Application of HMDSO Plasma Polymerization as a Novel Textile Finishing Process

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Abstract

The application of plasma as a novel textile finishing technology is a powerful possibility to fulfil environmental requirements and very specific functions. Plasma treatment is an effective technique for modifying homogeneously the uppermost atomic layers of a material surface leaving the bulk characteristics unaffected, due to its very low penetration.
This communication summarizes the most recent works, carried out at CNR-ISMAC institute, concerning the LTP (low temperature plasma) treatment of wool.
The attention was focused on the plasma polymerization of hexamethyldisiloxane (HMDSO), a silicon-containing organic monomer, as an alternative, ecological finishing process for improving pilling performance of wool fabrics. Wool fabrics were coated by a $Si:O_x:C_y:H_z$ thin film by means of a radio frequency glow discharge using HMDSO as precursor, in mixture with argon and oxygen gases. Different discharge powers, treatment times and reaction pressures were investigated, showing that all treated fabrics had a better pilling performance respect to untreated ones.
The structure of deposited films was characterized by means of Fourier transform infrared (FTIR) and X-ray photoelectron (XPS) spectroscopies, and surface morphology of treated fabrics by means of scanning electron (SEM) and atomic force (AFM) microscopies.
Moreover, the determination of bursting properties allowed to verify that plasma treatments did not damage and weaken the fabrics from a mechanical point of view.
Further studies concerned the characterization of physical, low-stress mechanical and surface properties (such as bending rigidity, shear rigidity and air permeability) of the plasma coated wool fabrics. In particular, bending, tensile and shear behaviour was characterized by means of FAST (Fabric Assurance by Simple Testing) integrated set of instruments.
Finally, when the treated fabric was subjected to strong washing stress, the deposited film seemed to be removed from its surface. However, studies about improvements in order to guarantee a better adhesion of the plasma polymerized film to wool surface are in progress.

Introduction

The pilling phenomenon is related to the surface characteristics of a fabric; it is an unresolved problem for the textile industry, and one of the most important quality issues, particularly for the wool industry. It is a physical process that leads to the formation of bundles or balls of tangled fibres that cling to the fabric surface (Figure 1), thereby affecting the appearance and handle of the fabric and reducing its value. Pilling affects mainly knitted fabrics and woollen fabrics. It depends on repeated mechanical stresses, like rubbing, external pressure and fibre-fibre friction; therefore, to improve pilling resistance, processes should reduce the fabric surface fuzzing, modify inter-fibre friction coefficient and reduce the mobility of the fibre in the yarn.

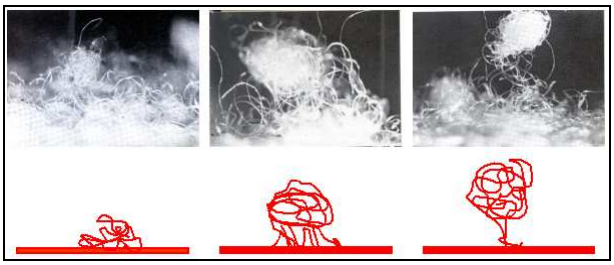

Figure 1. The formation of pilling.

