[
dry \text{ add on} = \frac{W_{\text{after}} - W_{\text{before}}}{W_{\text{before}}} \times 100\%
\]

in which \( W_{\text{before}} \) is the weight of the fabric before thiourea impregnation and \( W_{\text{after}} \) is the weight of the fabric after drying.

2.5. Capillary Rise Tests. Wicking properties were measured to evaluate the increase in surface hydrophilicity after plasma treatment by quantification of the capillary rise after contact between the treated fabric and distilled water. Strips of 10 × 4 cm of PA fabric were held vertically with an end dipped in a stained solution of distilled water. To evaluate the wicking behavior of these textiles, the height of capillary rise of the solution on the fabric was measured after 6 min.

2.6. Fourier Transform Infrared Spectroscopy. The evaluation of surface chemical modification of the fabric after plasma exposure was carried out by Fourier transform infrared spectroscopy (FTIR) analysis. Spectra of treated and untreated PA fabrics were collected with a Thermo Scientific Nicolet iS50 FT-IR Spectrometer using a Smart iTR attenuated total reflectance (ATR) sampling accessory equipped with a diamond crystal. All the spectra were collected in the 4000–650 cm\(^{-1}\) wavenumber range with 64 scans and a 4 cm\(^{-1}\) resolution. In order to assess the homogeneity of the treatment, samples of 12 × 12 cm were cut and analyzed at five different points (in the center and at 1.5 cm from the four edges of the sample) immediately after the functionalization.

2.7. Thermogravimetric Analysis. A second evaluation procedure of thiourea absorption was done by thermogravimetry. TGA analyses were carried out with a Q600 SDT (TA Instruments) analyzer under air atmosphere at a flow rate of 100 mL/min and a constant heating rate of 20 °C/min from room temperature up to 700 °C.

2.8. Limiting Oxygen Index. The reaction to small flames, also known as flammability, of thiourea-treated fabric samples was examined by measuring the LOI in accordance with ISO 4589 standard. Samples 80 mm × 15 cm in size were tested after conditioning in a climatic chamber at 23 °C and 50% relative humidity for 24 h.

2.9. Scanning Electron Microscopy. Scanning electron micrographs of the fabrics were collected with a Hitachi S-3400N SEM on gold sputtered samples (SC7620 Sputter Coater) to provide evidence of the effect of plasma treatment on the surface of the material.

2.10. Design of Experiments. After the initial screening activity on the suitable conditions for plasma fabric functionalization, an optimization of the process has been carried out to identify the best plasma parameters to obtain the highest LOI performance. This investigation was conducted through a design of experiment (DoE) approach by using a randomized I-optimal design for the construction of a response surface with the Design-Expert software (Stat-Ease, Minnetosa, USA).

3. RESULTS AND DISCUSSION

3.1. Vacuum Plasma Treatment. Vacuum plasma equipment is capable of tuning the functionalization of a given substrate by a proper choice of the different parameters that can be employed during the treatment process. For this reason, in order to obtain a clear proof of the effect of the different variables on the functionalization of the fabrics, a series of screening experiments has been realized with the target to provide evidence of the relevance of the selected factors. Subsequently, the relevant factors were selected and employed in a statistical analysis of the process to optimize their combination with the aim of maximizing the LOI performance of thiourea-impregnated fabric.

