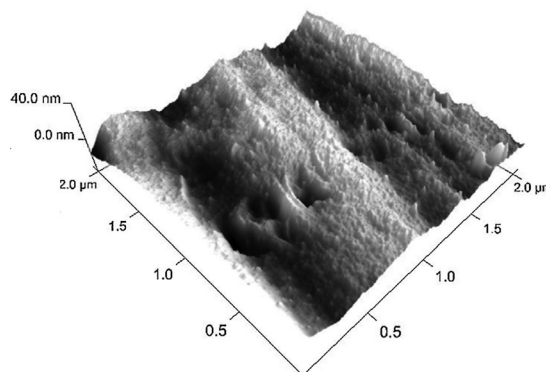


Plasma Treatment in Textile Industry

Andrea Zille,^{*,†} Fernando Ribeiro Oliveira,[†] Antonio Pedro Souto

Plasma technology applied to textiles is a dry, environmentally- and worker-friendly method to achieve surface alteration without modifying the bulk properties of different materials. In particular, atmospheric non-thermal plasmas are suited because most textile materials are heat sensitive polymers and applicable in a continuous processes. In the last years plasma technology has become a very active, high growth research field, assuming a great importance among all available material surface modifications in textile industry. The main objective of this review is to provide a critical update on the current state of art relating plasma technologies applied to textile industry.



1. Introduction

Nowadays, due to the increasing growth competition textile materials cannot be restricted to clothes, linen, tablecloth and curtains, but they also have to be regarded also as high-tech products that, in addition to the traditional clothing industry, find application in many technological fields, like construction, agriculture, automotive, aerospace and medicine. In this context, plasma technology has assumed a great importance among all available textile surface modifications processes.^[1] It is a dry, environmentally- and worker-friendly method to achieve surface alteration without modifying the bulk properties of different materials.^[2] Plasma, the ‘fourth state of matter’, is an electrically neutral ionized gas (i.e. electron density is balanced by that of positive ions) and contains a significant number of electrically charged particles not bound to an atom or molecule. The free electric charges make plasma

electrically conductive, internally interactive and strongly responsive to electromagnetic fields.^[3] Although there are plenty in nature (it is estimated that plasmas are more than 99% of the visible universe), plasmas can also be effectively produced in laboratory and industry. For the surface modification of polymers, the power is usually obtained from an electric field. This is responsible for accelerating the electrons, which collide with atoms or molecules producing new charged particles, such as ions or atomic molecules, electrons and photons.^[4] This provides opportunity for many applications, in particular to produce microelectronics, medical cauterization, plasma TVs and also for the treatment or modification of polymer films and textile fibres.^[5] Essentially, depending on the treatment conditions and processing requirements of the materials (sheets, membranes, fabrics, polymers) four main effects can be obtained with plasma treatments (Figure 1): (i) Cleaning effect. Mainly associated with changes in wettability and surface texture of the material may increase dye or finishing agents absorption; (ii) Increased microroughness. This can improve the adhesion of finishing agents, stamping and the behaviour of anti-felting finishing agents; (iii) Generation of free radicals. May induce secondary reactions such as crosslinking thus allowing graft polymerization and the reaction with oxygen or other gases to generate hydrophobic or hydrophilic surfaces; (iv) Plasma Polymerization. Allows the deposition of solid polymer with desired properties.^[6–8]

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There are numerous types of plasma and it is therefore very difficult to carry out a universal classification. However, a first simple and objective way to classify different kinds of plasma is to divide it into two categories: thermal and non-thermal.^[9] Thermal plasmas can also be artificially generated using several methods, such as DC or AC electrical discharges (free burning, pulsed and transferred arcs, plasma torches, lamps), laser, RF and microwave discharges at near-atmospheric pressure.^[10] In thermal plasmas, the temperatures are extremely high (some thousands degrees Celsius) and are characterized by the condition of thermal equilibrium between all the different species contained in the gas. Thermal plasma can be observed in the stars, lightnings, northern lights and other celestial bodies. No textile material can withstand the destructive nature of this type of plasma, thus it is not a topic for discussion. Non-thermal plasmas are those in which the thermodynamic equilibrium is not reached even on a local scale between the electrons and the higher mass particles (neutral atoms or molecules, ions and neutral molecules fragments). In this type of plasma, the temperature of the electrons is much higher than the temperature of other particles. The electrons can reach temperatures of 104–105 °K (1–10 eV), while gas temperature remains near to room temperature. Non-thermal plasmas, also called cold plasmas, are particularly suited for textile surface modification and processing because most textile materials are heat sensitive polymers.^[11] It has been shown that such forms of discharge have the major advantage of inducing significant surface chemical and morphological modifications thereby improving hydrophilicity and making fibres more accessible to various chemical species without altering the bulk properties of the materials.^[12,13] Cold plasmas may be divided into atmospheric pressure plasmas and vacuum or low-pressure plasmas. The advantages and disadvantages of these two types of plasmas are still topic for debate. The choice of the process to be applied depends on the processing speed, sample size and extent of the intended modification.^[14] Several research groups have concentrated their efforts on modifying polymer surfaces with plasma treatments using various gases. Most of the work done on that field has been accomplished with low-pressure plasma treatments. Vacuum plasma is often used to achieve various effects by etching, polymerization or formation of free radicals on the surface of the textile substrate.^[15] However, low-pressure plasma (LPP) technology requires expensive vacuum systems, therefore, making it difficult to upscale and obtain continuous processing. These factors have seriously limited the commercial viability of this technique in the textile industry.^[16]

In the past, it was believed that plasmas generated at atmospheric pressure were neither uniform nor stable. However, recent research on plasma generated at atmospheric pressure demonstrated excellent results for



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stability, uniformity, and workability in surface modification of textiles and many other types of material.^[6,7,11] Atmospheric plasmas are an alternative, cost-competitive methods to low-pressure plasma and wet chemical treatments, avoiding the need for expensive vacuum equipment and allowing continuous and uniform processing of fibres' surface.^[17]

There are four main types of atmospheric plasmas applied to textiles: (i) Corona is the oldest plasma technology applied on the modifications of polymer surfaces. Corona discharge is usually generated at atmospheric pressure by applying a low frequency and a high voltage (10–15 kV) between two electrodes of different shapes and sizes. The discharge energy density falls rapidly

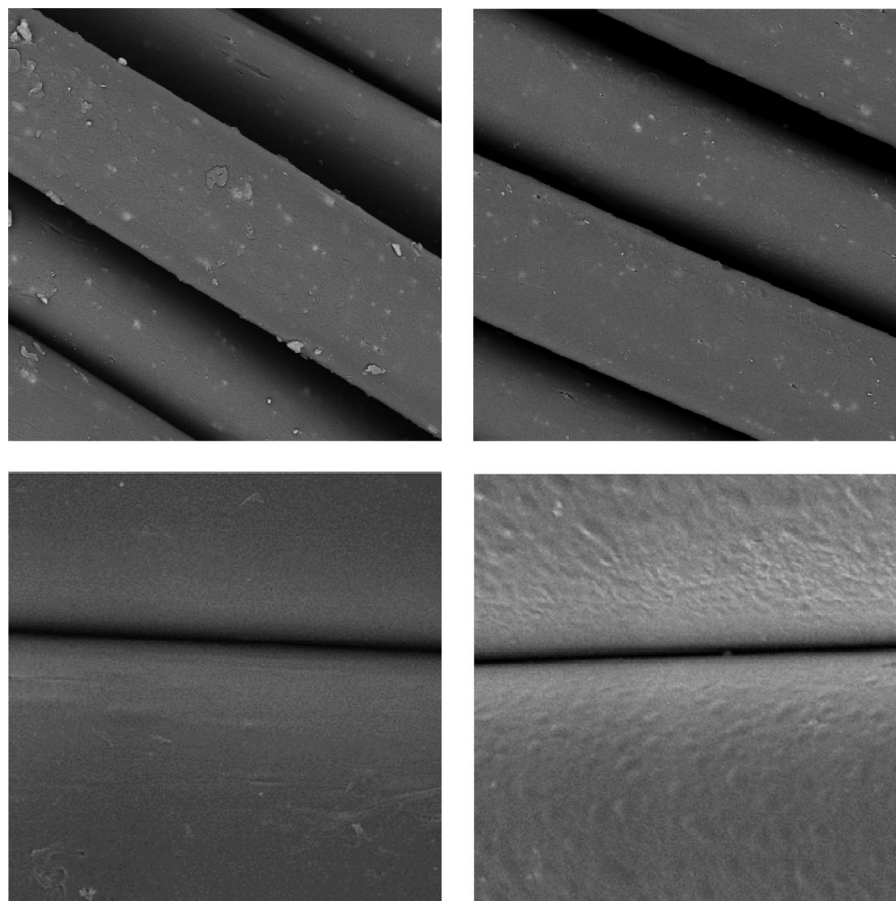


Figure 1. SEM images of a cleaning effect (4 000 \times) and surface microroughness (10 000 \times) of untreated (left) and air DBD plasma treated (right) polyamide 6,6.

in function of the distance between the electrodes consenting very small interelectrode spacing (≈ 1 mm), which are incompatible with thick materials and rapid, uniform treatments. Corona treatment may increase the fibres surface area and the surface roughness, however, it is an uneven treatment for textiles because it has a weaker ionization being non-uniform and only affecting loose fibres and not penetrating deeply into the fabrics;^[18] (ii) The dielectric barrier discharge technology (DBD) in air is one of the most effective non-thermal atmospheric plasma sources and has been attracting increasing interest for industrial applications due to its scalability to very large systems.^[7] In DBD plasma at least one of the electrodes is covered by a dielectric layer that accumulates the transported charge on its surface. The dielectric layer has two functions: it limits the amount of charge transported by a single micro-discharge and distributes the charge over the entire area of the electrode. However, DBD is not completely uniform and has short duration. This can interrupt the sequence of chemical reactions required to produce important species. It should be noted that occasionally in

literature, the term corona discharge or corona treatment has been improperly used in connection with DBD, but the corona term should only be used only for discharges between bare metal electrodes without dielectric;^[19] (iii) Glow discharge (APGD) is generated by a lower voltage and a higher frequency when compared with DBD plasma and it is characterized by a relatively long duration, uniformity, and low-to-moderate areal power densities avoiding surface heating or damaging. A radio-frequency source can be connected between two parallel electrodes, which are separated by few millimetres. To sustain a DC glow discharge, the electrodes must be conductive. In the simplest case, a discharge is formed by applying a potential from few kV up to 100 V between electrodes inserted into a cell comprising a gas, usually helium or argon, at atmospheric pressure;^[20] (iv) Atmospheric pressure plasma jet (APPJ) is significantly milder than a plasma torch but still highly effective at room temperature. Plasma jet has advantages over DBD because it can generate uniform reactive gases and can also be applied to the surface of any shaped object. However, APPJ can

only be applied to one side of the treated material directly facing the plasma jet.^[21]

Currently preserving a cleaner environment has become a major global concern. In recent decades, there has been the introduction of strict environmental legislations, especially in developed countries. However, the resolution of the environmental problems of textile industry is not a simple task. The numerous steps of textile processing such as desizing, bleaching, alkali treatment, mercerization, dyeing, printing, washing and finishing originate several different toxic, hazardous, and poorly biodegradable compounds. Due to the enormous environmental, economic potential and possibilities of using plasma discharge to modify the textile materials, this review offers the opportunity to update and critically discuss the latest advances on plasma technologies and applications for the textile industry.^[11,22]

2. Plasma in Textile Industry

Despite the high potential advantages, environmentally friendly approach and application possibilities of plasma technology its use in textile industry is still limited. Some responsibility can be attributed to the traditional and rigid management structure of the textile industry, but probably the real causes are intrinsically related to the properties of textile materials. Three main drawbacks may be reported: (i) Surface cleanliness. Since plasma treatment only influences the top layer, contaminations or different surface conditions (e.g. weft and warp direction) of the textile could have significant negative effects. (ii) Three-dimensional structure of textiles. Textiles are porous three-dimensional structure and plasma species could not penetrate deep enough into fabric structure to ensure proper treatment as the wet processes do. In this context, the pressure at which the plasma treatment is performed is a crucial variable. (iii) Large surface area. Textile materials whereas composed of individual fibres, are characterized by a large surface area, usually one order of magnitude larger than flat films.^[23]

In spite of that limitation, in the last years due to constant technological improvements and scientific research efforts, plasma technology is already used for several niche applications in textile industry and its use in new and improved methods for wider application is close to breakthrough. In the textile industry vacuum plasma technology has advanced significantly faster than atmospheric-pressure plasma technology because: (i) it is more simple produce large volumes of plasma at reduced pressure than at one atmosphere; (ii) it is easier to control the concentration, composition and process chemistry of the gas atmosphere in a closed system under vacuum; (iii) atmospheric plasmas are characterized by a higher

collisionality and a lower fractional ionization than vacuum discharges.^[24] Low-pressure plasmas are successfully employed in textile industry. Italian (HTP Unitex), Belgian (Europlasma) and Austrian (Textilveredelungs GmbH Grabher) manufacturers produce and sale roll-to-roll low-pressure gas plasma systems for surface activation in textiles to improve wettability and adhesion, and for a hydrophobic/oleophobic finishing with a plasma polymerization. The English P2i and the Italian SAATI companies employ low-pressure plasma chemical vapour deposition techniques to produce extremely durable water proofing textiles and to enhance the meshes durability for screen-printing, respectively. Other European plasma equipment providers also develop low-pressure plasma products for the textile market such as Grinp, Softal, iplas, Ahlbrandt Systems, and Arioli.^[23] In large roll-to-roll equipment low-pressure vacuum plasma treatment is in general economical viable. A typical full costing for plasma activation is in around $0.02 \text{ €} \cdot \text{m}^{-2}$.^[25] On the other hand, the costs of plasma coating at low pressure are higher ($\approx 0.05 \text{ €} \cdot \text{m}^{-1}$) because of the lower web speed and the more expensive process gases. The coating deposition is one of the most important processes in thin-film and composite manufacturing. In this field, the physical sputtering and the chemical vapour deposition under low-pressure plasmas are the dominant technologies. In coating application, atmospheric pressure plasma is limited by a few high process temperatures with very sophisticated configuration, huge energy loss from collisions and short mean free path. Atmospheric pressure plasma also requires high flow rates of the filling gas in order to provide an adequate plasma atmosphere and to obtain a drift of the reactants to the surface, since convection processes have to be overcome.^[26] Even when a gas recycling system is present, recovering around 80% of the used gas, the low-pressure plasma remains the more cost-efficient technology. Additionally, due to the fact that textiles contain large quantities of water when plasma treatment is done at atmospheric pressure, the influence of humidity on the treatment efficiency should be taken into careful account due to the potential formation of undesired chemical interfering species.^[27]