Nowadays, no well-established and specific anti-pilling treatment exists in textile industry. In many cases organofunctional silicone softeners are used. They have been developed as finishing auxiliary with a softening and swelling action, to reduce inter-fibre (or inter-yarn) friction and felting and improve drawing. Their application on textile substrate is conventionally made by exhaustion in aqueous bath or in foulard. They modify fibres surface properties but imply many disadvantages. In fact, they are short time stable and sensitive to temperature and pH variations. If not well controlled, they could cause some defects like yellowing, a decreased resistance to abrasion and rubbing, a low shearing stability [1].
Moreover, the required wet chemical processes are not environmentally friendly at all, owing to the use of great amount of heated water and the production of polluting liquid effluents. The replacement of wet-finishing treatments with low-or-zero effluents processes is a target for the textile industry, also considering the increasing awareness of legislators and citizens for the ecological sustainability.
Taking into account such problems, the study started mainly with the focus on hindering the propensity to surface fuzzing and to pilling of knitted wool fabrics by means of silicon-based plasma polymerized coatings.
Low temperature plasma (LTP) treatment could be a promising, economic and ecological alternative to conventional processes; it affects the surface of polymeric materials physically and chemically without altering their bulk properties, due to its very low range penetration. Traditionally, cold plasma is generated by glow discharges in a gaseous environment at low pressure, and is characterized by a low density of reactive electrons, ions, radicals which react with the surface of the samples [2]. Electron temperatures are much higher (up to 10^4-10^5 K) than gas temperatures (near room temperature), making possible to treat materials under very mild thermal conditions, avoiding heat damage of the substrates. In particular, plasma polymerization is a thin film-forming process, where thin films deposit directly

on surfaces of the substrates without any fabrication, and where the growth of low-molecular-weight molecules (monomers) into high-molecular-weight molecules (polymers) occurs with the assistance of the plasma energy [2]. This process can be accomplished with small quantities of starting materials and is not energy intensive.
Hexamethyldisiloxane, an easy and safe organosilicon monomer to handle, has been used to achieve either inorganic SiO_2-like or silicone-like plasma coatings; it has been extensively employed for polymer layers deposition in rather different fields, but relatively few works focused on the application of HMDSO plasma deposited films in the textile field: the polymeric films produced by HMDSO RF plasma techniques on polypropylene fabrics are used to create a plasma polymerized HMDSO coated fabric with high contact angle and consequent lower wettability in comparison to the untreated fabric [3]; elsewhere, it has been reported that HMDSO plasma treatment on cotton fabric resulted in the self-cleaning property of the surface (Lotus effect) [4].
Instead, it is possible to retrieve a lot of scientific publications regarding studies on chemical, physical and mechanical properties and surface characteristics of wool, cotton, linen and silk fabrics treated with non-depositing LTP plasma. In particular, wool is an interesting substrate for plasma surface modification, because of the presence of an external thin membrane, the epicuticle, a 5-7 nm thicknessed surface layer rich in lipids and ionisable functional groups. Therefore, the plasma treatment has a great potential in the wool surface modification, particularly as regards non-felting property, waterproofness, anti-soiling, handle and pilling.

Plasma application: aims, equipment and process conditions

To verify the effectiveness of silicon-based plasma polymerized coatings in improving the pilling performance, $Si:O_x:C_y:H_z$ thin films were deposited on knitted wool fabrics, from the precursor HMDSO, using argon and oxygen as carrier and reactive gases. In the next work, plasma aided coatings were deposited on fabric samples cut from standard undyed worsted fabric (ISO 105-F01), with the aim to characterize physical, low-stress mechanical and surface properties of the plasma coated wool fabrics.
Treatments were made on 30 cm x 30 cm wool samples, and were carried out using a steel plasma reactor (Figure 2), with front and back aluminium flanges, which employed two capacitively-coupled cylindrical electrodes to achieve the glow discharge. The power electrode was RF (13.56 MHz) driven by a generator tuned by means of an impedance-matching network. The reactor was pumped by a turbo-molecular and a rotary pump. Fabric sample was fixed on a rotating roller below the electrodes, allowing homogeneous plasma irradiation on the surface area.

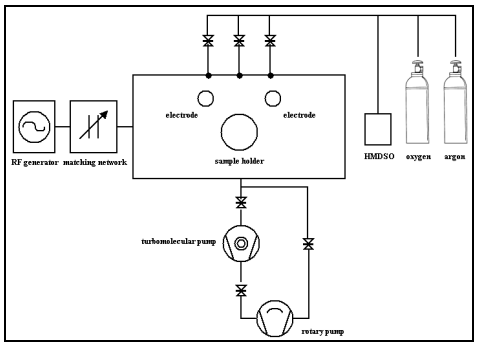

Figure 2. Schematic diagram of plasma system.