3.1.1. FTIR Analysis. The FTIR spectrum of the pristine fabric was compared with the treated samples with a He/O\(_2\) gas mixture functionalization (5:1 feed gas mixture volumetric ratio, 80 W of power and 5 min of treatment taken as reference conditions) to identify possible modifications induced. Due to the nature of the technique, FTIR is only a qualitative analysis for the evaluation of changes in the surface chemistry of plasma treated polymers, which can, however, provide a quick screening for the discrimination on the relevance of the effects of plasma working parameters. Figure 1 shows the FTIR spectrum of the pristine fabric, which presents the characteristic peaks of PA66. The first peak at 3295 cm\(^{-1}\) is the absorption related to the stretching of hydrogen bonded N–H groups, while the two peaks at 2932 and 2859 cm\(^{-1}\) are characteristic of the asymmetric and symmetric C–H stretching of the aliphatic polymer backbone. The fingerprint region of the spectrum presents two dominant sharp peaks at 1362 and 1563 cm\(^{-1}\), which are usually identified as amide I and amide II bands and can be assigned to the C=O stretching and N–H bending, respectively. Further peaks of high absorbance can be found at 720 cm\(^{-1}\), where there is the presence of a shoulder due to hydrogen-bonded secondary amines and at 680 cm\(^{-1}\), which has been assigned to the bending motion of the N=C=O group.

For the treated sample, no new peak has been observed in comparison to the 1730, 1234, 1247, and 965 cm\(^{-1}\) wavenumbers nor a shoulder in correspondence to the 1700–1860 cm\(^{-1}\) region, which have been attributed to the vibrations of the C=O or C–O groups due to new introduced functionalities in plasma-treated samples. Upon this comparison, it has been clear that no significant modifications were present in terms of new functional groups but rather a change in the relative intensities between the peaks of PA66, as can be seen in Figure 1. Indeed, the absorption intensity of the peaks associated to PA66 functional groups can be altered as a consequence of the plasma treatment. For this reason, the
comparison has involved the evaluation of the height of the absorption peaks of the spectrum regions related to the stretching of N–H (at 3296 cm\(^{-1}\) and 1532 cm\(^{-1}\)) and C=O (at 1632 cm\(^{-1}\)) groups after normalization by using the C–H stretching at 2932 cm\(^{-1}\) as reference peak.\(^{51}\) The analysis of the spectra has shown that this last peak is not affected by the plasma treatment, and therefore, it can be used as internal standard. For this reason, in the following analysis, the normalized peak height (NPH), that is, the ratio between the height of the N–H or C=O peak and the height of the internal C–H standard has been used to draw conclusions. For this purpose, the reference baseline for the peak at 3296 cm\(^{-1}\) was taken in the 3680–2380 cm\(^{-1}\) interval, while the 1800–856 cm\(^{-1}\) interval was considered for the 1532 and 1632 cm\(^{-1}\) peaks.

3.1.2. Effect of the Unconstrained Variables on the Fabric Functionalization. Among the selected variables to carry out the functionalization with vacuum plasma (Table 2), the initial screening activity involved the He/O\(_2\) volumetric ratio of the feeding gas, plasma MW power, and treatment time, using FTIR spectroscopy and capillary rise height to check the effects. The following results have been obtained as the average of three different samples to assess the relevance of the different levels of the factors.

### Table 2. NPH and Capillarity Test Results at Different Volumetric Ratios for the Three Functional Groups

| He/O\(_2\) ratio | wavenumber [cm\(^{-1}\)] | NPH | NPH % increase | capillary rise height [cm] |
|-----------------|--------------------------|-----|----------------|--------------------------|
| 0 (pure PA66 fabric) | 3296 | 1.967 | | 3.50 ± 0.43 |
| | 1632 | 2.812 | | |
| | 1532 | 2.870 | | |
| 1:1 | 3296 | 2.031 | +3.3% | 5.20 ± 0.34 |
| | 1632 | 2.855 | +1.5% | |
| | 1532 | 3.310 | +15.3% | |
| 5:1 | 3296 | 2.156 | +9.6% | 5.50 ± 0.25 |
| | 1632 | 3.054 | +8.6% | |
| | 1532 | 3.429 | +19.5% | |
| 10:1 | 3296 | 1.952 | −0.8% | 4.60 ± 0.47 |
| | 1632 | 2.721 | −3.2% | |
| | 1532 | 3.165 | +10.3% | |

