Plasma technology in fashion and textiles

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Andrea Zille
2C2T, Centro de Ciência e Tecnologia Têxtil, Departamento de Engenharia Têxtil, Universidade do Minho, Guimarães, Portugal

6.1 Introduction

The production of textile materials has grown significantly in recent years. Global fiber production rose to approximately 111 million metric tons in 2018, a rise over the past decade of 35 million tons, and they expect to grow 3.7% per year to 2025 (Koszewska, 2018). Of the global total, natural fibers accounted for 32 million tons of production during 2018 (cotton production is estimated at 26.72 million tons), an increase of less than 2 million tons in 10 years. The share of natural fibers in global fiber production fell from 41% in 2008 to less than 30% in 2018. Until today the global production of synthetic filament rose to 50 million tons; of this, polyester filament alone was about 45 million tons. Synthetic staple production rose to 22 million tons, and production of cellulosic fibers rose to 7 million tons (Bremen Cotton Report No. 05-06, 2019).

Recently, there have been many efforts at the industrial level to adopt cleaner production processes and technologies. The introduction of a new environmental regulation in European countries called REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) has forced companies to tackle environmental problems by encouraging innovation with the aim of promoting sustainable development (Europa, 2019). Nowadays, textile industries show clear signs of divergence in the face of decades of stagnation with regard to innovative textile processes and products. The progress of the world textile industry, especially in the processing sector, is linked to the changes coming from new research fields such as micro- and nanotechnology, functionalization, and intelligent fabrics. In this context, plasma technologies emerge as a way to achieve significant improvements in almost all phases of the textile processing, modifying conventional treatments, obtaining important results in rising efficiency, and increasing the durability of functional properties such as capacity for adhesion, dyeing, reactivity, grafting of new chemical groups, and coating of polymers (Zille et al., 2015).

Generally, plasma is produced by applying a flow of voltage over a gas to ionize the atoms/molecules. There exist multiple methods to create ionized gases, in which the following are the typical ones. (a) Glow discharge: Plasma is produced by putting a radio frequency of 40 kHz, 13.56 MHz, microwave, and direct current at low frequency 50 kHz voltage through either a pair or a series of electrodes. This method

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uses reduced pressure and ensure to reach the greatest level of flexibility and uniformity of all plasma usage. (b) Corona discharge: It is known to be producing plasma using atmospheric pressure by putting it through a pair of different size electrodes at a low frequency or high voltage flow. This method is only compatible to certain types of fabrics due to its inability to achieve uniformity (Zille et al. 2014); if not, it could cause some problems. (c) Dielectric-barrier discharge: It is produced using a pulse voltage flow on a pair of electrode, of which one of them is covered in dielectric material. Its biggest advantage that outweighs corona is the ability to reach uniformity.

Plasma technology is based on a simple physical principle. When energy is supplied to matter, it changes state from solids to liquid, and liquids to gaseous. If more energy is supplied to a gas, it becomes ionized and goes into the energy-rich plasma state, the fourth state of matter into which electrons are free from atoms or molecules allowing both species to coexist. Plasma was first discovered by Irving Langmuir in 1928 and is the most common state of matter in the universe. More than 99% of the visible matter in the universe is in the plasma state (Muthu, 2018).

The development of plasma discharge for application in textile materials is very recent. The first continuous system developed was proposed by Bradley in the year 1971 (Surface Activation Corporation, USA); however, it was a vacuum system, which limited its application due to the high cost involved (Bradley and Fales, 1971). Since then, different systems for application in textile materials have been developed by several manufacturers and research institutes around the world, namely: Sando Iron Works Ltd. (Uzu, Wakayama, Japan); Fraunhofer IGB (Stuttgart, Germany); NIEKMI institute in Russia (Tecnoplasma, S.A); Europlasma (Outdenaarde, Belgium); Polyplas (Emmerthal, Germany); Fourth State (Belmont, USA); Softal Electronic GmbH (Hamburg, Germany); University of Minho (Guimarães, Portugal); Sherman Treater Co (Oxon, UK); Paladin (North Carolina State University); and Dow Corning Plasma Solutions (APGD, AP 100).

There are a large number of plasma types, and an universal classification it is not straightforward; however, they can be primarily divided into thermal and nonthermal plasma (Xi et al., 2008). Thermal plasma can be naturally observed in the stars, lightings, northern lights, other celestial bodies, and the corona of the sun during an eclipse. Thermal plasmas can be also artificially generated using electrical discharges of DC (direct current) or AC (alternate current), laser, radio frequency, and microwave discharges at near-atmospheric pressure (Gleizes et al., 2005). In thermal plasmas, the temperatures are extremely high, in the order of thousands degrees Celsius, and all the different species contained in the gas are in thermal equilibrium.

Since textile materials are heat-sensitive polymers and they cannot withstand the temperature of thermal plasma, nonthermal plasma (or cold plasma) are the only viable option for textile surface modification and processing (Morent et al., 2008). In cold plasmas, the temperature of the electrons is higher (104−105°C at 1−10 eV) than the temperature of other particles (that can remain at room temperature) since the thermodynamic equilibrium is not reached even on a local scale between the electrons and the neutral atoms or molecules, ions and neutral molecules fragments. Cold plasmas, that can be divided into atmospheric pressure plasmas and low-pressure plasmas, have the major advantage of inducing significant surface

chemical and morphological modifications onto fibrous materials without altering the bulk properties of the materials (Borcia et al., 2005; Oliveira et al., 2010a).