The surface of wool samples was covered by a ultra-thin layer of plasma polymer obtained from HMDSO by means of a two steps LTP process. An activation and etching of the substrate by a RF excitation of Ar (mantaining Ar flow rate at 20 sccm, discharge power at 50 W, chamber pressure at 20 Pa, for 3 minutes) was followed by the polymerization performed in a mixture of HMDSO vapour and feed gases (O_2 and Ar) at constant flows (3 sccm of HMDSO, 20 sccm of Ar, 20 sccm of O_2). Different discharge powers (20÷60 W), deposition times (5÷9 minutes) and reaction pressures (2 and 20 Pa) were investigated. After treatment, RF power was switched off and the system returned to atmospheric pressure by introducing air into the plasma chamber.

Chemical characterization of deposited films and coated wool

Plasma polymers are different in chemical composition from conventional polymers, even if the same monomers are used in the two polymerization processes. The appearance and characteristics of plasma polymers are strongly dependent on the nature of the monomer and the operational conditions, *e.g.*, the magnitude of the input power to maintain the glow discharge, the flow rate of the gases, the pressure in the reaction chamber, the exposure time and the distance from electrodes [2].
FTIR and XPS spectroscopies were used to follow changes in the chemical structure of plasma deposited films. Since coated wool showed complex FTIR signals that did not allow a clear interpretation of film structure (changing operational parameters), it was chosen to evaluate those modifications repeating the depositions on a substrate like potassium bromide (KBr) tablets; the characteristics absorption bands of the coating were found and their variations investigated. Similar behaviour of the different plasma deposited films were observed; however both FTIR and XPS analysis pointed out that an increase of discharge power led to the formation of a more inorganic film.

Peak position (cm^{-1})	Band assignment
3400	ν (O-H) in Si-OH
2960	ν_a (C-H) in CH_3
2900	ν_s (C-H) in CH_x
1410	δ_a (CH_3) in Si-$(CH_3)_x$
1260	δ_s (CH_3) in Si-$(CH_3)_x$
1020	ν_a (Si-O) in Si-O-Si
840	ρ (CH_3) in Si-$(CH_3)_x$
800	δ (Si-O) in Si-O-Si
ν stretching; δ bending; ρ rocking; a asymmetric; s symmetric	

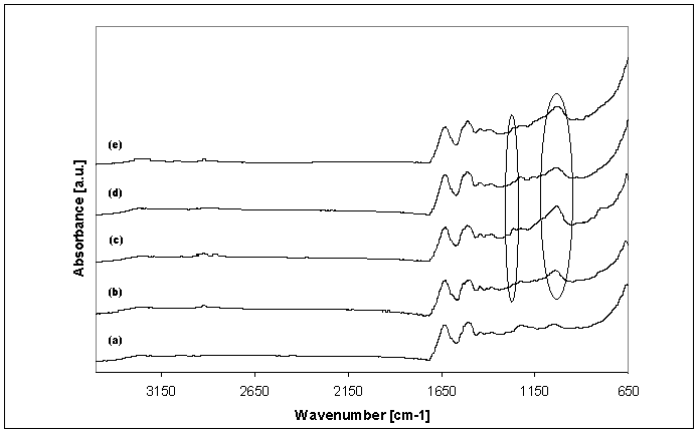

Figure 3. FTIR band assignments of pp-HMDSO film and typical FTIR spectra of untreated wool sample (a) and coated wool samples: deposition at 40 W and (b) 5 min 2 Pa, (c) 9 min 2 Pa, (d) 5 min 20 Pa, (e) 9 min 20 Pa.