FTIR results show also that there is a clear dependence of the extent of functionality on the amount of oxygen present in the feeding gas. Still, at a 10:1 volumetric ratio, some effects take place, although the extent of functionalization is limited, due to the low oxygen amount, as evidenced by the NPH and capillary rise height results. The best results in terms of capillary rise height and NPH increment are obtained at a 5:1 volumetric ratio, as seen in other studies,\(^{57}\) while a higher oxygen content (1:1 ratio) leads to worse results. This could probably be ascribed to a more pronounced molecular etching effect of the plasma, which favors the bond breaking of the more liable polar groups of the polymer backbone rather than promoting a net increase of surface hydrophilicity due to the formation of new oxygenated functionalities. Since the 5:1 volumetric ratio showed the best results and represented also an optimum compromise to minimize the amount of reflective power (i.e., lost energy) generated by the plasma, it has been used in all the subsequent trials.

3.1.2.2. Microwave Source Power. For plasma source power investigation, the samples were treated similarly to the previous case for both treatment time and specimen sampling point, using a 5:1 He/O\(_2\) gas mixture. In this case, by looking at the results of NPH (Figure 2) and capillary rise height (Figure 3), it is possible to notice the presence of an optimum power value to maximize the functionalization of the fabric. Indeed, there is a common trend for the two indexes with a smooth increase up to 80 W. After that, the values decrease appreciably by increasing the source power. Similar results are provided also for the points analyzed on the edge of the samples (results not reported here).

In general, similar to what was discussed elsewhere,\(^{54,55}\) the effect of treatment conditions on the fabric surface modification can be related both to a building and to a damaging effect, and these phenomena may counteract one another or overtake the other. Therefore, depending on the MW power, different effects can be seen. At lower power, the building effect, that is, the breaking of the more liable covalent bonds of the polymer chain and the interactions with oxygen active species, is predominant and produces an increase in the surface functionalities due to creation of more radical sites and reaction with the ionized species.

However, at high input power (higher than 80 W), the formation of active sites on the surface slows down and the damaging effect eventually dominates. At this stage, the damaging effect of the plasma treatment leads to a drop in the amount of functional groups produced which reduced the NPH to values close to the untreated PA fabric, thus decreasing also the capillary rise height.

3.1.2.3. Treatment Time. For the treatment time effect, the previous optimal values for power (80 W) and feeding gas composition (He/O\(_2\) = 5:1) were employed. FTIR spectra comparison, both at the center and at the edge of the specimen, have been used to understand the extent of homogeneous fabric activation at different time intervals (2, 5, and 10 min). In this case, an increase in the content of functional groups with respect to the pristine material is present, especially for the N–H stretching at 1532 cm\(^{-1}\) (Figure 4), and the PA fabrics treatment in the vacuum reactor also provides a uniform modification of the material surface from the center to the edge of the sample. However, different from the previous parameters, the time factor seems not so relevant, at least in the selected intervals of treatment. From this point of view, the results suggest the possibility of
selecting small treatment times, among 2 and 5 min, to reduce the duration of the process and the energy expenditure for fabric surface activation.

3.2. Thiourea Impregnation. The optimal plasma functionalization parameters found for the feeding gas composition (He/O₂ mixture with a 5:1 volumetric ratio), MW power (80 W), and treatment time (2 min) were combined together to understand if the final amount of absorbed thiourea was increased as a consequence of the plasma treatment. Samples of optimal plasma treated and untreated fabric were soaked in thiourea solution, passed through the pad mangle, dried, and subsequently analyzed. The reference concentration of thiourea solution was fixed at 10% to obtain more distinguishable results from the analysis since FTIR is less sensitive to spectrum variations with additive content below this concentration. The FTIR spectroscopy analyses of plasma-treated and untreated fabrics are reported in Figure 5 in comparison with the pure thiourea spectrum.