Despite the obvious advantage of low-pressure plasma in numerous applications, vacuum plasma must operate off-line in batch mode. Atmospheric pressure plasmas have a major throughput advantage in textile process that operate in open perimeter mode allowing continuous, on-line processing easily integrated into conventional textile finishing lines. In this context, assuming that the personal, infrastructure, maintenance and energy costs are comparable in both technologies, low-pressure systems are considered non-competitive since the running costs are higher due to the expensive vacuum pumping system and the Meissner trap (cryogenic coil) often required to avoid

the water evaporation in the vacuum chamber during unwinding of textiles.^[26] Extra requirements such as the ability to treat full width textiles of at least 2 m wide, and higher processing speeds at $20 \text{ m} \cdot \text{min}^{-1}$ are more economically addressed by atmospheric plasma treatment systems.^[28] Today several atmospheric plasma technologies and configurations meet the basic manufacturability criteria for textile processing. However, capital investment and processing costs must be carefully considered as well as the cost-benefit analysis for each case. For example, in the case of textile surface modifications using non-polymerizing gas, it is important taking in consideration the aging effect, which leads to gradual deterioration of the modified performance due to the reorientation and migration of polar groups into bulk material. Anyhow, successful examples of atmospheric-pressure plasma technologies applied to textile processes are available. A pilot-scale DBD apparatus build by the German company Softal in collaboration with the textile engineering department of the University of Minho (Portugal) was tested by a textile industry in order to replace the sizing, scouring and bleaching pre-treatments of cotton (Figure 2). The total costs of DBD were compared using a Jet and Pad-steam methods in a continuous process. All the costs of the conventional methods (between 0.147 and $0.055 \text{ €} \cdot \text{kg}^{-1}$) resulted higher than DBD ($0.013 \text{ €} \cdot \text{kg}^{-1}$). It is clear the economic advantage of applying the DBD technology in the cotton pre-treatment consuming only 23% of the direct variable cost in a continuous method.^[29] Already in the marketplace exist mature atmospheric pressure plasma technologies that are offering new textile properties and performances such as plasma-deposited functional coatings for technical applications. Softal, claims a payback time of only 9 months single-shift operation for its Aldyne plasma adhesion primer system versus conventional liquid priming.^[30] Sefar AG/Switzerland is a company specialized in high-performance filtration solutions and uses the world largest atmospheric pressure plasma systems for industrial applications. The machine is

installed inline textile processing and is capable of treating textiles up to 4 m wide with a speed up to $25 \text{ m} \cdot \text{min}^{-1}$. APJET (USA) company commercialize a proprietary all-dry APPJ[®] technology to produce 'dual-functional' textile fabrics repelling oil and water on the outside, while retaining its original qualities and comfort on the inside. Recently the Green Theme Technologies LLC company (USA) designed a so called ChemStik[®] technology to be compatible with a Dielectric Barrier Discharge (DBD) plasma, that could be operated using less expensive gases than helium such as nitrogen, oxygen and argon eliminating the need for a costly gas recycling system.^[26] These commercial atmospheric pressure plasma technologies are based on the most used configuration compatible for textile treatment: the corona, DBD and Glow Discharge.^[31] However, newer atmospheric devices have been recently developed: (i) the atmospheric pressure non-equilibrium plasma (APNEP) developed by EA Technology Ltd. in conjunction with the University of Surrey, and (ii) the APPJ, developed by researchers at Los Alamos National Laboratory. Both the system have already demonstrated great potential in wide range of applications such as surface cleaning, altering surface energy, surface oxidation and cross-linking.^[24] With the constant rise of the costs of raw materials, energy and water, the increasing cost advantages of atmospheric plasmas over wet processing in terms of low power, water and chemicals consumption, there is no doubt that atmospheric pressure plasmas stand on the edge of a revolution in textile processing.

3. Hydrophilicity

Plasma discharge is widely used to improve the wettability and/or hydrophilicity of numerous textile materials.^[32,33] Several studies were published in the last 10 years on the increase in hydrophilicity in several fibres such as polyester (PET),^[34,35] polyethylene (PE),^[36] polypropylene (PP),^[37] polytetrafluoroethylene (PTFE),^[16] silk,^[38] polyamide

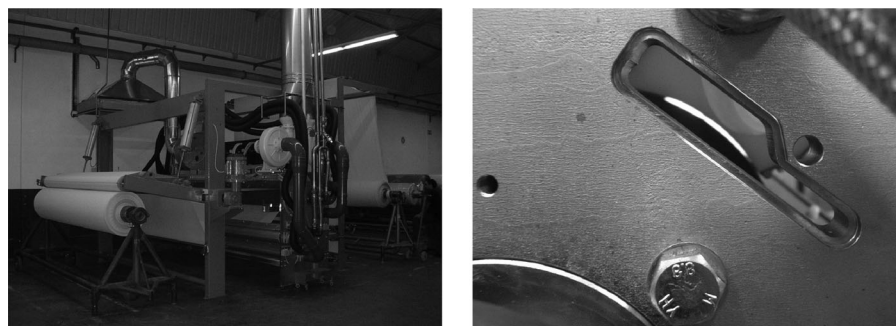






















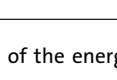
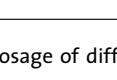
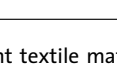
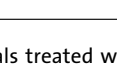
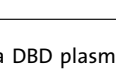
Figure 2. Industrial air DBD plasma apparatus (left) and detail (right) of the plasma discharge (white halo in the centre) for cotton pre-treatment in a Portuguese textile company.

(PA),^[39] nylon–cotton–elastane (NCE),^[7] polyimide (PI),^[16] hemp,^[6] aramid,^[9] carbon fibres,^[40] wool,^[21] cellulose^[41] and also leather.^[42] Plasma treatments to introduce hydrophilic functional groups such as $-\text{COOH}$, $-\text{OH}$ and $-\text{NH}_2$ are unquestionably the most studied over the last years. Freitas and collaborators modified para-aramid fibres (Kevlar) with O_2 , N_2 and Ar vacuum plasmas in order to study the effects on the hydrophilicity of the material. The results show a substantial improvement in hydrophilicity using O_2 and N_2 plasma treatments.^[43] Similar results were obtained in other researches with meta-aramid fibres after application of a DBD plasma discharge at atmospheric pressure.^[9,17] Canal et al. studied the role of the active species involved in the wool and polyamide 6 modifications using different gases (N_2 , O_2/N_2 , O_2) in microwave generated post-discharge plasma.

The action of these gases on the surface of the fibres was analysed by using dynamic contact angle technique, revealing greater wettability in all cases.^[22] The increase in wettability was assigned to the generation of new chemical groups and to the reduction/elimination of the fatty layer on the wool surface. Pappas et al. have also studied the effect of glow discharge plasma at atmospheric pressure with different gases (N_2 , C_2H_2) and treatment times (0.6–9.6 s) for films and fibres of polyamide 6.^[14] The results showed an improved wettability, stable for several weeks after treatment. Wool fibres were modified by low-frequency plasma glow discharge polymerization of acrylic acid. After plasma treatment the hydrophobic wool fabric became hydrophilic and the breaking strengths of fabrics were increased up to 26%. Average wrinkle recovery angle of the treated fabrics were between 157 and 178° , while that of untreated fabric was 180° .^[44] Significant decrease in contact angle and increase in surface energy of polyethylene, polyamide and polytetrafluoroethylene fabrics was observed after DBD plasma treatments in presence of He– O_2 gases.^[16] Xu et al. studied the modification of a polyester fabric after a Corona plasma irradiation. The wicking property of the material showed that the optimum hydrophilicity can be obtained with a treatment of 10 kV and a speed of $5\text{ cm} \cdot \text{min}^{-1}$ preserving hydrophilicity for a long period of time.^[45] Recently, Gorjanc et al. modified polyester cloth using corona treatment at the power 900 W , speed of $4\text{ m} \cdot \text{min}^{-1}$ and 30 passages. The X-ray Photoelectron Spectroscopy (XPS) analysis observed an increase in the O/C atomic ratio, confirming that oxygen is the main functional groups induced on the fibres surface.^[1] The influence of the number of passages was evaluated by Carneiro et al. in a DBD prototype equipment onto unbleached and bleached cotton fabrics under an applied energy of $1.2\text{ kW} \cdot \text{min} \cdot \text{m}^{-2}$. They found that the increase in hydrophilicity greatly depends on the cotton fabric properties; while raw fabric requires four passages to

achieve good wettability, only two passages are required for bleached cotton to reach similar wettability.^[46] Karahan and Özdogan also studied raw-cotton fabrics treatment in DBD plasma. They found that the hydrophilicity and the capillarity of the plasma treated samples in air and argon increased considerably. This study showed that a reduction in static contact angle is inversely proportional to the intensity and duration of plasma treatment. The best results were obtained when samples were subjected to a power of 60 W for $40\text{--}60\text{ s}$.^[47] Energy dosage parameters are also considered (Figure 3). Oliveira et al.^[48] showed the effect of different energy dosages of atmospheric DBD plasma in several textile fabrics.

Hwang et al. evaluated the physical and chemical changes induced by capacitively coupled atmospheric pressure helium plasma in non-woven polypropylene (PP). The results showed that by increasing the treatment time a rapid decrease in contact angle could be observed. The values went from the 105° of the untreated sample to 55° in the plasma-modified sample treated for 120 s . According to the authors, the longer the exposure of the material to plasma discharge the more hydrophilic functional groups are formed on the fabric surface.^[49] Another study confirms that the DBD plasma jet in argon and an argon/water vapour mixture can effectively enhance the hydrophilicity of several textile layers of PET and cotton and can thus modify the inner surface of porous materials.^[50,51] Similar results with the same type of plasma, but using He/ O_2 gas were observed in raw and grey cotton knitted fabric. The results showed a great improvement in hydrophilicity and in addition a huge improvement in combining de-waxing process with He/ O_2 plasma jet treatment.^[52,53] Another APPJ with oxygen demonstrated improved wettability by the simultaneously formation of polar groups and etching-promoted enhanced capillary flow on the surface of polyamide and polyester fabrics. On the other hand, this plasma jet treatment did not show any significant improvement in dryability when compared with untreated fabrics.^[54] The application of APPJ on woven wool fabric showed a great wettability improvement and uniform plasma treatment. These effects decreased with the increasing oxygen flow rate and jet-to-substrate distance, and increased with the increasing of treatment time.^[55] The surface modifications of viscose, Modal[®] and Lyocell[®] samples using standard chemical pre-treatment procedures were compared with a low-pressure oxygen plasma treatment. Bleaching and alkaline treatments increased the surface carboxylic acid content by approximately 4.8% and hydrophilicity by 24% while plasma treatment increased it by approximately 9.7 and 70%, respectively.^[56] Another research using a glow-discharge atmospheric-pressure plasma treatment showed that polylinen[®] fabric has a higher wettability than normal polyester fabric due to the combined effect of plasma

Dosage (W min m ⁻²)	Polyester	Polyamide	Acetate	Acrylic	Wool
0					
300					
600					
1200					
1800					

■ Figure 3. Contact angles in function of the energy dosage of different textile materials treated with a DBD plasma discharge in air.

treatment and modified yarn structure.^[57] Polyester fabrics were treated by atmospheric pressure plasma to enhance hydrophilic behaviour of the fibre surfaces. It was found that the plasma exposure not only increased the wettability, oxygen concentration and roughness of the polyester fibre surface, but the water wicking, antistatic property, detergency and dyeability were also successfully enhanced.^[35]

The wettability of a solid material is directly related to its surface energy and determines surface and interfacial phenomena including chemical reactivity, adsorption, desorption, wet processing and adhesion.^[58] The use of plasma discharge to improve this property in low-surface energy textile materials such as polyethylene, polypropylene and polyester is today a well-established technology. De Geyter and colleagues investigated the effect of plasma treatment on the surface energy of polyethylene. The results showed an increase in free energy of the material from 31.3 to 56.2 MJ · m⁻² after plasma treatment. They also verified that this increase is directly related to exposure time.^[59] Another exhaustive study using plasma with oxygen, argon and air for the modification of polyester fabric obtained a considerable increase in surface energy from 40 to 71 dynes cm⁻¹ after a treatment of only 60 s.^[60] These results were also corroborated in others substrates, such as polypropylene, polyester and polyethylene.^[61–64]

The increase in hydrophilicity/wettability is undoubtedly one of the most simple and quickly studied properties to identify surface modification of plasma treated textile

materials. As can be observed in Table 1, a wide number of different plasma techniques, especially atmospheric plasmas in air, were used in the last years to impart hydrophilicity properties onto textile surface. However, plasma–surface interactions are not yet fully understood because they are influenced by many complex factors, such as the chemistry of plasma gases, the nature of the substrate and the treatment operating parameters. Energy or power density is one of the most important parameters to understand the extension of plasma treatment and to calculate its cost-benefits. However, it is also one of the most disregarded parameters in literature. Often, only the output power of plasma machine is reported and frequently other different parameters, such as frequency, current and voltage are singularly reported without any other information. Albeit, recently, an effort to develop a quantitative tool to evaluate, understand and predict fabric surface modifications was proposed. It is clear that an uniformization of the hydrophilicity and wettability measures is imperative.^[65] Moreover, numerous methods are used including contact angle, wicking, capillary rise, feathering, wettability, drop-adsorption diameter, spreading time, absorptive capacity, etc. The most common is without a doubt, the contact angle technique. However, contact angle does not provide sufficient information about the wetting characteristics of textiles materials because it is very difficult to measure in irregular and high porous structures. On the other hand, wicking properties (expressed in height or time) may provide more reliable information about the wetting properties of textiles, but are not consistently used.

Table 1. Hydrophilicity of plasma treated textiles fabrics.