FTIR spectra of coated wool samples confirmed the presence of the silicon-based coating. Figure 3 shows typical FTIR spectra of coated wool samples in the region from 4000 to 650 cm^{-1}. They confirmed the presence of the plasma polymerized HMDSO (pp-HMDSO) film, whose main vibrational modes are clearly visible: the absorption at 1025 cm^{-1} and the band at about 1260 cm^{-1} can be assigned to the symmetric stretching of Si-O bond in Si-O-Si and the symmetric bending of CH_3 in Si-

$(CH_3)_x$, respectively; the absorption bands at about 2960 and 2900 cm^{-1} can be assigned to the asymmetric and symmetric stretching of the C-H bond in CH_x groups. Figure 4(a) shows that there was a decrease in the C/Si (the film tended to be more inorganic) and an increase in O/Si atomic ratios with the increase of power. Figure 4(b) shows a typical XPS Si_{2p} spectra for a plasma deposited film (on Si wafer) at 2 Pa and 50 W for 8 minutes. The broad scan XPS spectra of these films reveal the presence of distinct bands at binding energies (BE) which correspond to Si_{2p}, C_{1s} and O_{1s} core levels. The interpolation of signals reveals the presence of several peaks. The Si_{2p} band has been resolved into four components: $SiOC_3$ (BE=100.8 eV), SiO_2C_2 (BE=101.6 eV), SiO_3C (BE=102.4 eV) and SiO_4 (BE=103.1 eV). The oxygenated structure (Si-O) prevail on the silicon environment (Si-C) relative to the monomer, producing a film with a more inorganic character.

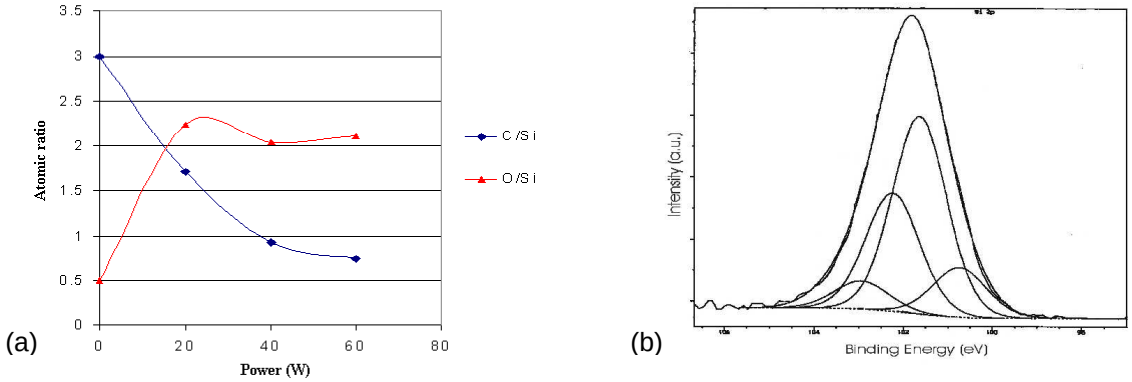

Figure 4. (a) C/Si and O/Si atomic ratios vs. power; (b) XPS Si_{2p} spectra for plasma deposited film at 2 Pa and 50 W for 8 minutes.

Morphological characterization of plasma coated fabrics

Surface morphology of coated fabrics was investigated by means of scanning electron (SEM) and atomic force (AFM) microscopies. Even if SEM micrograph (up to 5000 x) did not show significant morphological changes and no signs of the plasma polymer covering the wool surface were detected, the AFM analysis demonstrated the presence of a coating with a grain size of the order of 150 nm width. Anyway, owing to the irregularity of wool fabrics surface, the depositions were repeated on Si wafers, and it was possible to confirm that the film presented deposit islands, and the root mean square (RMS) roughness was of the order of 0.4 nm (Figure 5).