The FTIR spectrum of pure thiourea (Figure 5a) shows the characteristic absorptions due to the presence of the N−H groups, capable of generating intense broad bands due to hydrogen bonding, and the C=S and C−N groups. The high wavenumber region presents several peaks at 3380, 3279, 3180, and 3092 cm⁻¹, which are associated to the symmetric and asymmetric N−H stretching vibrational bands of primary amines, while the strong band observed at 1620 cm⁻¹ was assigned to the NH₂ bending vibration. The absorption peak at 1474 cm⁻¹ is due to asymmetric N−C−N stretching vibrational mode. The characteristic bands of thiourea at 1414 and 1084 cm⁻¹ were assigned to the NH₂ rocking vibration, N−C−N, and C=S stretching vibrations. The band located at 730 cm⁻¹ in the thiourea spectrum is attributed to the C=S stretching. Analyzing the spectra of nylon samples (Figure 5a), for both FTIR spectra, there is a general shift to lower wavenumbers of the 3177 cm⁻¹ peak of thiourea, related to N−H stretching vibration, which means an increase in hydrogen bonding, compared to thiourea itself (Figure 5b), while the position of the other characteristic peaks of thiourea, in particular that at 730 cm⁻¹ related to C=S bond (Figure 5c), remains unchanged. This means that the interaction between thiourea and nylons (both untreated and plasma-treated one) is through hydrogen bonding, while the C=S bond is not involved. Indeed, it is frequently reported in the literature that metal−thiourea complexes are characterized by a shift to higher wavenumbers in the high frequency region of N−H absorption, due to weakening of hydrogen bonding because of the formation of S→M (metal) bond, and to a shift to lower wavenumbers for the 730 cm⁻¹ peak, due to the involvement of the C=S bond in the complex formation, that is the opposite situation compared to that observed in our work. In other words, we can assess that the interaction between thiourea and nylons is through the N−H group by...
hydrogen bonding without affecting the C=S bond of thiourea. To gain semi-quantitative information about the increase in thiourea content because of the plasma treatment, the calculation of NPH was carried out with reference to the two previously identified characteristics peaks of thiourea molecule at 1084 and 733 cm$^{-1}$. For this specific case, the reference baseline chosen for the comparison was in the 1790–860 cm$^{-1}$ interval. These values are compared in Table 3, where it is possible to evaluate a significant increase in the intensity of the C=S and C–N stretching of the plasma treated samples in comparison to the untreated reference.

More quantitative data were obtained by the analysis of the dry add-on results, as summarized in Table 4, where a comparison between the results obtained from microbalance and TGA calculation, at a reference thiourea concentration of 10% by weight, is shown.

The amount of thiourea content on the dry fabric was calculated by TGA, knowing the thermogram of pure thiourea as reference, by analyzing the weight residue at a specific temperature in comparison with that of the pure polymer. Since this compound loses most of its weight (around 87.5%) up to 330 °C, where the weight of PA66 treated samples is constant (Figure 6a), the amount of weight loss on thiourea impregnated samples can be used for the calculation of the amount of adsorbed FR. Indeed, it is possible to observe that no significant modifications are present in the weight loss before the first degradation stage, between the plasma-treated sample and the pristine reference, while after thiourea treatment the degradation profile in that region is shifted due to the different amounts of FR absorbed, as can be seen in Figure 6b. Although about a 10% difference is present between the two methodologies, the use of the microbalance can provide faster and more reliable results due to the more representative amount of sample to be measured. Despite this, the results demonstrate that the higher surface functionalization due to the plasma activation is capable of increasing the amount of thiourea uptake up to 14% more than the untreated fabric. Further evidence was obtained by comparing the two fabrics using thiourea solutions at different concentrations, as reported in Table 5.