Plasma Type	Textile Substrate	Power (W)	Gas	Hydrophilicity (Control) Contact angle (°)	Reference	
APGD	Cotton	200 ^{a)}	Air	50 (0) ^{d)}	[66]	
	PA6	850	N ₂ , C ₂ H ₂ —He	58 (76)	[14]	
	PA6	50	He	1.1(540) ^{f)}	[60]	
	PET	50	He	6.7 (700) ^{f)}	[60]	
	PET	0.3 ^{a)}	Ar	51 (37) ^{d)}	[60]	
	PET	0.3 ^{a)}	Air	64 (37) ^{d)}	[60]	
	PET	0.3 ^{a)}	O ₂	83 (37) ^{d)}	[64]	
	Polylinen [®]	460	O ₂	4.3 ^{d)}	[57]	
	PP	0.005 ^{c)}	He	55 (105)	[49]	
	Wool	150	Air	780 (135) ^{g)}	[67]	
	Wool	40–100	C ₃ H ₄ O ₂	14 (0) ^{d)}	[64]	
	APPI	Cotton	40	O ₂ —He	100 (141)	[52]
		Cotton	40	O ₂ —He	17.2 (139)	[53]
Cotton (hexane)		40	O ₂ —He	0 (137)	[52]	
PA		13.6 ^{c)}	O ₂ —He	0 (86)	[54]	
PET		14–20	Ar	0 (150)	[68]	
PET		13.6 ^{c)}	O ₂ —He	0 (87.5)	[54]	
PET		100	O ₂ —He	0 (200) ^{f)}	[69]	
PET filament		n.a.	Air	25 (0) ^{d)}	[35]	
PET spun		n.a.	Air	55 (18) ^{d)}	[35]	
PP		14–20 ^{b)}	Ar	60 (120)	[68]	
Wool		40	O ₂ —He	300 (1200) ^{f)}	[21]	
Wool		40	O ₂ —He	0 (10) ^{f)}	[55]	
Wool		13.56 ^{c)}	O ₂ —He	59 (116)	[70]	
Corona		Cotton	530	Air	1 (100) ^{f)}	[46]
	PA6	n.a.	Air	47 (332) ^{f)}	[71]	
	PET	n.a.	Air	134 (877) ^{f)}	[71]	
	PET	7.1 ^{a)}	Air	450 (40) ^{h)}	[72]	
	PET	6 000	Air	17 (5) ^{d)}	[45]	
	Wool	n.a.	Air	91 (>2 000) ^{f)}	[71]	
DBD	Acrylic	600	Air	≈0 (85)	[48]	
	Aramid	23.33 ^{a)}	Air	140 (100) ^{d)}	[9]	
	Aramid	33.33 ^{a)}	Air	175 (100) ^{d)}	[9]	
	Aramid	27.6 ^{a)}	Air	35.9 (64.3)	[17]	
	Carbon fibres	0.008 ^{c)}	Air	42.7 (98.6)	[40]	
	Cotton	50	Air	98.3 (107.8)	[47]	
	Cotton	100	Air	32.8 (107.8)	[47]	
	Cotton	130	Air	0 (107.8)	[47]	
	Cotton	50	Ar	0 (107.8)	[47]	
	Cotton	100	Ar	0 (107.8)	[47]	
	Cotton	130	Ar	0 (107.8)	[47]	

Table 1. Continued

Plasma Type	Textile Substrate	Power (W)	Gas	Hydrophilicity (Control) Contact angle (°)	Reference
LPP	Diacetate	600	Air	≈0 (0)	[48]
	NCE	5 ^{b)}	Air	10 (39) ^{e)}	[7]
	PA	600	Air	≈0 (110)	[48]
	PA	5 ^{b)}	Air	9 (28) ^{e)}	[7]
	PA12	5.7 ^{b)}	Air	42 (101)	[73]
	PA6	5.7 ^{b)}	Air	36 (75)	[73]
	PA6	1 200	He—O ₂	30.2 (68.2)	[16]
	PA66	2 400 ^{a)}	Air	50.4 (323.5) ^{f)}	[74]
	PA66	500–1 500	Air	≈50 (≈80)	[39]
	PE	2 ^{a)}	Air	37 (70)	[75]
	PE	0.7 ^{a)}	N ₂	30 (70)	[75]
	PE	0.12 ^{a)}	Ar	24 (70)	[75]
	PE	1 200	He—O ₂	42.3 (92.4)	[16]
	PE	6	Air	53.5 (101.7)	[59]
	PET	2 ^{a)}	Air	30 (58)	[75]
	PET	0.12 ^{a)}	Ar	15 (58)	[75]
	PET	600	Air	≈0 (120)	[48]
	PET	5 ^{b)}	Air	7 (10) ^{e)}	[7]
	PET	50 ^{b)}	Air	730 ^{g)}	[76]
	PET	50 ^{b)}	He	500 ^{g)}	[76]
	PET	50 ^{b)}	Ar	570 ^{g)}	[76]
	PET	n.a.	Air	1 000 (600) ^{h)}	[77]
	PET	500–1 500	Air	≈50 (≈80)	[39]
	PET	500 ^{b)}	Air	12 (80)	[61]
	PI	1 200	He—O ₂	15.8 (62.7)	[16]
	PP	2 ^{a)}	Air	46 (103)	[75]
	PP	0.7 ^{a)}	N ₂	32 (103)	[75]
	PP	0.12 ^{a)}	Ar	30 (103)	[75]
	PP	200 ^{b)}	Air	350 ^{g)}	[76]
	PP	200 ^{b)}	He	300 ^{g)}	[76]
	PP	200 ^{b)}	Ar	340 ^{g)}	[76]
	PP	0.5 ^{b)}	N ₂	3.2 ^{f)}	[78]
	PTFE	1 200	He—O ₂	82.1 (121.3)	[16]
	Wool	600	Air	≈0 (145)	[48]
	Wool	5 ^{b)}	Air	137 (202) ^{e)}	[7]
	Aramid	n.a.	Ar	45 (35) ^{d)}	[43]
	Aramid	n.a.	N ₂	68 (35) ^{d)}	[43]
	Aramid	n.a.	O ₂	80 (35) ^{d)}	[43]
	Aramid	0.38 ^{a)}	O ₂	600 (0) ^{d)}	[79]
	Cotton	0.64 ^{a)}	O ₂	25 ^{h)}	[80]
Cotton	300	O ₂	19.7 (60.6)	[81]	

Table 1. Continued

Plasma Type	Textile Substrate	Power (W)	Gas	Hydrophilicity (Control) Contact angle (°)	Reference
	Lyocell [®]	500	O ₂	18 (74)	[56]
	Modal [®]	500	O ₂	25 (83)	[56]
	PA6	60	N ₂	43.2 (71.4)	[22]
	PA6	60	O ₂	35.5 (71.4)	[22]
	PE	40	Ar	28 (88)	[36]
	PET	150	SiCl ₄	58 (89)	[82]
	PET	n.a.	O ₂ , N ₂ , H	80 (1) ^d	[83]
	PET	0.4 ^b	O ₂ , N ₂	1 000 (20) ^h	[84]
	PET	7.7 ^b	Air	>10 (350) ^f	[85]
	PET	0.38 ^a	O ₂	500 (0) ^d	[79]
	PP	300	O ₂	46 (99)	[86]
	PP	500	O ₂	83.9 (121.5)	[37]
	Viscose	500	O ₂	16 (66)	[56]
	Wool	300	O ₂	23.8 (79.7)	[81]
	Wool	60	N ₂	67.7 (102.8)	[22]
	Wool	60	O ₂ –N ₂	69.6 (102.8)	[22]
	Wool	60	O ₂	58.2 (102.8)	[22]

^a)Power density (W · cm⁻²); ^b)Energy density (J · cm⁻²); ^c)Frequency (MHz); ^d)Wicking height (mm); ^e)Wicking time (mm); ^f)Wettability (s); ^g)Absorptive capacity (%); ^h)Feathering area (mm²); n.a. not available.

4. Hydrophobicity

The hydrophobicity of a textile substrate can be obtained by introducing hydrophobic functional groups as coating or graft co-polymerization. The most commonly used methodology consists of the graft polymerization of the fibres with fluorocarbons or novel finishes such as silicones. Another frequently used method involves the immersion of the fabric in a liquid formulation containing a polymer and hydrophobic activators. Later, the textile material is treated with plasma, which promotes the graft polymerization onto the fibre surfaces.^[87] However, the method with the highest potential is the deposition of a polymer onto the fibres during the plasma treatment. The deposition can occur while the plasma is excited (plasma polymerization) or in a two-step process: (i) creation of radicals on the fibre surface by plasma in inert gas (e.g. argon) and (ii) reaction of these radicals with unsaturated monomers.^[11] As can be observed in Table 2, numerous studies with different plasma discharges were conducted with the objective of increasing the hydrophobicity of various textile fibres, such as polyesters (PET),^[88–90] polyacrylonitrile (PAN),^[91] polypropylene (PP),^[92] cotton,^[24,93–96]

cellulose,^[97] cellophane,^[92] silk,^[98] poly(lactic acid) (PLA)^[99] and cotton/polyester blends.^[20] In particular, the increase in fabric hydrophobicity using plasma with polymerizing fluorocarbon gases such as hexafluoropropylene,^[100] fluoro-decyl acrylate,^[101] hexafluoroethane^[102] and tetrafluoromethane^[92] were deeply investigated. In a study by Iriyama and Yasuda, it was observed that the plasma treatments with tetrafluoromethane and hexafluoroethane did not provide good coating durability to the fabrics. This effect was assigned to the formation of small polymer chains adsorbed on the fabric surface.^[103] Hodak et al.^[104] used a radio frequency (RF) inductively coupled plasma in an atmosphere of hexafluoroethane to modify the surface of silk to increase hydrophobicity obtaining a significant increase of the contact angle from 0 to 145°. Another research using the same gas and fabric was performed using a low-pressure plasma obtaining an increase of contact angle from 70 to 130°.^[105] Shen and Dai studied the influence of plasma discharge in vacuum with hexafluoroethane in silk and cotton. After just a minute of treatment, the contact angle was increased from 0 to 120°. XPS technique confirmed that both sides of the fabrics were functionalized.^[106] A vacuum RF plasma discharge was

Table 2. Hydrophobicity of plasma treated textiles fabrics.

Plasma Type	Textile Substrate	Power (W)	Monomer (Carrier Gas)	Contact Angle (°)	Reference
APDG	Cellulose	0.019 ^{c)}	C ₄ H ₆ (He)	142	[97]
	Cellulose	250–400	CH ₄ (He, Ar)	113	[94]
	Cotton	750	C ₁₁ H ₇ F ₁₃ O ₂ (He)	159	[117]
	Cotton	250–400	CH ₄ (He, Ar)	150	[94]
	Cotton	0.019 ^{c)}	C ₈ H ₈ (He)	126	[120]
	Cotton/PET	600	C ₁₃ H ₇ F ₁₇ O ₂ /C ₁₅ H ₇ F ₂₁ O ₂ (Ar)	140	[121]
	PET	200	C ₆ H ₁₈ OSi ₂ (Ar)	9 ^{a)}	[113]
	PET	4 000	C ₆ H ₁₈ OSi ₂ (He)	142	[119]
	PET	4 000	C ₈ H ₂₀ O ₄ Si (He)	136	[119]
	Viscose	0.022 ^{c)}	C ₄ H ₆ (He)	143	[118]
Corona	PET	5 000 ^{d)}	(CH ₃) ₃ SiO[(CH ₃)(H)SiO] _n Si(CH ₃) ₃	127	[111]
DBD	Cotton	2 000	C ₆ H ₁₈ OSi ₂ (Ar)	140	[122]
	Cotton/PET	4 000	C ₆ H ₁₈ OSi ₂ (He, Ar)	150	[123]
	PET	1 000	Unidyne TG-571 [®]	141	[90]
LPP	Cellophane	150	CF ₄	75	[92]
	Cellophane	450	CF ₄	132	[92]
	Cellulose	120	CF ₃ CHF ₂	167	[108]
	Cellulose	50	CF ₄ (O ₂ , Ar)	153	[124]
	Cellulose	300	CHF ₃	155	[125]
	Cotton	100	C ₃ F ₆	128	[100]
	Cotton	80	C ₂ F ₆	85	[104]
	Cotton	40	C ₈ F ₁₇ CH ₂ CH ₂ OCOCH=CH ₂	>145	[107]
	Cotton	50	Diamond-like carbon (O ₂)	146	[95]
	Cotton	50	Diamond-like carbon (Ar)	145	[95]
	Cotton	50	Diamond-like carbon (H ₂)	123	[95]
	Cotton	5 000	Dynasylan F 8815 [®] (H ₂ O)	154	[96]
	Cotton/PET	30	C ₃ F ₈	5 ^{b)}	[20]
	Cotton/PET	40	C ₈ F ₁₇ CH ₂ CH ₂ OCOCH=CH ₂	>145	[107]
	Nomex [®]	40	C ₈ F ₁₇ CH ₂ CH ₂ OCOCH=CH ₂	>145	[107]
	PA	40	C ₈ F ₁₇ CH ₂ CH ₂ OCOCH=CH ₂	>145	[107]
	PA6	100	CF ₄	>900 ^{e)}	[126]
	PA66	40	C ₆ H ₁₈ OSi ₂ (O ₂)	150	[112]
	PAN	100	C ₁₃ H ₇ F ₁₇ O ₂ (Ar)	132	[91]
	PET	40	C ₆ H ₁₈ OSi ₂	138	[127]
	PET	400	SF ₆	132	[127]
	PET	40–400	SF ₆ , C ₆ H ₁₈ OSi ₂	143	[127]
	PET	13.56 ^{c)}	H ₂ C=CHCO ₂ CH ₂ CH ₂ (CF ₂) ₇ CF ₃ (He)	9 ^{a)}	[99]
	PET	150	CF ₄	109	[92]
	PET	450	CF ₄	115	[92]
	PET	100	CH ₃ (CH ₂) ₁₇ Si(OCH ₃) ₃	>150	[115]
	PET	100	CH ₃ Si(OCH ₃) ₃	>150	[115]

(Continued)

Table 2. Continued

Plasma Type	Textile Substrate	Power (W)	Monomer (Carrier Gas)	Contact Angle (°)	Reference
	PET	40	C ₈ F ₁₇ CH ₂ CH ₂ OCOCH=CH ₂	>145	[107]
	PET	50	C ₆ H ₁₈ OSi ₂	135	[110]
	PET	40	C ₆ H ₁₈ OSi ₂ (O ₂)	150	[112]
	PET	80	C ₆ H ₁₈ OSi ₂ (Ar)	145	[128]
	PLA	13.56 ^{c)}	H ₂ C=CHCO ₂ CH ₂ CH ₂ (CF ₂) ₇ CF ₃ (He)	9 ^{a)}	[99]
	PP	150	CF ₄	140	[92]
	PP	250	CF ₄	153	[92]
	Silk	50	SF ₆ (Ar)	130	[98]
	Silk	100	C ₃ F ₆	122	[100]
	Silk	50	SF ₆	145	[104]
	Silk	50	SF ₆	140	[105]
	Wool	80	C ₂ F ₆	88	[102]
	Wool/PET	40	C ₈ F ₁₇ CH ₂ CH ₂ OCOCH=CH ₂	>145	[107]

^{a)}3M Water repellency rating number; ^{b)}Bundesmann test rate; ^{c)}Frequency (MHz); ^{d)}Voltage (V); ^{e)}Wetting time (s).

used to polymerize a fluoro-acrylate monomer (PFAC8) on cotton/polyester, cotton, polyester, polyamide, Nomex and wool. The experiments demonstrate that the combination of fluoropolymer coatings with 'hairy' fibres is particularly beneficial for optimizing liquid repellence. However, none of the investigated textile surfaces can be regarded as super-repellent to low-surface tension liquids.^[107] Superhydrophobicity on cellulose paper was obtained by selective etching in oxygen plasma followed by a coating with a thin fluorocarbon film deposited via plasma-enhanced chemical vapour deposition using pentafluoroethane as precursor. Variation of plasma treatment yielded two types of superhydrophobicity: 'roll-off' (contact angle 166.7°; hysteresis 3.4°) and 'sticky' (contact angle 144.8°; hysteresis 79.1°).^[108] Over the last decades, fluorocarbons were used to reduce fibre friction thanks to their low-friction coefficients and hydrophobic properties. However, the price of these fibres remains high and is a major limitation for the textile market. Another commonly used method of obtaining hydrophobic surfaces by plasma polymerization is the use of ultrathin SiO_x (siloxane coatings) or amorphous hydrogenated carbon films on polymers due to their biocompatibility and wetting properties.^[109] Previous studies on plasma-polymerized hexamethyldisiloxane (HMDSO) coatings on fabrics or directly on the fibres have shown a reduction of the friction on flexible substrates thanks to their hydrophobization by the retention of -CH₃ groups within a Si-O network.^[110] Lei et al. performed a superficial copolymerization on polyester using fluid hydrogen silicone onto fabric through a corona plasma discharge. The

polyester fabric showed a significant difference in contact angle as a function of treatment time passing from 71 to 127° after 30 s.^[111] The effects of HMDSO coated on PA and PET using RF plasma were investigated to evaluate the frictional properties. The water repellence of the fabrics coated with HMDSO (contact angle increased to around 150°) has a positive effect on reducing friction coefficient under wet conditions. However, the hardness of the coating and the nature of the counterpart influence the coating delamination and the skin-to-textile frictional properties negatively. Thus, the use of fluorocarbon fibres remains nowadays, the most efficient solution to lower the coefficient of friction between textiles and the skin.^[112] Highly hydrophobic polyester fibres were obtained with atmospheric pressure middle frequency (MF) and radio frequency (RF) plasma system using HMDSO and Argon as carrier gas. The increase of plasma exposure time shows a proportional increase of Si-O-Si, Si-(CH₃)₂ and Si-C bonds in relation to untreated PET fibres.^[113]