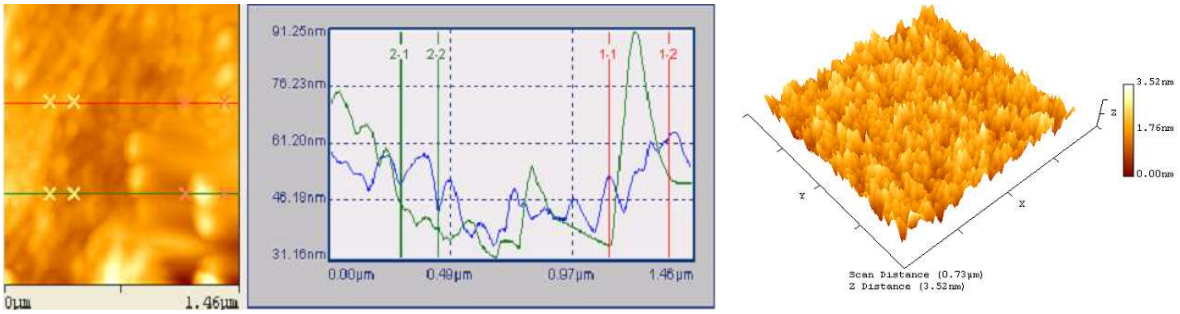

Figure 5. AFM images of the plasma coating on wool (right) and on silicon wafer (left).

Effects of the plasma process on pilling behaviour

The determination of fabric propensity to pilling and to surface fuzzing of knitted fabrics was assessed according to ISO 12945-2 modified Martindale method: a circular test specimen is subjected to a defined load and rubbed against a friction surface comprising the same fabric in a movement tracing a Lissajous figure; fuzzing and pilling are assessed visually after defined stages of rub testing, in accordance with a grading range from 5 (no change) to 1 (severe pilling and pills covering the whole specimen surface). Dealing with knitted fabrics the evaluations were made at six different assessment stages: 125, 500, 1000, 2000, 5000 and 7000 rubs.
Tables 1 shows the pilling grading of knitted wool fabrics, at each assessment stage, for treated and untreated fabrics. All plasma coated samples showed a reduction in the propensity to surface fuzzing and to pilling, at each assessment stage. Probably, the plasma polymerization determined the creation of a coating that slowed down the coming out of the fibres and, consequently, reduced pilling tendency. Evaluating the influence of the deposition parameters (power, deposition time and pressure), it was not possible to outline significant tendencies. An illustrative visual comparison between the pilling ratings of untreated and treated fabric is presented in Figure 6.

Assessment stage	Number of rubs	Untreated	Deposition 40 W 5 min 2 Pa	Deposition 40 W 9 min 2 Pa	Deposition 40 W 5 min 20 Pa	Deposition 40 W 9 min 20 Pa
1	125	3-4	4-5	4-5	4-5	4-5
2	500	3	4	4	4	4
3	1000	1-2	3-4	3-4	3	3-4
4	2000	1	3	3	2-3	3
5	5000	1	2-3	2-3	2	2-3
6	7000	1	2	1-2	2	2

Table 1. Surface fuzzing and pilling of knitted wool fabrics.

Figure 6. Knitted wool fabrics untreated (left, grade 1) and plasma coated (right, grade 2) at 5000 rubs.

After pilling test, the samples were analyzed by means of FTIR spectroscopy. Spectra of plasma coated sample before and after pilling test showed that the tested samples were characterized by a decrease of the absorption intensity of Si-O bond in Si-O-Si at about 1025 cm^{-1} compared to the coated sample. Moreover, also the absorption peak of CH_3 in $Si-(CH_3)_x$ at around 1260 cm^{-1} decreased and resulted in a little shoulder of Amide III peak of the wool. The mechanical stress during pilling test caused a partial removal of the deposited film. The results were encouraging and strengthened by a preliminary work, in which plasma coating was compared with a

wet anti-pilling treatment, carried out by impregnating the knitted wool fabric in an aqueous solution containing a softener and an amino-functional silicone emulsion. On that occasion, the results showed that the plasma deposition of the $Si:O_x:C_y:H_z$ thin film was a method to reduce pilling more effective than the conventional chemical treatment.