The trend is confirmed for every concentration tested, although more significant improvements are associated with the cases of lower thiourea content in solution where there is a +31 and +38% increase for 5% and 7.5% concentration, respectively. This behavior could be explained in terms of a kinetic effect due to the diffusion phenomenon along the surface of the fabric. Since all the samples, independently of the concentration of the solution, were dipped for 15 min, it is possible that at lower concentrations there is a more marked effect related to the affinity between the treated sample and thiourea. Indeed, thiourea is about 160% more polar than water (4.93 D vs 1.85 D of dipole moment) and once the high hydrophilic surface of the plasma activated fabric is placed in the solution, the adsorption of thiourea along the surface of the fabric is faster than that along the untreated fabric, generating a local decrease of thiourea concentration, which drives a high diffusion flux from the surrounding solution. Increasing the concentration of thiourea in the impregnating solution increases the speed of the phenomenon, for both the fabrics, and lowers the time to reach the final equilibrium adsorption.
concentration, which in turn results in a lower difference in adsorbed thiourea.

Generally speaking, this increment in thiourea uptake is beneficial since it can be translated in a better fire performance due to the lower flammability of the material.

### 3.3. LOI Tests

The fire performance of the different fabrics was tested in terms of LOI values, and the results are reported in Table 6. A first comparison was realized among non-impregnated pristine and plasma-treated fabrics to compare the possible alteration of fire response due to the plasma activation but no statistically significant difference was detected. Upon addition of thiourea, the samples displayed a higher LOI value, as expected, but the burning behavior of the fabrics was the same as untreated PA66, with a degradation mechanism based on dripping. LOI values of the samples exposed to plasma treatment increased for all the concentrations tested, in agreement with the previous results relative to the FR pick-up values. To identify the solution concentration capable of providing the best results, Table 6 also shows the ΔLOI (difference between the LOI of the plasma-treated and untreated sample) versus the percentage of thiourea concentration in solution. From those values, it can be noted that up to 10%, by increasing the solution concentration of thiourea, there is a corresponding rise in ΔLOI, followed by an abrupt decrease for 15% concentration. These results also highlight that, by comparison among the absolute LOI value at 7.5 and 15% thiourea solution content, the same fire behavior of pristine fabric can be obtained for plasma-treated samples by halving the fire retardant concentration in the finishing solution.

Such evidence can provide interesting improvements in terms of economic and environmental costs of the process by reducing the fire retardant consumption and the amount of wastewater to be treated for a given fire performance. Indeed, by combining these results with the previous findings from the gravimetric tests, it is interesting to note that there is a 35% decrease in the FR amount needed to obtain the same LOI performance. This result can be explained by considering that although the amount of absorbed fire retardant is lower for a 7.5% solution concentration, its more homogeneous distribu-

### Table 3. NPH Values for Samples Soaked in 10% Thiourea Solution (NPH Maximum Standard Deviation: ± 0.1)

| wavenumber [cm$^{-1}$] | NPH (no plasma) | NPH (plasma treatment) |
|------------------------|-----------------|------------------------|
| 1084 (C=S) or (N−C−N) | 0.25            | 0.37                   |
| 733 (C−N)              | 0.46            | 0.62                   |

### Table 4. Dry Add-On for PA66 Textiles After Soaking in 10% Thiourea Solution

| sample                | microbalance add-on [%] | TGA add-on [%]   |
|-----------------------|-------------------------|------------------|
| untreated PA66 fabric | 9.8 ± 0.1               | 8.9 ± 0.05       |
| plasma treated PA66 fabric | 11.2 ± 0.3           | 10.2 ± 0.4       |

![Figure 5. FTIR spectra comparison between the plasma-treated and untreated samples, after soaking in thiourea (TU) solution: whole range (a); detailed view of the 3177 (b) and 730 cm$^{-1}$ peaks (c).](image-url)
tion on the surface of the fibers increases the amount of oxygen required to start the combustion reaction. However, based on the best LOI values provided, a 10% thiourea content was identified as the reference solution concentration for the subsequent analysis.

3.4. Statistical Analysis of the Plasma Treatment by Response Surface Methodology. Treatment time and plasma power were selected as discrete independent variables and \( \Delta \text{LOI} \), expressed as difference between the LOI of plasma-treated sample and the LOI of the reference PA66 impregnated with 10% thiourea solution (40.9 \( \pm \) 0.2%), was selected as response variable. The interval of variation for the selected variables was divided into three different levels, whose values were selected in the ranges previously analyzed and are reported in Table 7. Among them also a very short treatment time (30 s) has been considered to try to fasten the treatment procedure.