Another strategy to obtain hydrophobic surface in textiles is the plasma-assisted nanofunctionalization through the deposition of nanoparticles, sol-gels or by nanotexturing the surfaces. Zhang et al.^[114] obtained a contact angle of 164° on cotton coated with a thin-film of hydrophobic nanoparticles. Nanostructured PET has been prepared by domain-selective O₂ plasma etching. Subsequently, to reduce its surface energy, a hydrophobic layer was formed on the nanotextured substrate by means of chemical vapour deposition. Since the nanotextures remained after the organosilane layer coatings, the

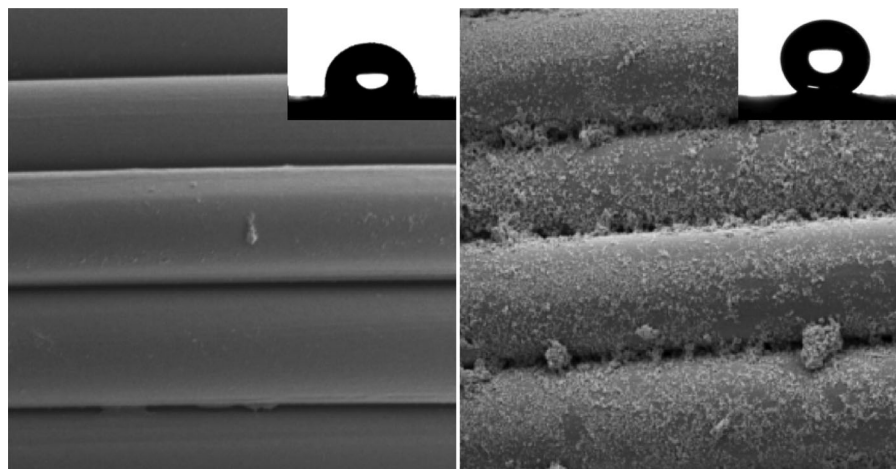


Figure 4. SEM images of untreated (left) and atmospheric DBD plasma treated polyamide 6,6 coated with a superhydrophobic nanolayer of ZnO/PMMA. Inset: water contact angles before and after treatment.

substrates showed ultra-water-repellence with water contact angles higher than 150° .^[115] Super hydrophobic nanotextured surfaces robust and stable in time were also obtained by O_2 plasma etching in poly(methyl methacrylate) (PMMA) and poly(ether ether ketone) (PEEK) following by C_4F_8 deposition. Aging of super hydrophilic surfaces (contact angle of 153°) was significantly retarded because of the valuable effect of the nanotextured topography.^[116]

Most of the available literature about superhydrophobic coating of textiles was carried out using vacuum plasmas that is very expensive, difficult to upscale and obtain continuous processing. However, in the last 5 years several research groups have developed superhydrophobic coatings on textiles using cost-competitive atmospheric pressure plasmas demonstrating excellent results (Figure 4).^[90,113,117–120]

5. Desizing

The application of sizing agents to warp yarns plays an important role in high weaving efficiency by increasing yarn strength and reducing yarn hairiness. Carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA) and polyacrylic acid esters (PAA) are the most utilized sizing agents. Sizing agents must be completely removed by desizing prior to dyeing and finishing fabrics with many disadvantages such as high energy and water consumption.^[28] Plasma can effectively aid desizing since it does not involve such large quantities of chemicals and water as the conventional desizing does. However, an efficient fibrous surface cleaning needs a careful selection of the type of plasma treatment in order to avoid fibre damage. Most of the research efforts are clearly focused in the plasma desizing of cotton. Cai et al. used an atmospheric glow

discharge plasma treatment with two different gas compositions Air/ O_2 /He and Air/He for the desizing of cotton sized with PVA. They found that both treatments removed a portion of the film of PVA and significantly facilitated the removal of PVA with a simple cold wash. The XPS analysis of the samples treated with PVA revealed plasma surface chemical changes, such as chain scission and formation of polar groups, which were deemed responsible for the solubility of PVA in cold water. They also verified that the plasma using oxygen was more effective.^[129]

Also atmospheric DBD plasma treatment has been proven to be an effective technique for improving efficiency of size removal in cold water, thereby reducing energy cost. It was observed that the rate of cotton desizing increases when the fabric is pre-treated with plasma. This phenomenon of surface etching and chemical modifications can be used advantageously for industrial processing.^[130] Another author suggested a mechanism of the PVA particle extraction during the plasma discharge. In this study, different treatment times and gases mixtures including He/ O_2 and He/ CF_4 were used. The results showed a progressive reduction in average molecular weight of PVA chains increasing treatment time. This reduction was attributed to chain scission caused by plasma discharge.^[131] In two surveys conducted by Carneiro et al. it was possible to observe a considerable increase in the quality of preparation of cotton fabrics treated with DBD plasma in air. According to the authors, the increase in hydrophilicity observed after DBD treatment becomes crucial in textile desizing, alkaline boiling, bleaching, dyeing, printing and finishing processes.^[132,133] The effect of plasma discharge on the bleaching of grey cotton fabric has also been studied by varying power discharge and number of discharges. To achieve a high

degree of whiteness, a two-stage process is suggested wherein the plasma discharged fabric is further treated with hydrogen peroxide.^[134] The same authors have also studied the cotton mercerization after DBD plasma treatment. The effect of mercerization is greater when the plasma treatment is applied as observed in the analysis of the frequency of the ratio between the axes of the cross sections of the raw cotton mercerized with wetting agent with and without plasma treatment. The change in cross sections is obtained even without the use of wetting agents. The mercerization without the use of wetting agents means better conditions of recovering the sodium hydroxide in the bath, with low costs and smaller environmental impact.^[135] The effect of argon/oxygen atmospheric DBD treatment on desizing and scouring of PVA on cotton fabric was studied regarding the treatment duration by Peng et al. Solubility measurement revealed that plasma treatment increased PVA solubility in hot washing but was less effective in cold washing. The results of the yarn tensile strength test showed that the plasma treatment did not have a negative effect on fabric tensile strength.^[136] The same author also investigated the moisture influences in the desizing of PVA on cotton fabrics treated with an APPJ. Solubility measurement reveals that the sample with the lowest moisture regain has the highest desizing effectiveness and the desizing ratio reaches 96% after 64 s exposure plus a 20 min hot wash.^[137] A study combining the influence of the He/O₂ APPJ and ultrasound treatment on desizing of the blended sizes of starch phosphate and PVA on cotton fabrics shown higher effectiveness in desizing. Wickability analysis reveals that the capillary height of the fabrics treated by plasma and ultrasound was higher than that of the fabrics treated by plasma and hot washing under different plasma exposure time.^[138] Several plasma treatments in desizing of PVA from cotton have been recently investigated confirming that plasma treatments are effective in improving efficiency of PVA size removal in cold and hot water and reinforcing the idea that the time of their industrial scalability is mature.^[139–143]

Few examples of plasma desizing applied to other textile substrates are available in literature. The most studied substrate after cotton is polyester. Bae et al. used a low-pressure plasma treatment as an alternative for desizing cleaning of a PET fabric. As indicated by weight loss, O₂ plasma treatment efficiently removed sizing agents such as PVA, polyacrylic acid esters (PAA) and their mixture on fabric. Additionally, the desizing effluent from the treated fabric gave lower TOC, COD and BOD values.^[144] Li and Qiu studied the influence of He/O₂ APPJ treatment on subsequent wet desizing of polyarylate on PET fabrics. A 99% of desizing ratio was achieved after 65 s plasma treatment followed by a 5 min NaHCO₃ desizing. Compared to conventional wet desizing, plasma treatment could significantly reduce desizing time.^[145,146] In another work, the

effect of atmospheric DBD plasma treatment on desizing PVA on PET fabric was compared with desizing in alkali bath. The results confirmed that DBD plasma treatment can improve desizing rate, surface colour depth and dye-uptake for polyester fabric.^[147]

A new degumming method was also recently developed also for silk using a low-pressure and glow discharge argon plasma. In comparison with a conventional degumming process, the suggested method achieved comparable degumming efficiency and properties of silk fabric, and it was more environmental friendly by shortening the conventional wet-chemical treatment process, saving the dosage of degumming agents, water and energy.^[148]

6. Dyeing

In general, conventional dyeing processes have a low yield, and the percentage of dye lost in the effluents can reach up to 50%. Besides the obvious aesthetic problem, dye wastewaters without an appropriate treatment can persist in the environment for extensive periods of time and are deleterious not only for the photosynthetic processes of the aquatic plants but also for all the living organisms since the degradation of these can lead to carcinogenic substances.^[149] In this context, plasma technology inducing significant surface modifications and removing the natural or synthetic occurring grease and wax in textile fibres, has proved to increase dyeing rates of textile polymers, to improve the diffusion of dye molecules into the fibres, to enhance colour intensities and washing fastness of several fabrics such as cotton,^[81,150,151] polyamide,^[13,74,126] polyester,^[152,153] polypropylene,^[154,155] silk,^[156] and wool.^[157–160] The higher dye exhaustion provided by plasma application improves dyeing uniformity achieving high levels of strength and decreasing the amount of dyestuff and water necessary for a desired shade.^[161,162] The possibility of reusing the water effluent contributes to a reduction of the effluent load with a significant diminution in costs and environmental impact.^[163] As can be noted in Table 3, plasma technology has been employed to improve the dyeability of the most important industrial textile fabric materials. Despite the low-pressure plasmas being already largely investigated, during the last 5 years the atmospheric pressure plasmas have revealed to be an effective alternative to dye polyamide and wool fibres. Excellent results were obtained by dyeing polyamide (PA) fabrics with acid, direct and reactive dyes after DBD plasma treatment. The chemical and physical effects of the plasma discharge, such as the formation of strong bonds between the dye and the polyamide fibres, which contribute to achieve high levels of colouristic and fastness properties.^[13,164,165] In a study by Oktem et al. carboxylic acid groups were

Table 3. Plasma assisted dyeing of textile fabrics.

Textile Substrate	Plasma Type	Plasma Method	Power (W)	Dye (C.I.)	K/S (Control)	Wash Fastness (ΔE) [*]	Reference
Cotton	APPJ	He + O ₂	150	Red Pigment	2.3 (1.2)	n.a.	[199]
	Corona	Air	380	Reactive Blue	4.7 (4.1)	n.a.	[197]
	Corona	Air	660	Reactive Black 5	n.a.	4–5 (4–5) ^{a)}	[151]
	Corona	Air	660	Reactive Red 158	n.a.	5 (5) ^{a)}	[151]
	Corona	Air	1 000	Direct Red 80	60 (55) ^{d)}	5 ^{a)}	[46]
	Corona	Air	1 000	Direct Red 243	70 (65) ^{d)}	5 ^{a)}	[46]
	DBD	Air + TETA	100	Acid Red 99	1.1 (0.7)	5 (5) ^{a)}	[150]
	DBD	Ar + TETA	100	Acid Red 99	1.4 (0.7)	5 (5) ^{a)}	[150]
	LPP	EDA	20	Reactive Black 5	13.6 (10.5)	5 (5) ^{a)}	[200]
	LPP	TETA	20	Reactive Black 5	14.1 (10.5)	5 (5) ^{a)}	[200]
	LPP	Ar + EDA bath	20	Reactive Black 5	17.3 (10.5)	5 (5) ^{a)}	[200]
	LPP	Ar + TETA bath	20	Reactive Black 5	21.1 (10.5)	4–5 (5) ^{a)}	[200]
	LPP	Air	40	Reactive Red 1	102.7 (100) ^{e)}	n.a.	[195]
	LPP	Air	40	Direct Red 28	97.9 (100) ^{e)}	n.a.	[195]
	LPP	Air	40	Natural Amazon	103.2 (100) ^{e)}	n.a.	[195]
	LPP	O ₂	120	Basic Blue 9	3.7 (5.4)	n.a.	[201]
	LPP	Air	20	Direct Red 81	18.3 (13.6) ^{d)}	n.a.	[201]
	LPP	O ₂	70	Direct Red 81	20.7 (13.6) ^{d)}	n.a.	[201]
	LPP	O ₂	120	Direct Red 81	18.1 (13.6) ^{d)}	n.a.	[201]
	LPP	O ₂	300	Acid Red 330	35 (25) ^{d)}	n.a.	[81]
PA	DBD	Air	1 000	Direct Orange 57	100 (80)	4–5 (4–5) ^{a)}	[167]
	DBD	Air	1 000	Direct Orange 57	125 (65)	5 (4–5)	[202]
	DBD	Air	1 500	Reactive Yellow 27	88.9 (84.4)	n.a.	[74]
	DBD	Air	1 500	Reactive Red 231	24.9 (15.6)	n.a.	[74]
	DBD	Air	1 500	Reactive Yellow 26	102.6 (43.1)	n.a.	[74]
	DBD	Air	1 500	Realan Red EHF [®]	48.6 (36.1)	n.a.	[74]
	DBD	Air	1 500	Realan Yellow EHF [®]	60.9 (54.8)	n.a.	[74]
	DBD	Air	1 500	Realan Blue EHF [®]	86.8 (49.9)	4 (4) ^{a)}	[74]
	DBD	Air	1 500	Sirius Scarlet KCF [®]	185.5 (111.6)	n.a.	[74]
	DBD	Air	1 500	Direct Violet 47	138.7 (100.8)	n.a.	[74]
	DBD	Air	1 500	Direct Orange 57	199.3 (68.4)	3 (4) ^{a)}	[74]
	DBD	Air	1 500	Telon Blue MGWL [®]	66.1 (51.5)	4–5 (4–5) ^{a)}	[74]
	DBD	Air	1 500	Telon Red A2FR	95.9 (80.7)	n.a.	[74]
	DBD	Air	1 500	Telon Rot M-6BW	149.3 (131.2)	n.a.	[74]
	DBD	Air	600	Reactive Yellow 125	202.2 (42.7)	n.a.	[48]
	DBD	Air	600	Acid yellow 240	142 (112)	n.a.	[48]
	LPP	Acrylic acid	10	Basic red 18	9.16 (8.17)	7 (12)	[166]
	LPP	Water	10	Basic red 18	8.6 (8.17)	6.5 (14)	[166]
	LPP	Ar	10	Basic red 18	6.7 (8.17)	6.5 (11.5)	[166]
	LPP	Air	10	Basic red 18	6.46 (8.17)	8 (15)	[166]

(Continued)