Effects of the plasma process on bursting properties

To evalutate possible damages and weakenings occurred to fabrics after plasma treatments their bursting strength was determined according to the pneumatic method described in ISO 13938-2. The bursting strength values of plasma coated samples were quite similar to (in many cases greater than) those of untreated ones. Thanks to these results it could be asserted and confirmed that plasma treatment did not weaken and damage the fabrics from a mechanical point of view.

Effects of the plasma process on low-stress mechanical properties

FAST integrated set of instruments had permitted to analyse low-stress mechanical properties regarding fabrics treated with different operating conditions, and to assess possible differences introduced by the plasma process in the compression, bending, tensile and shear behaviour of the fabrics. FAST measures fabric properties that are closely related to the ease of garment making-up and the durability of worsted finishing, and represents an inexpensive, robust, and simple to use alternative to the more complex Kawabata Evaluation System for Fabrics [5]. First of all, the results highlighted that the plasma process caused an increase in fabric thickness (Table 2).

	T2 (mm)	T100 (mm)
Untreated	0.473	0.336
Ar activation + Deposition 2 Pa 20 W 5 min	0.479 (+1.3%)	0.358 (+6.5%)
Ar activation + Deposition 2 Pa 20 W 8 min	0.487 (+3.0%)	0.355 (+5.6%)
Ar activation + Deposition 2 Pa 40 W 5 min	0.477 (+0.8%)	0.357 (+6.3%)
Ar activation + Deposition 2 Pa 40 W 6 min	0.496 (+4.9%)	0.357 (+6.3%)
Ar activation + Deposition 2 Pa 40 W 7 min	0.484 (+2.3%)	0.351 (+4.4%)
Ar activation + Deposition 2 Pa 40 W 8 min	0.494 (+4.4%)	0.357 (+6.3%)
Ar activation + Deposition 2 Pa 60 W 5 min	0.489 (+3.4%)	0.358 (+6.5%)
Ar activation + Deposition 2 Pa 60 W 6 min	0.496 (+4.9%)	0.354 (+5.3%)
Ar activation + Deposition 2 Pa 60 W 7 min	0.506 (+7.0%)	0.359 (+6.8%)
Ar activation + Deposition 2 Pa 60 W 8 min	0.500 (+5.7%)	0.358 (+6.5%)

Table 2. Measured fabric thickness at 2 gf/cm^2 (T2) and 100 gf/cm^2 (T100).

The plasma polymerization was responsible for the deposition of a thin polymeric film (the thickness of the deposited films, at different conditions, was measured by means of a profilograph resulting less than 100 nm), so it could not be the only answerable of the general increase in thickness revealed by compression measurements after the plasma process (from 4 to 33 μm). All these increments are at least one order of magnitude greater than the thickness of the plasma polymerized film. So the general thickening must be a consequence of the whole plasma process. As described above, prior to the deposition, Ar pre-treatment was carried out to clean, etch and activate the surface; besides, the polymerization step was carried out in a mixture of HMDSO, Ar (as neutral gas carrier for HMDSO vapour whose presence improves the

decomposition of the monomer) and O_2 (added to dilute the input gas mixture). It is known that O_2 and Ar plasma treatments lead to an increase in fabric thickness: the treated fabrics become fuller and a certain roughness on the surface is created, enhancing the inter-spaces between fibres and yarns and thus increasing the fabric thickness and compressibility [6, 7].
From bending measurements, it was possible to state that the plasma process induced an increase in bending length, and consequently in bending rigidity (Figure 7): this means greater resistance to bending and minor flexibility of the fabric.