The experimental design obtained produced nine final runs with all the possible combinations between the variables under investigations. After carrying out the treatments, as stated by the design, the fabrics were tested for LOI performance, and the results obtained are presented in Table 8.

After analyzing the results, the suggested approach was to fit the response variable by using a linear model without introducing interactions among the two factors. However, the \( R^2 \) value was only 0.6223 and there was a significant difference between the Adjusted (0.4965) and Predicted (0.1848) \( R^2 \). A Difference in Fits (DFFITS) analysis, which evaluates the influence of the \( i \)-th observation on the predicted value, identified an outlier in the first run. As a consequence, a second statistical analysis was run by ignoring the result of the first experimental run to understand if it was possible to

Table 5. Dry Add-On for PA66 Textiles after Soaking in Thiourea Solutions with Different Concentrations

| thiourea solution concentration [%] sample | microbalance add-on [%] |
|----------------------------------------|-------------------------|
| 5 untreated PA66 fabric | 4.2 \( \pm \) 0.4 |
| plasma-treated PA66 fabric | 5.5 \( \pm \) 0.5 |
| 7.5 untreated PA66 fabric | 6.2 \( \pm \) 0.2 |
| plasma-treated PA66 fabric | 8.6 \( \pm \) 0.3 |
| 10 untreated PA66 fabric | 9.8 \( \pm \) 0.1 |
| plasma-treated PA66 fabric | 11.2 \( \pm \) 0.3 |
| 15 untreated PA66 fabric | 13.3 \( \pm \) 0.3 |
| plasma-treated PA66 fabric | 14.4 \( \pm \) 0.1 |

Table 6. LOI Values for the Test Samples (\( \Delta \text{LOI} \) is Expressed as the Difference in LOI Results Between the Treated and Untreated Samples on the Basis of the Same Solution Concentrations in Thiourea)

| thiourea solution concentration treatment [%] | LOI untreated sample [%] | LOI plasma-treated sample [%] | \( \Delta \text{LOI} \) [% increment] |
|-------------------------------------------|--------------------------|-------------------------------|-----------------------------------|
| 0 (PA66 fabric without thiourea impregnation) | 35.6 \( \pm \) 0.2 | 35.3 \( \pm \) 0.2 | 1.0 (+2.7) |
| 5 | 37.5 \( \pm \) 0.2 | 38.5 \( \pm \) 0.2 | 1.0 (+2.7) |
| 7.5 | 40.1 \( \pm \) 0.2 | 41.7 \( \pm \) 0.2 | 1.6 (+4.0) |
| 10 | 40.9 \( \pm \) 0.2 | 42.7 \( \pm \) 0.2 | 1.8 (+4.4) |
| 15 | 41.5 \( \pm \) 0.2 | 42.4 \( \pm \) 0.2 | 0.9 (+2.2) |

Table 7. Levels of the Two Discrete Variables Selected for the Optimization Study

| variable unit | level 1 | level 2 | level 3 |
|----------------|---------|---------|---------|
| time (t) s | 30 | 120 | 300 |
| MW power (P) W | 40 | 80 | 200 |

Table 8. Experimental Matrix for Runs Performed for the Response Surface Analysis

| run | factor A: time [s] | factor B: MW power [W] | response: \( \Delta \text{LOI} \) [%] |
|-----|---------------------|-------------------------|-----------------------------------|
| 1   | 30                  | 40                      | 1.7                              |
| 2   | 300                 | 40                      | 1.5                              |
| 3   | 120                 | 80                      | 1.8                              |
| 4   | 300                 | 40                      | 1.3                              |
| 5   | 300                 | 200                     | 0.9                              |
| 6   | 300                 | 80                      | 0.6                              |
| 7   | 120                 | 40                      | 2.7                              |
| 8   | 30                  | 80                      | 2.9                              |
| 9   | 120                 | 200                     | 1.3                              |
identify a better statistical regression model. Between the suggested models, the quadratic one was chosen due to the highest Adjusted $R^2$ provided. From the data of the analysis of variance (ANOVA) reported in Table 9, it is possible to observe that all terms, checking the $p$-values, are significant and only $A^2$ is a borderline term with a $p$-value of 0.071, which is still acceptable. Moreover, the $R^2$ is rather close to 1 and the predicted $R^2$ is not defined, since the leverage is 1.