Table 3. Continued

Textile Substrate	Plasma Type	Plasma Method	Power (W)	Dye (C.I.)	K/S (Control)	Wash Fastness (ΔF) [*]	Reference
PET	LPP	O ₂	10	Basic red 18	6.26 (8.17)	8.5 (9.5)	[166]
	LPP	Acrylic acid	10	Basic red 24	26 (6)	4 ^{b)}	[203]
	LPP	O ₂ + acrylic acid bath	800	Acid dye	1.46 (1) ^{c)}	n.a.	[204]
	LPP	O ₂ + HEMA bath	800	Acid dye	0.95 (1) ^{c)}	n.a.	[204]
	LPP	CF ₄	100	Acid Blue 62	10 (50) ^{d)}	5 (5) ^{a)}	[126]
	LPP	CF ₄	100	Disperse Blue 56	30 (20) ^{d)}	4–5 (4–5) ^{a)}	[126]
	APGD	Air	n.a.	Disperse Red 127	4.2 (3.6) ^{e)}	n.a.	[35]
	APGD	Air	n.a.	Disperse Yellow 211	9.2 (7.2) ^{e)}	n.a.	[35]
	APGD	Air	n.a.	Disperse Violet 57	6 (4.2) ^{e)}	n.a.	[35]
	Corona	Air	900	Disperse Red 73	0.83 ^{c)}	n.a.	[170]
	Corona	Air	6 000	Disperse Blue 79	60 (35) ^{d)}	n.a.	[45]
	DBD	Air	30	Disperse Blue 19	6.8 (6.6)	n.a.	[172]
	DBD	Air	30	Disperse Brown 1	6.2 (6)	n.a.	[172]
	DBD	N ₂	30	Disperse Blue 19	6.6 (6.6)	n.a.	[172]
	DBD	N ₂	30	Disperse Brown 1	6.1 (6)	n.a.	[172]
	DBD	O ₂	30	Disperse Blue 19	7 (6.6)	5 (5) ^{a)}	[172]
	DBD	O ₂	30	Disperse Brown 1	6.8 (6)	5 (5) ^{a)}	[172]
	DBD	Ar	30	Disperse Blue 19	6.6 (6.6)	n.a.	[172]
	DBD	Ar	30	Disperse Brown 1	6.1 (6)	n.a.	[172]
	DBD	Air	1 000	Curcumin	22 (22)	n.a.	[177]
	LPP	Acrylic acid	20	Basic red 18	0.82 (0.34)	8.5 (16.6)	[205]
	LPP	Ar + acrylic acid bath	20	Basic red 18	1.88 (0.34)	14.7 (15.2)	[205]
	LPP	N ₂	n.a.	Disperse Red 60	39.3 (9.3) ^{d)}	4–5 (4–5)	[171]
	LPP	N ₂	n.a.	Acid Red 138	26.2 (8.7) ^{d)}	n.a.	[171]
	LPP	N ₂	n.a.	Basic Violet 16	0.01 (2.7) ^{d)}	n.a.	[171]
	LPP	O ₂ + poly-DADMAC	600	Acid Red 18	0.35 (0.05)	2 ^{a)}	[173]
	LPP	O ₂ + poly-DADMAC	600	Acid Blue 80	0.3 (0.05)	2 ^{a)}	[173]
	LPP	NH ₃ + C ₂ H ₄	600	Acid Blue 127	0.36	3 ^{a)}	[168]
	LPP	Air	10	Direct Red 79	80 (65) ^{f)}	n.a.	[169]
	LPP	NH ₃ + C ₂ H ₂	475	Acid Blue 127	1.2 (0.2)	3–4 ^{a)}	[153]
	LPP	Acrylic acid	10	Basic red 18	0.92 (0.34)	8 (16.5)	[166]
	LPP	Water	10	Basic red 18	0.75 (0.34)	7.5 (21)	[166]
	LPP	Ar	10	Basic red 18	0.72 (0.34)	8 (18.5)	[166]
LPP	Air	10	Basic red 18	0.76 (0.34)	8 (16)	[166]	
LPP	O ₂	10	Basic red 18	0.53 (0.34)	7 (10)	[166]	
LPP	Acrylic acid	25	Basic red 24	4 (1.1)	1 ^{b)}	[203]	
LPP	Air	120	Disperse Blue 94	104 ^{e)}	n.a.	[152]	
LPP	Ar	130	Disperse Blue 94	104 ^{e)}	n.a.	[152]	
LPP	SiCl ₄	n.a.	Basic Blue	1.6 (0.4)	n.a.	[206]	

(Continued)

Table 3. Continued

Textile Substrate	Plasma Type	Plasma Method	Power (W)	Dye (C.I.)	K/S (Control)	Wash Fastness (ΔE) [*]	Reference
PET/Cotton	LPP	Acrylic acid	10	Basic red 18	3 (1.8)	15 (17)	[207]
	LPP	Water	10	Basic red 18	3 (1.8)	18 (20)	[207]
PP	DBD	Ar	100	Vat Yellow 46	489.2 ^d	4 ^a	[179]
	DBD	Air	100	Vat Yellow 46	562.1 ^d	3–4 ^a	[179]
	DBD	Air	130	Basic Yellow 28	850 ^e	4–5 ^a	[208]
	DBD	Air	130	Basic Red 18	100 ^e	4–5 ^a	[208]
	DBD	Air	130	Basic Red 46	25 ^e	2–4 ^a	[208]
	DBD	Ar	200	Basic Blue 3	450 ^e	3 ^a	[155]
	DBD	Ar	200	Basic Red 18	190 ^e	3–4 ^a	[155]
	DBD	Ar	200	Basic Red 46	120 ^e	3–4 ^a	[155]
	DBD	Ar	200	Acid Blue 264	130 ^e	3 ^a	[155]
	DBD	Ar	200	Acid Violet 17	320 ^e	3–4 ^a	[155]
	LPP	Acrylic acid	75	Basic red 24	25 (2)	2 ^b	[203]
	LPP	Ar + Acrylonitrile	100	Basic dye	4.25 (0.6)	n.a.	[209]
Silk	LPP	O ₂	50	Reactive Black 5	400 (240)	n.a.	[156]
	LPP	N ₂	50	Reactive Black 5	350 (240)	n.a.	[156]
	LPP	H ₂	50	Reactive Black 5	340 (240)	n.a.	[156]
Wool	APGD	He	5 000	Acid Red 13	29.1 (14.3)	n.a.	[186]
	APGD	He	5 000	Reactive Red 84	17.7 (12.3)	n.a.	[186]
	APGD	He	5 000	Natural Caspian	150 (100) ^e	3–4 ^a	[160]
	APGD	He + N ₂	5 000	Natural Caspian	140 (100) ^e	3–4 ^a	[160]
	APGD	He	5 000	Natural Thar	160 (100) ^e	3–4 ^a	[160]
	APGD	He + N ₂	5 000	Natural Thar	150 (100) ^e	3–4 ^a	[160]
	APGD	Air + He	n.a.	Acid blue 113	93 (92.9) ^d	4–5 (4–5) ^a	[157]
	APGD	O ₂ + He	n.a.	Acid blue 113	92.8 (92.9) ^d	4–5 (4–5) ^a	[157]
	Corona	O ₂ + N ₂	2 500	Acid Blue 158	0.3 (1.5) ^c	n.a.	[189]
	Corona	O ₂ + N ₂	2 500	Acid Blue 113	1 (1.1) ^c	n.a.	[189]
	DBD	Air	600	Reactive Yellow 125	88 (25.1)	n.a.	[48]
	DBD	Air	600	Acid yellow 240	73.9 (46.1)	n.a.	[48]
	DBD	N ₂	30	Acid Orange 19	19 (14.7) ^d	n.a.	[158]
	DBD	N ₂	30	Acid Green 9	50.6 (44.9) ^d	n.a.	[158]
	DBD	N ₂	30	Acid Red 249	73.7 (69.5) ^d	n.a.	[158]
	DBD	N ₂	30	Acid Blue 83	83.5 (81.6) ^d	n.a.	[158]
	DBD	N ₂	30	Acid Blue 25	65.6 (56.9) ^d	n.a.	[158]
	DBD	N ₂	30	Acid Green 27	94.6 (91) ^d	n.a.	[158]
	DBD	N ₂	30	Reactive Blue 19	82.2 (81) ^d	n.a.	[158]
DBD	N ₂	30	Reactive Red 4	57.5 (37.7) ^d	n.a.	[158]	
DBD	N ₂	30	Reactive Red 194	54.4 (34.9) ^d	n.a.	[158]	
DBD	N ₂	30	Reactive Black 5	52.6 (30.3) ^d	n.a.	[158]	
DBD	N ₂	30	Reactive Red 120	52 (29.6) ^d	n.a.	[158]	

(Continued)

Table 3. Continued

Textile Substrate	Plasma Type	Plasma Method	Power (W)	Dye (C.I.)	K/S (Control)	Wash Fastness (ΔE) ^a	Reference
	LPP	O ₂	20	Acid Orange 19	15.4 (8.8)	5 (3–4) ^{a)}	[185]
	LPP	O ₂	20	Acid Violet 90	11.5 (5.1)	5 (4) ^{a)}	[185]
	LPP	O ₂	20	Reactive Red 194	3.7 (1)	5 (4–5) ^{a)}	[185]
	LPP	Air	100	Acid Red 27	35.2 (28.2) ^{d)}	n.a.	[159]
	LPP	N ₂	40	Acid Blue 83	83.5 (81.4) ^{d)}	n.a.	[158]
	LPP	N ₂	40	Acid Red 249	73.9 (69.8) ^{d)}	n.a.	[158]
	LPP	N ₂	50	Reactive Blue 50	95 (75) ^{d)}	n.a.	[210]
	LPP	O ₂	300	Acid Red 330	90 (80) ^{d)}	n.a.	[81]

^{a)}Washing fastness according to AATCC test method; ^{b)}Washing fastness according to UNI EN 20105 test method; ^{c)}C.I.E. colour change (ΔE)^{*}; ^{d)}Dye exhaustion (%); ^{e)}Color depth; ^{f)}Reflectance (%); n.a. not available.

introduced on the surface of polyamide and polyester fabrics by a low-pressure plasma discharge and then dyed with cationic dyes. The results showed a significant increase in the colouristic strength (K/S) for both the PET and PA fabrics.^[166] Yip et al. treated a PA fabric with tetrafluoroethane using low-temperature plasma and dyed this substrate with acid and disperse dyes. The dyeing results showed that plasma treatment slowed the dye exhaustion without lowering the total amount of absorbed acid dyes. The disperse dyes showed significant changes when comparing samples with and without plasma treatment. A slight increase in the strength of the tissues was observed for all the treated samples.^[126] A recent research showed that a relatively low-DBD plasma dosage, of around 2.5 kW · min · m⁻², could promote the breakages of the polyamide chains thus generating micro-channels and open paths that favour the dye diffusion into the fibres' interior (Figure 5). At the same time, plasma generated low-molecular weight aliphatic chains tend, by oxidation, to form acidic and partially soluble species that act as a sort of dye 'carrier' into the fibre. This is a great advantage for all anionic dyes since darker shades are obtainable using lower amounts of dyestuffs at lower temperature and dyeing time.^[167]

Several studies have shown good results in the plasma assisted dyeing of polyester (PET) fabrics.^[35,45,168–173] Surface modification of polyester fabrics was studied using a radio frequency plasma treatment and argon gas. The dyeing properties of fibres treated with plasma were correlated with the topographical features and surface chemical composition.^[152] Ren et al. studied a combined method of caustification and plasma discharge to modify the surface of polyester fibres. The results showed a significant improvement in dyeing properties in the

combined process. A caustification pre-treatment can accelerate plasma 'etching' and surface oxidation of polyester.^[174] Xiaoliang et al. continuously treated polyester fabrics with a DBD plasma discharge in Ar–O₂. The results revealed that the dyeability of polyester fabric was greatly improved. The K/S values after plasma treatment increased about 50% and relative absorption at around 18% without affecting the dye fastness. According to these authors, the improvement in dyeability of the polyester can be attributed to the introduction of functional groups on the surface of the material during treatment.^[175] El-Nagar et al.^[176] significantly increased the dyeability of polyester fibres by using a low-pressure plasma. Hossain et al. performed a plasma deposition with mixture of ammonia and acetylene gases on polyester fabrics. The colouristic strength of the dyed polyester fabric was improved at low temperature by enhanced binding of dye molecules to the plasma polymer coating. It was further observed that the increase in dyeability depends on the exposure time, gas mixture composition and applied energy.^[153] Dyeing of polyester fabric with curcumin was studied with and without a prior surface activation using DBD plasma and an ultraviolet excimer lamp. It was observed an increase in colour yield for the ultraviolet excimer lamp only because the surface of PET activated by plasma lost all the hydrophilic species when subjected to the dyeing conditions. The excimer treatment yields hydrophilic species that are more resistant to high temperature and pressure dyeing.^[177]

The fibres of polypropylene (PP) display an excellent combination of important properties such as high tensile strength, low density and resistance to many chemicals. However, these fibres cannot be dyed with conventional dyes due to the high hydrophobicity, crystallinity and

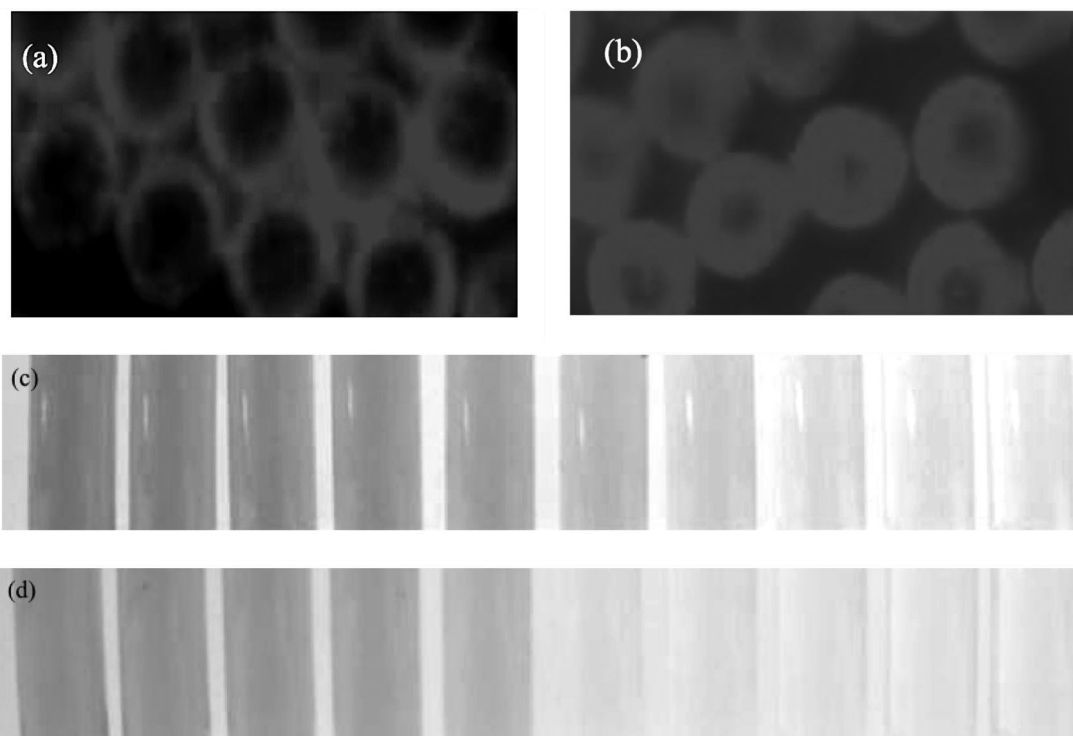


Figure 5. Fluorescence Microscopic images ($40\times$) of the cross-section of untreated (a) and plasma treated (b) PA66 fibres dyed with a direct dye. Dye bath concentrations taken during the dyeing process without (c) and with (d) plasma treatment.