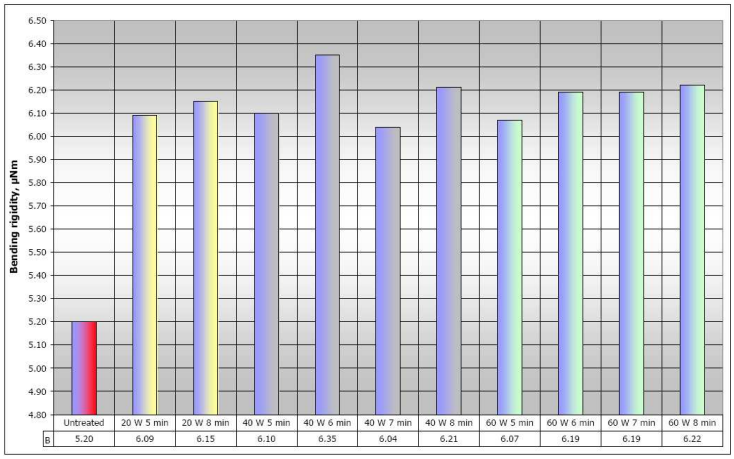

Figure 7. Bending rigidity (B) for untreated and plasma coated fabrics at different coating conditions (varying power and time) at 2 Pa.

Bending properties are important non only to aesthetic characteristics such as drape and hand, but also to the making up of an acceptable garment: a fabric of higher bending rigidity may be more manageable during sewing, resulting in a flat seam, but may cause problems during moulding [5, 8]. No particular trend related to changes in operating conditions was observed.
Starting from the considerations made for thickness measurements, the enhance of bending rigidity could be explained, in accordance with Yip *et al.*, with the rough surface that might impart more contact points between the fibres/yarns and thus enhance the fibre to fibre and yarn to yarn inter-friction; this increased friction develops a greater cohesive force among the yarns during the application of tensile, bending and shearing stresses [7]. The bending properties of a fabric depend, among other things, on the fabric structure and increase when the fabric thickness increases [6]: the results were consistent with the increase in fabric thickness reported above.
Finally, great influence of the plasma application was reported as concerns bias extensibility EB5: the plasma process caused a drastic decrease in bias extensibility, and consequently there was a great increase in shear rigidity (Figure 8), defined as shear load required to deform unit width of fabric to unit strain, and calculated as G = 123/EB5. The increase in shear rigidity might be explained in the same manner used for the explanation of the enhance of bending rigidity after the same process.
No particular trend related to different operating conditions was observed. Shear rigidity gives a measure of the ease with which a fabric can be deformed into a three-dimensional shape. With low shear rigidity the fabric easily distorts, giving rise to difficulties in laying up, marking and cutting; on the other hand, a high value means a fabric that is difficult to mould and where there are problems with sleeve insertion [8].

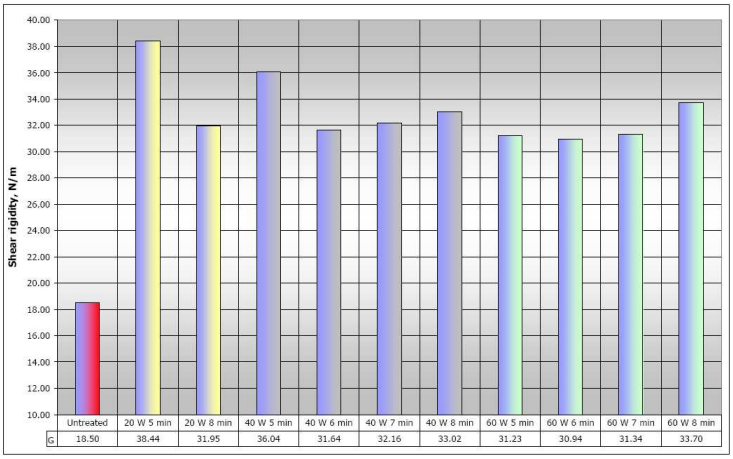

Figure 8. Shear rigidity (G) for untreated and plasma coated fabrics at different coating conditions (varying power and time) at 2 Pa.