On the basis of the ANOVA results, it was possible to construct a surface response of the quadratic model developed. The final equation in terms of actual factors is:

$$\Delta = -6.036 - 0.019t - 0.044P + (3.2 \times 10^{-5})tP$$
$$+ (2.4 \times 10^{-5})t^2 + (12.9 \times 10^{-5})P^2$$

From the contour plots in Figure 7a it is possible to analyze the time-power dependence and the general behavior of the process. Specifically, the graph shows that for a fixed value of power, increasing the treatment time leads to a decrease of the response parameter while, for a fixed value of time, increasing the power decreases the response variable as well. This means that to have the same $\Delta$LOI value, when increasing the time, it is necessary to decrease the power and vice versa. However, since the optimization is devoted to maximize the response of the model, this also allows us to obtain the best performances coupled with lower energy consumption and minimal treatment time, as previously suggested from the preliminary screening analysis.

From this point of view, the physical reason to justify such results could be that, since plasma is a surface treatment, after the initial modification of the first molecular layers of the material, a prolonged treatment period increases the degradation of the fabric surface. Such an effect is due to superficial interactions which develop low molecular weight species as a consequence of the removal of the generated or pre-existing functional groups. On the other hand, increasing the plasma power produces higher concentrations of high energy species which can interact more significantly and frequently with the polymer substrate, favoring etching or crosslinking reactions that can produce an opposite effect to the functionalization.62 These aspects are summarized by the shape of the 3D surface (Figure 7b) that displays the relation between these three factors. The surface is not flat, and its curvature is due to the interaction between treatment time and

Table 9. ANOVA and $R^2$ Statistics for the Quadratic Model Developed

| source      | sum of squares | degrees of freedom | mean square | $F$-value | $p$-value |
|-------------|----------------|--------------------|-------------|-----------|-----------|
| model       | 4.59           | 5                  | 0.9179      | 72.67     | 0.0136    |
| A-time ($t$) | 1.84           | 1                  | 1.84        | 146.02    | 0.0068    |
| B-power ($P$) | 1.20           | 1                  | 1.20        | 95.01     | 0.0104    |
| AB          | 0.2547         | 1                  | 0.2547      | 20.17     | 0.0462    |
| $A^2$       | 0.1586         | 1                  | 0.1586      | 12.55     | 0.0713    |
| $B^2$       | 0.5200         | 1                  | 0.5200      | 41.16     | 0.0234    |
| residual    | 0.0253         | 2                  | 0.0126      |           |           |
| lack. of fit| 0.0053         | 1                  | 0.0053      | 0.2632    | 0.6983    |
| pure error  | 0.0200         | 1                  | 0.0200      |           |           |
| cor total   | 4.62           | 7                  |             |           |           |