nonpolar groups in their structure. Yaman and colleagues performed a pre-treatment with argon plasma in order to activate the PP surface followed by a surface graft with different compounds like 6-aminohexanoic acid, acrylic acid, ethylenediamine, acrylamide and hexamethyldisiloxane. The results showed superior dyeability with acid and basic dyes depending on the grafted compound.^[155] PP fabric was also coated with an aqueous solution of acrylic acid using DBD plasma pre-treatment with nitrogen and air. The plasma activation with nitrogen was more efficient than plasma with air, showing improved water transport and dyeing properties.^[178] Another recent work also used an atmospheric DBD discharge in air and argon to modify the surface of PP fabrics. The effects on dyeability were investigated when the treated fabrics were dyed by leuco and pigment forms of vat dyestuffs. Vat-dyed samples showed a significant increase in colour strength. The enhance in dyeability was attributed to the increased microroughness, augmented surface area, and the addition of functional groups, such as carbonyl, carboxyl and hydroxyl, to the fabrics' surface.^[179]

A process that involves enormous difficulties is the dyeing of thermostable material such as meta- and para-aramids. These materials need the development of new dyeing methods, since the existing technology does not offer satisfactory results.^[9,180] Aramids have high degree of

orientation of the macromolecules in the polymer chain, high crystallinity, dense structure and they are also coloured. Studies to develop dyeing methods for these fibres using traditional technologies are in progress.^[181,182] However, the use of plasma discharge has been also explored in order to improve and facilitate the dyeing process of aramid fibres. Three different types of aramid fabrics (Technora[®], Conex[®] and Kevlar[®]) were dyed with disperse dyes at low temperature after an argon plasma pre-treatment with contradictory results.^[183]

Plasma assisted dyeing of wool, which is one of the most important fibres in the textile industry, was also deeply investigated. Wool fibres has a complex surface structure and comprise a hydrophobic surface, which directly affects its dyeability due to the presence of a high number of disulphide bridges and fatty acids. Many harmful chemical methods are used to change the surface property to improve fibres hydrophilicity. Currently, plasma discharge appears as an environmental friendly alternative treatment to improve the dyeability of wool.^[157,160,184–190,191] Kan et al. treated wool with oxygen plasma and dyed with acids, reactive and metal complex dyes. The results demonstrated that the plasma treatment increase the dyeing kinetic with acid dye and metal complex with small gain in the exhaustion rates. However, reactive dye showed an considerable improved exhaustion

of the dyebath.^[192] El-Zawahry et al. have studied the effect of plasma discharge in the dyeing properties of wool fabrics in detail. The DBD plasma discharge using N₂ gas resulted in the creation and introduction of NH₂ groups at the surface of the wool fibres, improving their wettability and enhancing the acid dye exhaustion. The treatment has also increased the initial dyeing rate and decreased the time to reach the equilibrium between the fibres and the dye in the bath.^[158] Jin and Dai studied the increase in the colouristic strength of a wool fabric after a nitrogen plasma treatment.^[193] Jovic et al.^[159] compared the effect of plasma treatment and chitosan in the dyeing of wool with acid dyes. Sun and Stylios^[81] improved the dyeability properties of woven wool blended with cotton up to 50% using a low-temperature plasma discharge.

Furthermore, silk fibre surfaces were modified using oxygen and argon plasma treatments. The dye adsorption capacity for the pre-treated silks was improved when compared with that of the untreated sample especially for the argon plasma treatment.^[194]

Cotton fibres are usually dyed with low affinity direct or reactive dyes using high level of electrolytes. Therefore, the dyeing process of cotton fibres is highly demanding in term of water and energy and results in low-dye fixation with a significant amount of chemicals and colour in the effluent. It was observed that plasma treatment can improved the dyeing behaviour of cotton fabrics when reactive and natural dyes were used. On the other hand, the dyeability was found to have slightly decreased with direct dyes.^[195] Karahan et al. studied the effect of argon and air plasma discharge in cotton fabrics. The activated surfaces were coated with two amine compounds and dyed with acid dyes. The K/S results showed an increase in dyeability in the plasma treated coated samples.^[150] In another study, plasma technology has been used in the dyeing of a cotton fabric mixed with casein fibres. The results showed a considerable increase in K/S and exhaustion parameters.^[196] Carneiro et al.^[46] applied corona technology on cotton fabrics intending to study various properties including hydrophilicity, mechanical properties and ionization. The plasma treated fabrics dyed with three direct dyes, have proven to be a valid alternative to the classical method of processing cotton fabrics. Several other studies of the same authors have revealed that plasma treatment of cotton results in improving dyeability due to the creation of micro-channels for water penetration.^[132,133,135] Another research evaluates the differences between the functionalization obtained on the surface of cotton fibres with corona plasma, and the chemical cationization of the cotton fibres with an epihalohydrin by means of a dyeing process with a bifunctional reactive dye. Plasma treatment, previous to cationization increased the impregnation of the fabrics, but the effects of both treatments on dyeing parameters are additive only in column water rise and

generally the effects obtained by cationization with epihalohydrin prevail.^[197] Atmospheric plasma treatment was also used to improve the poor crocking fastness and low build-up of pigment dyeing of cotton. Low-pressure and atmospheric DBD plasma treatments were used to enhance the properties of pigment dyeing with satisfied colour fastness.^[198] Moreover, oxygen plasma treatment shows a positive influence on increasing colour yield and strengthening colour fastness to crocking of pigment application to cotton fabric. However, the levelness of pigmented fabric was higher using a helium-oxygen treatment.^[199]

Concluding, it is clear from Table 3 that over the last years the atmospheric plasma technologies have significantly improved in the efficient dyeing of polyamide and wool fabrics. Despite that, atmospheric plasmas are not yet investigated in the dyeing of other protein fibres such as silk. In the case of cotton the low-pressure plasmas are the most investigated, but more research is needed in the atmospheric plasmas due to promising results attained. In the case of polyester and polypropylene fabrics the low-pressure plasma technologies showed without any doubt the best results, especially for disperse dyes. As a last consideration, in the field of atmospheric plasma technologies, the corona discharge is practically discontinued due to its lack in uniformity.

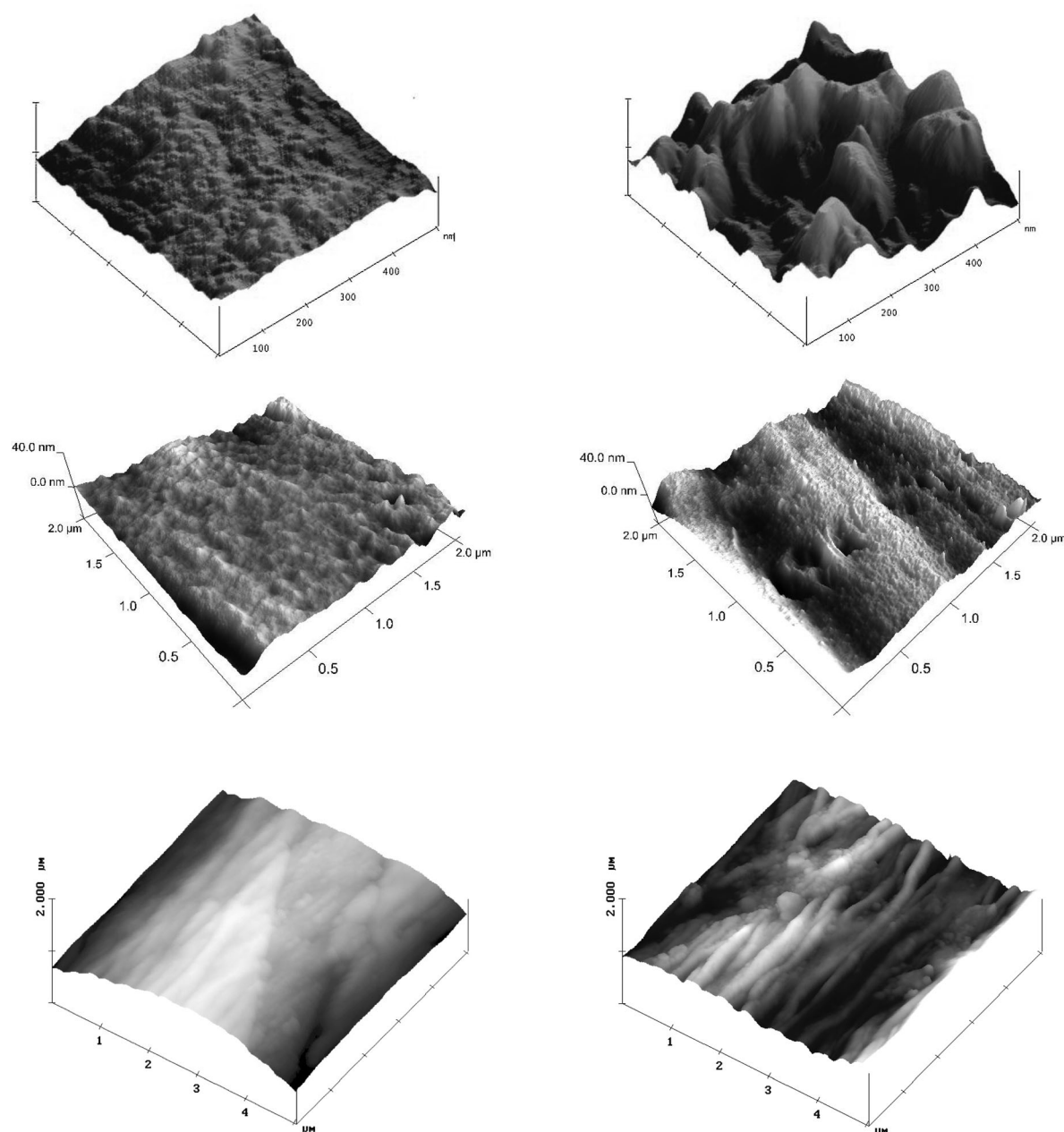
7. Printing

Inkjet printing is becoming increasingly widespread for the printing of textiles. Ink jet printed fabrics have demonstrated improved properties over the traditional textile printing methods, such as roller, screen and transfer printing. It displays excellent pattern quality, considerably little pollution, and especially a faster response to the frequent fashion changes. Moreover, inkjet printing furthermore allows visual effects namely tonal gradients and infinite pattern. However, without any pre-processing, some textiles have a lower capacity to retain water, inks, finish and embossing agents mainly due to the morphologies or chemical properties of the fibres providing low yield and low strength of the print. Nowadays, atmospheric plasmas offer an attractive pre-treatment method for pigment inkjet printing of textile, providing the necessary requisites for continuous and open process.^[211–214] Kan et al. used an atmospheric pressure plasma treatment to enhance the deposition of printing paste in order to improve the final colour properties of digital ink-jet printed cotton fabrics. Experimental results showed that plasma pre-treatment could increase the colour yield even after washing. In addition, other properties like outline sharpness, anti-bacterial properties, colour fastness to crocking and laundering were also improved when compared with those of the control cotton fabric printed without plasma

pre-treatment.^[215] Yuen and Kan also studied the influence of pre-treatment with low-temperature plasma and sodium alginate gel in the digital printing of cotton fabrics. The results confirmed an increase in colour strength and colour fastness when plasma treatment was applied.^[216]

Zhang and Fang studied an atmospheric plasma surface pre-treatment of PET fabrics with air and argon for pigment printing. The results showed better colour yield and drawing sharpness on the pre-treated polyester fabrics. The analysis of SEM and XPS analyses indicate that this performance is mainly due to the surface roughness and

polar groups on the surface of the fibres (Figure 6).^[217] Others plasmas types, such as radio frequency and DBD discharge have been employed for the pre-treatment of PET fabric before printing with pigment showing superior wettability in final properties of the printed polyester.^[218,219] The penetration depth of plasma modification on PET fabric using an inkjet printer was also investigated. Four layers of polyester fabric were exposed to plasma at atmospheric pressure using air. It was observed that plasma treatment was able to penetrate into the four PET layers, but the effect diminished in intensity throughout the



■ Figure 6. AFM images of untreated and DBD plasma treated PET (up), Polyamide 6,6 (middle) and cotton (down) for printing application.

number of layers. The properties of patterned, such as intensity and colour bleeding, revealed that the plasma discharge at atmospheric pressure can penetrate substantially into two layers of PET fabric thus improving the quality of inkjet printing.^[220]

A wool/polyester blended fabric (45/55) pre-treated with an atmospheric DBD plasma has been printed using two different dye mixtures. The experimental results indicated that the wettability and colour strength of treated fabrics are enhanced. Moreover, changes in surface morphology of treated samples are also observed.^[221]

Chvalinova and Wiener investigated the effect of a plasma treatment for printing on a wool fabric. The results showed that by increasing the time of plasma treatment the colour strength of the printed pigment was also increased.^[222]

Finally, Nasadil and Benesovsky studied the quality of a digitally printed polypropylene fabrics pre-treated with low-temperature plasma discharge. Polypropylene is known as very hard-to-print and hard-to-dye material. The use of conventional printing technologies is difficult and limited. Samples with and without treatment were printed with six colours, thermally fixed and then washed. Even before washing, the plasma pre-treated sample demonstrated much brighter colour shades. After two washing cycles the treated samples showed better colourfastness. It is clear that plasma pre-treatment is able to provide added value to inkjet printing on polypropylene.^[223]

8. Finishing

Compared with established finishing processes, such as pad-dry-cure or coating, plasma has the crucial advantage of improving the wettability, enhancing the interaction between fibres and finishing products reducing the usage of chemicals, water and energy.^[224] Moreover, it offers the possibility to obtain antimicrobial, anti UV, self-cleaning and flame retardant among others finishes with higher durability to washing and without changing the textile bulk properties.^[23]

Felting shrinkage is the most undesirable feature on wool clothes. When wool is agitated or washed in aqueous liquor the fibres come closer together forming a more compact and denser assembly, due to its instinctive characteristics and directional frictional effect. Currently, anti-felting treatment consists mainly of treating wool in a chlorine-containing solution. However, chemical methods produced harmful effluents, such as high-temperature wastewater, acidic pH, and chlorine discharges during the operation. Anti-felting plasma treatment of wool was conducted mainly in non-continuous vacuum and batch condition.^[225–228] For example, Shahidi et al. used

low-pressure plasma with non-polymerizing reactive gases, such as O₂, N₂ and Ar. The results proved that not only the topography of the surface is modified but also the wettability and dye ability of the wool could be increased under proper condition. It is also demonstrated that, plasma treatment imposes significant shrink-resistant and anti-felting effects to the wool fabrics.^[229] However, low-pressure methods are time and energy consuming and the material properties as in the case of thickness and size are highly dependent on the size of the equipment, which limited the industrial application. On the other hand, atmospheric plasma has many advantages when compared with low-pressure plasma, such as no vacuum systems with continuous and open perimeter fabric flow. Moreover, the temperature of the atmospheric plasma is relatively low, so the activating species in the plasma will easily lose their energy once they have reacted with the polymer material without affecting its interior.^[230] Kan et al. treated wool fibres and fabrics with nitrogen plasma jet under atmospheric pressure followed by a polysiloxan polymer deposition process to improve the anti-felting property. The results revealed that atmospheric plasma treatment alone could achieve the best anti-felting effect, but the hand feel was adversely affected. With the deposition of the polymer on the fibre surface, the anti-felting properties were retained with an acceptable hand feel.^[231] Also Kim and Kang applied three different silicone polymers, such as aminofunctional, epoxyfunctional and hydrophilic epoxyfunctional silicone polymers onto plasma pre-treated wool fabric to improve the dimensional properties. The results proved that plasma pre-treatment modified the cuticle surface of the wool fibre and increased the reactivity of wool fabric toward silicone polymers. Felting shrinkage of plasma and silicone treated wool fabric was decreased with different level depending on the applied polymer system. Furthermore, in this case, fabric tear strength and hand were adversely affected by plasma treatment, but favourably restored after polymer application.^[232] Xu et al. investigated the effect of environment relative humidity (RH) on the etching of wool fibres in atmospheric plasma treatments and the subsequent anti-felting properties of wool fabrics treated under the same conditions. In shrinkage test, plasma-treated wool fabrics preconditioned in 100% RH showed the lowest shrinkage ratio of 5% below 8% is required for machine-washable wool fabrics according to ISO standard.^[233]