Effects of the plasma process on air permeability

Air permeability is a property of textiles which influences the flow of gas from the human body to the environment and the flow of fresh air to the body. It depends mainly on fabric porosity, which means the number of canals in the textile fabric, its cross-section and shape, and has great influence on thermal properties.
The air permeability of a textile fabric is determined by the rate of air flow through a material under a differential pressure between the two fabric surfaces. It was measured according to ISO 9237. Figure 9 reports air permeability values for treated and untreated fabrics. It can be seen how the plasma process caused a lowering in air permeability of fabrics, in comparison with untreated ones (from 3.1 to 5.5%).

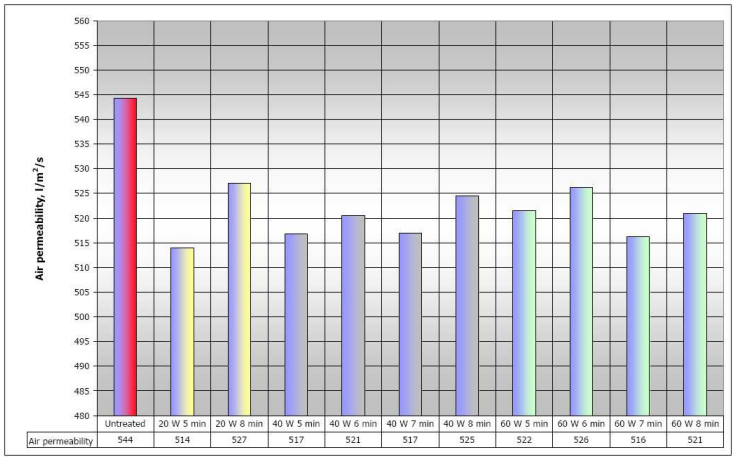

Figure 9. Air permeability for untreated and plasma coated fabrics at different coating conditions (varying power and time) at 2 Pa.

For plasma coated fabrics, no particular trend related to the variation of the process parameters was pointed out, at least for conditions tested in this work. All averaged values were quite similar and very near: the investigated LTP process decreased air permeability of the fabric. The air permeability is related to the construction characteristics (*e.g.* structure, thickness and surface) of the yarns and fabrics, and to the air entrapped within their structure. It is known that plasma etching did not alter

the fabric structure but rather fibre surface roughness and surface morphology [6, 7, 9]. Besides, the deposition of a thin polymeric film changes surface characteristics. As discussed before, these effects as a whole, closely related to the two-steps plasma process, enhance the inter-spaces between fibres and yarns, induce a certain degree of roughness on the fabric, and, as a consequence, increase the fabric thickness, resulting in changes that act as a boundary to hinder the air flow through the fabric and consequently reduce the air permeability of the fabrics [7, 9].

Evaluation of the washing resistance

To evaluate washing resistance, plasma coated samples were washed and dried according to ISO 6330. Two 7A wash cycles at 40±2 °C were used, with the total load of 1 kg for each cycle. To verify the persistence of the plasma deposited film on the fabrics after washing, washed treated samples were analysed by means of FTIR spectroscopy. All plasma coated and washed fabrics, at different process conditions, produced FTIR spectra with similar trend after the two wash cycles; the absorptions referable to the band of Si-O bond in Si-O-Si at 1020 cm^{-1} and to the band of CH_3 in Si-$(CH_3)_x$ at around 1260 cm^{-1} were no more present: when the coated fabric was subjected to washing stress, the deposited film was removed from its surface. It could be supposed that deposited coating was not bound to substrate through strong bonds (*e.g.* ionic bond and covalent bond), thus resulting in a poor adhesion to wool substrate. However, the washing procedure used is mainly specific to determine the dimensional changes and shrinkage of wool textile products; for this reason it may result too strong, and probably not suitable for our purpose. Anyway, different plasma pre-treatments (*e.g.* Ar/O_2 mixture), aiming to guarantee a better adhesion of the coating to the wool surface, will be considered in further investigations.

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