std. dev.    0.1124  
mean          1.63   
CV (%)        6.92

$R^2$ 0.9945  
adjusted $R^2$ 0.9808  
predicted $R^2$  NA

adeq. precision 23.1977

Figure 7. Graphical representation of the quadratic model developed: (a) contour plot of power against time parametric in $\Delta$LOI (%) and (b) response surface.
MW power. These results provide also an interesting aspect from an industrial point of view since this means that optimal conditions for plasma functionalization requires low energy consumption and reduced treatment time, which are essential requirement to provide economic sustainability for this type of technology. The validation of the treatment procedure has been carried out by identifying the best parameters to obtain a high response value within the experimental window investigated. Upon the analysis of Figure 7, a target %LOI of 2.9 was selected in order to combine optimal fire response with a sufficiently wide operative window. To get this improvement, the DoE software provided a specific set of conditions based on a numerical optimization related to the model developed, suggesting 50 W as MW power and 80 s as treatment time. After performing this last experiment, the obtained value for %LOI was 44 ± 0.2 with a %LOI of 3.1. By considering the standard deviation related to %LOI equipment (±0.2) and the rounding of the MW power and time parameters, it is possible to conclude that the model provides a good prediction of %LOI values. As a consequence, it is possible to relate the higher %LOI performance to the increased surface hydrophilicity of the fabric after the plasma treatment, which determined a higher thiourea uptake after the soaking treatment. A further advantage is also related to the final morphology of the treated samples, as shown by the SEM micrographs in Figure 8. The pristine fabric presents some circular and some square fibers which can be associated to different cross sections present in the samples or to the fact that heat setting during the textile production process has induced some deformation. The analysis of the surface of the pristine fibers (Figure 8a) reveals some surface irregularities, which were attributed to impurities present within the yarn structure and that could not be completely removed by washing. However, after the plasma treatment (Figure 8b), the surface of the fibers shows a lower roughness indicating that the treatment can also induce an effect of surface cleaning, which can be useful in increasing the absorption of FR. The comparison between the two samples at a higher magnification (Figure 8c,d) reveals that the plasma treatment produces some surface modification with the formation of white spots, as also shown in Figure 8b, that can be associated to an etching effect. Such a result is in accordance to the previous considerations on the concurring phenomena involved during functionalization. In this case, although the plasma-treated sample is slightly rougher than untreated one, the selected plasma conditions limit the damaging effect on the fabric surface, producing only a localized etching along the fibers while there were no apparent signs of significant surface ablation. This is probably related to the fairly low microwave power used, as already seen in another work, to the short treatment time, and also to the use of a mixture inert gas and oxygen (He/O2), instead of pure oxygen, since inert gas has lower ablation efficiency.

Figure 8. SEM micrographs of thiourea impregnated PA66: without plasma treatment (a,c); with plasma treatment (b,d).
Therefore, the optimized conditions not only effectively produced an increased functionalization but also did not alter significantly the surface characteristics of the fibers, which is an important point in order to preserve the mechanical and aesthetic properties of the fabric.

4. CONCLUSIONS

In this study, we implemented a vacuum plasma treatment for the surface activation of PA66 fabric to reduce the amount of fire retardant solution concentration employed to achieve optimal fire behavior performance.

A preliminary analysis on the process variables highlighted optimal conditions for surface activation by using a 5:1 He/O2 volumetric mixture of feeding gas, coupled with low treatment times and MW plasma power. The increased hydrophilicity of the fabric surface was qualitatively assessed by FTIR and confirmed both by capillary rise height tests and thiourea uptake by the impregnation procedure, which showed a maximum of +38% increase with respect to the untreated fabric. The increment was directly translated into a better fire performance for the same fire retardant concentration (LOI of 42.7, +5% higher than the reference value) and into a halving of fire retardant concentration for the same fire behavior (reference LOI of approximately 41.5). On the basis of these results, a subsequent optimization has been carried out by using a DoE approach and analyzing the % amount of LOI increase (ΔLOI) as response, for a fixed thiourea concentration of 10%.

The generated response surface was fitted with a quadratic relationship, and the significance of each term in the model was assessed with an ANOVA analysis. The model revealed that best results are obtained with a combination of low MW plasma powers and low treatment times, probably because of the higher efficiency and stability of surface activation. The best parameters found showed a good agreement between the measured and predicted ΔLOI and confirmed a higher amount of thiourea uptake with no significant morphology alterations of the fabric fiber surface.

Such results demonstrated the applicability of plasma technology to provide consistent and uniform FR properties of PA66 in the perspective of developing more sustainable processes in the context of the textile industry.

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Notes
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