Errifai et al. reported that plasma treatment could replace traditional method of finishing for fire retardancy of the polyamide fibres. In order to improve the property of resistance to fire spread of PA6, a low-pressure microwave plasma process has been investigated to graft and polymerize a fluorinated acrylate monomer. The rate of heat released of coated PA6 was decreased by approximately 50% in comparison to the control.^[234] In another

study on PA66, a nonwoven PP, Labay et al. analysed the influence of plasma treatment on drug release from textiles, a largely unexplored and very innovative area of research. The results showed that the increased hydrophilic properties after plasma treatment were important and provided higher drug release of around 10%.^[235]

The anti-static property of a polyester fabric was improved with a low-temperature plasma treatment by Kan and Yuen. Plasma modification allowed a greater ability to retain moisture and consequently increase the dissipation of the static charge. Comparing chemical and plasma antistatic finishing treatment, it was found that both acquire antistatic property, but achieve different values of recovering moisture. This shows that the mechanism of plasma treatment and chemical antistatic agent on the polyester fabric is not the same.^[236] Besides the smoothing of polyester fabrics was easily achieved with an atmospheric-air plasma process that coated a softening agent onto the fabrics' surface. The physical properties of the textiles indicated that the combination of plasma and emulsion treatments on polyester can improve crease resistance, drapeability and water repellency due to a uniform coating of the emulsion on the surface of the textiles.^[237] The way that atmospheric plasma acts on cellulosic substrates is still controversial and strongly depends on the plasma reactor parameters. Generally, free radical reactions take place in the plasma environment but also esterification reactions have been reported as a result of plasma treatment on cotton. Recently, Ahmed et al. reported the chemical modification of cotton with permanent attachment of a cyclodextrin derivative using cold glow discharge atmospheric plasma. Linoleic, ricinoleic, oleic acids were included in the grafted cyclodextrin fabrics as possible wound healing agents. Several plasma machines and conventional thermal techniques for fixation were studied. Iododeoxycellulose gave the best results by thermofixation and the in situ mode of the APPJ plasma machine. The cyto-compatibility of the treated samples either included or un-included with fatty acids show promising results. There is no significant difference in the cytotoxicity among the fabrics and the control.^[238]

Plasma enhanced coatings by chemical vapour deposition (CVD) methods have also been developed on nonwoven fabrics for industrial applications. Carbon coatings were developed on polypropylene nonwoven fabrics using glow discharge plasma and propane-butane in the gaseous phase for electromagnetic shielding applications.^[239] Substantial enhancement of wear resistance was observed in textiles on which a thin film of $\text{SiO}_x\text{C}_y\text{H}_z$ was deposited by plasma enhanced CVD method using hexamethyldisiloxane as a precursor compound.^[240] Malkov and Fisher^[241] used pulsed plasma enhanced CVD to obtain thin uniform coatings of poly(allyl alcohol) on silk, wool and cotton fibres. Tensile strength of wool and silk was found to improve after

treatment. Plasma enhanced CVD of TiO_2 films on cotton have been reported for photocatalytic applications. Using titanium tetrachloride as a precursor, depositions were performed in the presence of oxygen. Results showed a substantial enhancement of the bactericidal activity of UV irradiation for the surfaces modified with the presented process. A strong correlation was observed between the bactericidal efficiency of the films and their refractive index.^[242] Plasma induced CVD polymerization process of a flame retardant monomer was easily integrated in a cotton fabric as finishing process, totally compatible with reactive dyeing process and water repellent treatment. Moreover, the flame retardant properties are not affected by this post plasma treatment and exhibited excellent wash-fastness properties after 50 cycles of laundry.^[243] A cotton/polyester (50/50%) fabric was treated by plasma CVD deposition of a fluorocarbon to obtain a hydrophobic coating. Then, the fabric was treated with a quaternary ammonium salt to obtain antimicrobial properties. Good laundering durability and excellent antimicrobial properties were obtained.^[121]

Atmospheric plasmas were also applied in the finishing of cotton fabrics. Carneiro et al. reported a significant improvement in wrinkle recovery angle of a cotton fabric pre-treated with a DBD plasma discharge. The finishing was performed with a crosslinking resin of low-formaldehyde content. Results in semi-industrial and industrial DBD prototypes are presented giving wide overview for advantages and benefits achieved in fields, such as the shortening and preparation steps, the possibility of close combination of preparation and dyeing operations, the elimination of tensioactives in mercerization of the increase in efficiency of finishing agents and extension of durability of effects. A positive effect was also observed in the release of formaldehyde, with the use of less amount of catalyst.^[244] Lam et al. treated cotton fabrics with oxygen plasma and wrinkle-resistant finishing agents with polycarboxylic acid. The results of wicking rate, contact angle and wettability revealed that atmospheric plasma treatment significantly improved hydrophilicity of cotton fibre. Such improvement greatly enhances the effectiveness of post-finishing processes.^[245] A quaternary ammonium salt monomer was graft polymerized on Nylon-Cotton (50/50) standard military fabric by using atmospheric pressure glow discharge plasma to impart durable antimicrobial properties. Results showed almost 100% reductions in the bacterial activities.^[246]

Currently, nanotechnology is considered the most promising technology for commercial applications in the textile industry.^[247] This is mainly due to the fact that conventional fabric-treatment methods do not lead to permanent effects losing their functions after laundering or wearing. Nanotechnology can provide high durability for fabrics due to nanoparticles extremely large surface area

and high surface energy, without affect their breathability or hand feel.^[248–250] Over the last years nanotechnology has renewed the interest for finishing of textiles applied to the production of medical and protective technical products.^[251–253] Different textile materials have been functionalized with silver nanoparticles.^[254–256] However, most of these materials are based on synthetic fibres, which are often highly hydrophobic. Polyamide is one of the most important synthetic fibre materials used in textile industry due to its excellent mechanical, thermal and chemical properties. Its silver surface functionalization by atmospheric plasma has been broadly investigated especially in what concerns the antimicrobial activity.^[255,257–261] The size-dependent antimicrobial activity of silver nanoparticles has already been investigated concluding that the smaller the nanoparticle, the more it releases Ag^+ ions and the higher the antibacterial effect is.^[262–264] The fastness properties of a cotton fabric treated with corona plasma and finished with antibacterial silver nanoparticles were evaluated. The fabrics pre-treated with Corona, after twenty washings, had better effects than samples non-treated after five washings. All the results show that Corona improves performance and durability of finishing products offering a more economic production process of surgical fabric.^[265] Recently, the effect on the deposition of three different size silver nanoparticles onto a PA66 fabric pre-treated using DBD plasma in air was investigated. The result confirmed a dual effect on the wettability of the plasma treated PA fabric. AgNPs enhances hydrophobicity of the PA surface and, at the same time, protects it against the plasma aging effect.^[266]

The influence of atmospheric air plasma treatment on the performance of silicone nanoemulsion softener on PET fibres was investigated. Results indicated that the plasma pre-treatment modifies the surface of fibres and increases the reactivity of substrate toward nanoemulsion silicone. Moisture regain and microscopic tests showed that the combination of plasma and silicone treatments on PET can decrease moisture absorption due to uniform coating of silicone emulsion on surface of fibres.^[267]

Alongi et al. studied the impregnation of two nanoparticles suspensions (Hydrotalcite HT and SiO_2) on cotton fabrics in order to improve their stability and flame retardancy. The application of a pre-treatment through an oxygen low-temperature plasma discharge revealed an increased amount of nanoparticles on the treated fibres. Furthermore the thermal stability of cotton in contact with air was modified by the addition of nanoparticles, causing a decrease in the rate of degradation of the material.^[268] Horrocks et al. coated atmospheric plasma treated cotton with a nanoclay and hexamethylene disiloxane (HMDSO) improving its resistance to flash fires.^[269]

In another study carried out on natural cellulosic fibres, multifunctional properties were imparted to linen based

fabrics using oxygen or nitrogen plasma followed by the application of nanoparticles of Ag, TiO_2 or ZnO .^[270] PECVD has also been used to successfully deposit silica nanoparticles on non-woven polyester surface.^[271]

Degummed silk fabrics modified by cold oxygen plasma and titania sols demonstrated that titania nanoparticles were associated with silk fibres by forming organic–inorganic hybrid blends. The initial decomposition temperatures of finished samples were elevated by 23–35 °C with increased char residues at 600 °C, while the transmittance of UVA and UVB of finished samples decreased by 11.7, 17.7%, respectively.^[272]

The use of plasma in the finishing process proves to be effective for all types of textiles with a great variety of effects and durability. This wide variety recommends the use of plasma as an independent stage for the manufacturing process in textile finishing. Once again, despite the high efficiency of treatment with low-pressure plasma, the wide use of plasma technologies has been held back by a number of factors discussed earlier. Moreover, in the finishing of a textile the use of atmospheric-pressure plasma especially DBD plasma has been proposed as a suitable alternative.^[273] Nowadays, the elevated capacity of DBD plasma for oxidative degradation, including dyes and the comparatively easier plasma polymerization process show that DBD technologies have reached the technological maturity and are ready for commercial industrial applications.

9. Composites

The main purpose of plasma surface treatment of textiles used as reinforcements in composite materials is to modify the chemical and physical structures of their surface layer, tailoring fibre–matrix bonding strength or toughen, control interfacial bonding and adhesion, but without influencing their bulk mechanical properties.^[274] Plasma treatment improves the fibre–matrix adhesion by introducing polar groups, by deposition of a new layer of the same polymer or by changing the surface roughness of the substrate. These characteristics may favour the formation of strong bonds between the fibre and polymeric matrix.^[2,275,276] Radio frequency and microwave discharge at low pressures were for more than 15 years the most important plasma technologies due to their strong modification ability and relatively low-gas temperatures. However, the industrial uses of atmospheric pressure plasmas, such as APPJ and DBD have recently increased because they are easy to integrate into existing production lines and they can selectively treat specific parts of a substrate. Especially, APPJs are not only limited to the two-dimensional structures but can also be used for the three-dimensional structures.^[277]

Recently, Morent et al. have carefully reviewed the large amount of publication about plasma by improving composite materials as well as their resistance to fatigue, delamination and corrosion. They covered the most important fibre composites including the plasma surface treatment of carbon, polyolefin, aramid and glass fibres.^[11] For this reason, the literature review of this topic is only focused on the most important researches of the last 5 years.

Plasma polymerization is an effective and eco-friendly method, for the surface modification of the cellulosic and ligno-cellulosic fibre, to increase the compatibility between the hydrophobic matrix and the hydrophilic fibres. Cotton fabrics when exposed to low-pressure DC glow discharge plasma in argon showed a significant increase in wicking behaviour, an effect that rises with increasing treatment time. Results also explain that plasma treatment leads to surface attrition of the cellulose fibres, accompanied by an incorporation of oxygen-containing groups.^[278] Ethanol pre-treated cellulosic ramie fabric followed by an atmospheric helium plasma treatment was prepared to test the degree of improvement in mechanical properties of ramie-fabric-reinforced polypropylene composites. The mechanical tests demonstrated increases in flexural and tensile strength of the treated composites when compared to the control group.^[279] The influence of different plasma treatments on the tensile characteristics of cellulosic lyocell[®] fibres and the interfacial interactions of lyocell[®] fibres in a PLA matrix were investigated. The best improvement of the fibre/matrix adhesion was obtained by a plasma treatment with a mixture of water vapour and ethylene resulting in an improved interfacial shear strength.^[280] Gibeop et al. studied the mechanical properties of jute fibre and its composites using poly (lactic acid) as the matrix. The results were compared with alkali and low-pressure plasma treated fibre composites. Plasma fibre composites exhibited superior mechanical properties and hardness properties comparing to other treatments. Moreover, plasma polymerization leads to a bigger increase (>20%) in the flexural strength than untreated fibre composites.^[281] Another study on low-pressure argon RF plasma modification of jute fibre surface showed approximately a 25% drop in tensile strength of jute fibres with little deterioration for high gas pressures.^[282] Jute fabric was also treated under atmospheric plasma using various gases. Different levels of improvement of up to 55, 62 and 40% in flexural strength, flexural modulus and interlaminar shear stress, respectively, were observed in composites produced from plasma treated fabrics. The storage modulus and glass transition temperature were also improved by up to 200% and 16 °C, respectively.^[283] Flax fibres were treated by argon and air atmospheric pressure plasma systems under various plasma powers to improve interfacial adhesion between the flax fibre and high-density polyethylene and unsaturated polyester. The result revealed that for the adhesion

between flax fibre and polyester matrix, air treatment is more efficient than argon treatment.^[284] Low-pressure glow discharge of air plasma was used to improve the adhesion properties of wood/polyethylene composites. The shear bonding strength test showed that the adhesion properties of the composites improve effectively after plasma treatment.^[285]

Several authors studied the effects of plasma on surface modification of ultra high molecular weight polyethylene textiles for biomedical applications. Fixation of polyethylene components is difficult because the molecules of this material are inert and non-polar by nature, and thus, chemical bonding with an adhesive is difficult. Modification with argon plasma treatment showed that the peel strength of textile/adhesive composites can be increased and the contact angle on the surface of polyethylene textile significantly decreased from 80 to 28°.^[36] On the other hand, corona discharge and radio frequency glow discharge plasmas were found to activate the surface increasing surface energy over 100% in less than a minute of treatment.^[286]

Also carbon fibres and polyetheretherketone (PEEK) have notable mechanical and chemical properties, such as high strength, good fracture and fatigue resistance, and excellent ability to resist wear and chemical exposure. However, neither carbon fibre nor PEEK are bioactive which limits their use in biomedical fields. Luo et al. performed a DBD plasma treatment in ambient air on the surface of a three-dimensional braided carbon fibre-reinforced PEEK composite. It was shown that DBD plasma treatment led to a significant decrease in water contact angle, an increase in roughness and the creation of new oxygen related functional groups on Carbon/PEEK composite. These changes were found to result in a significant improvement in its in vitro bioactivity.^[287] DBD in air was also used on carbon fibre to improve the fibre surface activity in carbon fibre-reinforced polystyrene composites. Contact angles of the plasma-treated carbon fibre and XPS results revealed a significant increase in oxygen and nitrogen concentration in the carbon fibres modified with the DBD at atmospheric pressure.^[288] The surface of carbon/epoxy mixture was modified using oxygen plasma to improve the delamination resistance behaviour of carbon/epoxy-laminated composites. The results showed that the delamination resistance behaviour and layer-to-layer adhesion were significantly improved by plasma modification.^[289] Another similar research studied the tribological behaviour of plasma treated carbon/epoxy composites showing significant improve in the wear resistance and durability of the coating layer.^[290] Good results were also obtained in the interfacial properties of carbon fibre reinforced non-polar structure polyarylacetylene and polyetherimide resin composites modified through low-pressure plasma treatment using different gases.^[291,292]

Aramid fibres have frequently been used for composite material fabrication because of their high thermal stability, modulus, strength and resistance to chemicals. The adhesion between aramid and other polymer matrixes is usually poor, resulting from the high crystallization and smooth surface of the fibres. In recent years, surface modification of aramid fibres with plasma treatment to improve composite properties has been largely investigated.^[293–296] However, recent researches showed a positive influence of inter-yarn friction on ballistic performance of woven fabrics and panels made from aramid fibres. Chu et al. explored the effect of coating by means of atmospheric pressure plasma-enhanced vapour deposition with organic chemicals on the inter-yarn friction. Inter-yarn coefficient of static and kinetic friction has increased. In addition, there is evidence that the mechanical properties of the treated yarns were not negatively affected by the treatment.^[297] A similar research on plasma aramid/phenol composites, despite the superior mechanical properties of the plasma composite, showed a lower ballistic behaviour than that of the untreated composite. The results suggest that for ballistic application, slightly weak fibre–matrix adhesion could lead to improved ballistic behaviour.^[298] Several authors have used DBD plasma discharge under atmospheric conditions obtaining excellent results in the interfacial adhesion between aramid fibres and polyphthalazinone ether sulfone ketone (PPESK) or polyester resin matrix.^[17,299,300] Despite the relevant literature available on plasma assisted aramid composites, some aspects including the effect of surface roughness or chemical compositions on mechanism and physical process of enhancement adhesive properties need further investigation.

10. Enzymatic Treatment

There is considerable interest in the use of enzymes in textile industries to achieve a variety of finishing effects on fibre such as wool, silk, cotton and also synthetic fibres. Several kinds of enzymes in particular amylase, cellulase, peroxidase, laccase, catalase, protease, pectinase and lipase/esterase are used in enzymatic treatments of textiles.^[301] Enzymes exhibit a number of features that make their use advantageous in comparison to conventional chemical or microbial catalysts, such as the high level of catalytic efficiency, the high degree of specificity and the absence of side-reactions. In addition, enzymes are biodegradable, easily removed from contaminated streams, easily standardized in commercial preparations and generally operated at mild conditions of temperature, pressure and pH.^[302] Several advantages are obtained after enzymatic treatment on textile substrates, namely cleaning of the surface of the tissue, improved surface

appearance, reduced tendency of pilling formation, improvement in touch and softening among others.^[303] Several investigations are still being conducted with the goal of translate this technology in different stages of textile processing.^[304–306] Because it is an environmentally friendly and gentle process, plasma discharge treatment is being studied in several applications together with enzymes.

Fatarella et al. studied the effect of plasma discharge in wool fabrics with gaseous oxygen, nitrogen and air in order to improve fibre accessibility to transglutaminase enzyme, to increase wool yarns and fabrics tensile strength. The results showed that plasma pre-treatment in air was the most efficient for the enzymatic process. Modifications induced an improved enzyme penetration into the fibres and no change in enzyme activity was observed.^[307] Jovancic et al.^[308] successfully achieved shrink resistance after an enzymatic treatment applied to wool fabrics previously treated with a RF low-temperature plasma. Zhang and Huang^[309] carried out an anti-felting finishing of wool fabric with plasma pre-treatment followed by a protease treatment. Results showed a good anti-felting effect and a soft handle with low-colour deviation and strength loss. Wool fabrics were also treated with atmospheric argon plasma, protease and chitosan. Atmospheric plasma treatment enhances the adhesion of chitosan to the surface and improves the hydrophilicity of the fibres. Enzymatic treatment improves the coating ability of chitosan showing high dyeing efficiency and shrink-resistance.^[310]

Plasma treatments can also be used to modify the structure of cellulosic and ligno-cellulosic fibres for a variety of applications. Radetic et al. applied a RF plasma discharge on flax followed by a treatment with cellulase enzyme. After the treatment, the fabrics were dyed at low temperature with direct and acid dyes. The results of the combined plasma/enzyme treatment showed a decrease of the dyebath exhaustion attributed to plasma-facilitate enzymatic degradation of the amorphous areas of the hemp fibres.^[311] Wong et al. obtained similar results after treating flax fibres in a low-temperature plasma using oxygen and argon gases.^[312] Pectinase enzyme treatment subsequent to atmospheric air or argon plasma surface modification was applied in flax fabric by Karaca et al. Results clearly proved that the efficiency of pectinase in improving flax water absorbency can be significantly enhanced by plasma pre-treatment.^[313] Nithya et al. investigated the effects of DC air plasma and cellulase enzyme treatments on the hydrophilicity of cotton fabric. Cotton fabric samples were treated with DC air plasma, cellulase enzyme, enzyme treatment preceded by plasma and plasma treatment preceded by enzyme to improve the hydrophilicity. The results revealed a synergetic effect of plasma and enzyme treatments.^[314] The same author also assessed the

anti-microbial activity of the treated cotton fabrics after processing it with *neem* leaf extract. Plasma treatment preceded by enzyme treated fabrics showed 100% bacterial reduction against *Staphylococcus aureus* and 98% against *Escherichia coli* up to 30 washing cycles.^[315] Yoon et al. treated cotton fabric with low-temperature oxygen plasma and enzymes, and examined it for mechanical and dyeing properties. Plasma-treated cotton showed reduced strength, while the rate of weight loss in subsequent cellulase treatments decreased when compared with untreated cotton. Equilibrium uptake of a direct dye remained unchanged.^[316] Two plasma-based treatments, DBD and low-pressure oxygen plasma were used as pre-treatment prior to cotton bioscouring with pectinase. Although both of the pre-treatments could enhance cotton bioscouring, DBD showed to be more suitable due to its continuous processing mode and lower costs.^[317]

Also synthetic polymers were considered for plasma/enzyme treatments. Horseradish peroxidase (HRP) was immobilized onto hydrophobic polypropylene microfiltration membranes through physical adsorption after plasma treatment. The results demonstrated that more HRP could be immobilized onto plasma pre-treated membranes.^[318] Karaca et al. investigated the effects of cutinase, lipase and atmospheric air and argon plasmas treatments on knitted PET fabrics in terms of hydrophilicity, surface modification and moisture management properties. Combined treatments have given the same or slightly better results than those of conventional alkaline treatments. Fabrics treated with plasma and then followed by enzymatic incubations have significantly improved the wetting time, absorption rates and spreading speed results.^[319] Schroeder et al. studied the efficiency of laccase covalent binding by grafting methacrylate monomers possessing different amino groups onto polypropylene using plasma pre-treatment. Strong covalent binding of functional groups onto the synthetic polymer's surface were observed, which could then be suitably tailored by enzymes possessing substrate specificity and regional selectivity.^[320]

Operating under mild conditions, plasma/enzymatic treatments of textiles are particularly intriguing for research on different types of fibres. However, enzymatic treatment and plasma parameters must be strictly controlled in order to avoid unacceptable weight loss and reduction of strength. Despite that, the synergetic combination of plasma and enzyme technologies reveals without any doubt a great potential for textile applications.

11. Plasma Textile Wastewater Treatment

Plasma degradation processes are generally regarded as a combined process of some other advance oxidation processes including ozonation, UV photolysis and pyrolysis

and have the advantages of no demands on temperature and pressure, insensitive to contaminants and environmental friendliness.^[321] Numerous researches focused on the viability of plasma discharge for the treatment of real textile wastewaters but this technology has only recently become an attractive and cost-competitive alternative.^[322] Jiang et al. employed methyl orange to evaluate the degradation efficiency of the synergistic effect of activated carbon fibres and pulsed discharge non-thermal plasma in aqueous solution. Plasma alone can obtain a decolouration of 77% after 30 min treatment. The presences of activated carbon fibres considerably improved dye decolouration and COD removal in the plasma reactor performing a 100% decolourization and above 90% COD removal during 30 min of treatment. It was also observed that activated carbon fibres can be well regenerated in combined processes and their adsorption behaviours contributed little for final organic removal.^[323] The same authors also studied the methyl orange plasma degradation parameters. It was found that dye degradation depends on the initial concentration and total volume of the compound, being slower for higher concentrations and larger volumes.^[324] The degradation of aqueous solutions of various textile industry dyes was performed by means of a gliding arc electric plasma discharge at atmospheric pressure and ambient temperature. The results demonstrate that the oxygen species formed in the discharge induce strong oxidizing effects in the target solution that result in bleaching of the solution and degradation of the solute.^[325] The same gliding arc plasma was also used in combination with titanium dioxide (TiO₂) as photo-catalyst by several authors. The results showed that the TiO₂-mediated Gliding Arc discharge result in the mineralization of the wastewater samples confirmed by chloride, sulphate and phosphate ions formation.^[326,327]

Sugiarto et al. investigated the degradation of organic dyes by the pulsed discharge plasma between needle-to-plane electrodes in contaminated water in three discharge modes: (i) streamer, (ii) spark, (iii) spark-streamer mixed mode. The result showed that the decolouration rate during the pulsed discharge plasma treatment was dependent on the initial pH values. The decolouration rates in the case of spark and spark-streamer mixed discharge modes, which are characterized by high intensity ultraviolet radiation, were found to be much higher than that in the case of streamer discharge, characterized by low-intensity ultraviolet radiation.^[328]

DBD plasma discharge is one of the most promising plasma technologies, because it allows various reactor configurations and depending on conditions, can produce large amounts of ozone and UV radiation. Low-energy consumption and short decolourization time suggested that DBD plasma method might be competitive technology for primary decomposition of hardly degradable textile



dyes in wastewater. Tichonovas et al. investigated the degradation of a wide variety of industrial textile dyes in a pilot DBD semi-continuously operated plasma reactor. Plasma was generated in a quartz tube with central liquid-filled electrode immersed in wastewater; ambient air was used as a feeding gas for the reactor. The performance of the reactor was evaluated based on the production of ozone. The treatment process was found to decrease the toxicity of the wastewater to near-zero values.^[329] Manoj et al. and Dojčinović et al. combined advanced oxidation process and DBD plasma at the gas water interface for the oxidative decomposition of dye-contaminated wastewater. Hydrogen peroxide, a powerful oxidant formed during the plasma reaction was confirmed and the addition of Fe^{+2} showed to significantly improve the performance, possibly due to Fenton type reactions.^[330,331] DBD plasma combined with photocatalysis revealed to be a viable technique for the degradation of textile dye wastewater. Jang et al. evaluated the dye degradation ability in a combined system with three different photocatalysts: (i) titanium oxide, (ii) zinc oxide, and (iii) graphene oxide. It was found that in general the combination of photocatalysis with plasma substantially improved dye degradation in comparison to plasma alone. Graphene oxide, which has a broad band gap, degraded the dye most effectively.^[332]

It is clear that in the last decade the atmospheric pressure plasmas, especially DBD plasma discharge demonstrated to be very stable and effective in the decomposition of synthetic dye effluents without requiring additional chemicals and without producing dangerous chloro-organic by-products. Moreover, the dye degradation products obtained by ozonation showed low to zero toxicity.^[331,333]

12. Conclusion

The choice of the best plasma process to be applied between atmospheric and low-pressure technologies depends on the processing type, speed, sample size and extent of the intended modification. However, from the literature analysis it is clear that over the last 5 years, atmospheric plasma technologies (APT) have been effectively implemented as a suitable alternative and cost-competitive method to low-pressure plasma and wet chemical treatments, avoiding the need of expensive vacuum equipment and allowing continuous and uniform processing of fibres surfaces. A specific reference must be made about corona plasma discharge that is becoming a discontinued technology due to its lack of uniformity. The main conclusions attained in this review about APT recent improvements are reported into the following points:

- (i) APT significantly improved the efficient dyeing of polyamide and wool fabrics.

- (ii) APT along with the use of siloxane or amorphous hydrogenated carbon, due to their biocompatibility and improved wetting properties, is becoming a valid alternative to the more expensive low-pressure plasma deposition of fluorocarbons in the production of superhydrophobic coatings;
- (iii) Nowadays, APT offers an attractive pre-treatment method for pigment inkjet printing of textile providing the necessary requisites for continuous and open process;
- (iv) APT, especially DBD plasma, demonstrates to be very stable and effective in the decomposition of synthetic dye effluents with low or zero toxicity, without requiring additional chemicals and without producing dangerous chloro-organic by-products;
- (v) Furthermore, in textile finishing and composite production the use of APT, especially DBD plasma, has been proposed as a suitable alternative. However, some aspects, such as the effect of surface roughness or chemical compositions on mechanism and physical process of enhancement adhesive properties need further investigation.
- (vi) The synergetic combination of APT and enzyme technologies proves to be quite intriguing for research on different types of fibres. However, enzymatic treatment and plasma parameters must be strictly controlled in order to avoid unacceptable weight loss and reduction of strength.
- (vii) Currently, nanotechnology is considered the most promising technology for commercial finishing applications in the textile industry. ATP shows to be very effective for the production of medical and protective nanotechnical products, especially for the deposition of antimicrobial silver nanoparticles.

Low-pressure plasma remains the preferred technology to achieve various effects by etching, polymerization or formation of free radicals on the surface of the textile substrate as in the case of superhydrophobic and flame retardant coatings. Moreover, in the case of polyester and polypropylene fabrics dyeing the low-pressure plasma technologies showed without any doubt the best results, especially for disperse dyes.

As demonstrated throughout this review, the use of non-thermal plasmas can bring great advantages to traditional wet methods employed in different textile materials and processes without modifying the bulk properties of a large spectrum of natural, synthetic or inert materials. The most attractive feature of atmospheric pressure plasma technology, especially DBD in air, is that it does not require any expensive carrier gas such as helium. Also, plasma processing and maintenance costs are very low as compared to other plasma techniques.

On the other hand, two of the most important limitations that make the atmospheric plasma industrial application in textile still a challenge are the (i) ageing factor of plasma treated material, leading to gradual loss in the imparted properties and (ii) the lack of adapted machines. Furthermore, plasma–surface interactions are not yet fully understood because they are complexly influenced by many factors, such as the chemistry of plasma gases, the nature of the substrate and the treatment operating parameters. Plasma treatment at atmospheric pressure is perhaps the less advanced plasma technology so far. There are few industrial systems in the world utilizing plasma at atmospheric pressure at the development stage, but no wide-ranging textile applications are available yet. However, atmospheric pressure treatments, especially DBD and glow discharges because of their appeal for continuous processing, uniformity and low temperatures, seem to be the best choice to lead with the constraints of treating textile fabrics. Thus, the future of atmospheric plasma technology appears to be extremely promising due to its potential for innovation, value creation and environmental sustainability.

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