The choice of the process to be applied depends on the processing speed, sample size, and extent of the intended modification (Pappas et al., 2006). Most of the work done to modify polymer surfaces with plasma treatments using different gases and chemicals has been performed at low pressure achieving various effects by etching, polymerization, or formation of free radicals on the surface of the textile substrate (Sarra-Bournet et al., 2006). On one hand, low-pressure plasma technology are considered noncompetitive 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 (Mohammad et al., 2011). These factors have seriously limited the commercial viability of this technique in the textile industry (Pappas et al., 2008). On the other hand, atmospheric cold plasmas are suited because they do not need expensive vacuum equipment and allow continuous and uniform processing of fiber surfaces.

In the last 10 years, plasma technology has become a very active, and high growth research field, assuming a great importance among all available material surface modifications in textile industry. There are several benefits of applying plasma technology, which are best suited with the current vital aspects of sustainability. The benefits are:

- Endless opportunity for the modification of surface properties, by appropriate gases.
- Plasma technology reduces the use of water, chemicals and energy, in comparison with the conventional wet method.
- In terms of economic benefits, the elimination of water sources and chemicals can be more cost-effective.
- Plasma treatment, especially closed plasma process, is environmentally friendly.

The main objective of this chapter is to provide an overview on the most important applications of plasma technology for the fashion and textile industries such as the dyeing and printing processes and the hydrophobic and hydrophilic surface treatments. This chapter also provides a brief description of other areas of application in fashion and textiles, advantages, and drawbacks of the new sustainable technology.

6.2 Plasma in textile dyeing and printing processes

Conventional dyeing processes have a low yield, and the dye lost in the effluents can reach up to 50%, creating obvious environmental problems. Most importantly, dye wastewaters without an appropriate treatment can persist in the environment pollution creating problems not only to the photosynthetic processes of the aquatic plants but also to all the living organisms (Schneider et al., 2004). Plasma technology can be used in this context for the removal of the natural or synthetic occurring grease and wax in textile fibers, but also to improve the diffusion of dye molecules into the fibers enhancing color intensities and washing fastness of several natural and synthetic textile materials (Karahan et al., 2008; Nourbakhsh et al., 2008; Souto et al., 2011; Raffaele-Addamo et al., 2006; Hossain et al., 2009; Shahidi et al., 2007; Yaman et al., 2009; Cai and Qiu, 2008; El-Zawahry et al., 2006; Jocic et al., 2005;

Ratnapandian et al., 2011). Plasma application improves dye exhaustion, dyeing uniformity; decreases the amount of applied dyestuff and water; and allows the reuse of effluents contributing to a significant diminution in costs and environmental impact (Deshmukh and Bhat, 2011; Shah and Shah, 2013; Radetic et al., 2007).

In the last 10 years, atmospheric pressure plasmas have proved to be an effective alternative to low-pressure plasma in dyeing. Excellent results were obtained by dyeing polyamide, polyester, and wool fabrics using different dyestuff such as acid and disperse dyes (Oliveira et al., 2009, 2014; Hossain et al., 2007; Lehocký and Mráček, 2006; Gotoh and Yasukawa, 2010; Gorensek et al., 2009; Mirjalili and Karimi, 2013; Kamel et al., 2011; Salem et al., 2011). The dyeing properties of fibers treated with plasma are correlated with the surface chemical composition and surface modifications (Ren et al., 2011; Xiaoliang et al., 2007; El-Nagar et al., 2006; Gawish et al., 2011; Naebe et al., 2009; Motaghi et al., 2009; Ghoranneviss et al., 2011; Fakin et al., 2009; Ke et al., 2008; Barani and Maleki, 2011). However, the increase in dyeability also depends on the exposure time, gas mixture composition, and applied energy (Kerkeni et al., 2012; Yaman et al., 2011; Carneiro et al., 2005, 2006; Patiño et al., 2011).

In the last 10 years, inkjet printing technologies have demonstrated improved properties over the traditional textile printing methods, such as roller, screen, and transfer printing. These digital technologies are becoming widespread in textile industries displaying excellent quality, low pollution, and very adaptable to the today rapid fashion changes. Despite inkjet printing allows visual effects such as tonal gradients and infinite pattern, the lack of an opportune pretreatment can considerably low the print quality due to the lower capacity to retain water, inks, finish and embossing agents of some textiles. Atmospheric plasma is a very effective pretreatment method to improve inkjet pigment uptake (Fang and Zhang, 2009; Radetic et al., 2000; Kan, 2007; Payamara et al., 2010; Kan et al., 2011; Yuen and Kan, 2007; Zhang and Fang, 2009, 2011; Wang and Wang, 2010; Rashed et al., 2009; Maamoun and Ghalab, 2013; Chvalinova and Wiener, 2008; Nasadil and Benesovsky, 2008).

Overall it is clear that over the last 10 years, atmospheric plasma technologies have significantly improved the dyeing and printing efficiency of textile materials. However, in some cases (e.g., cotton, polyester, and polypropylene fabrics), the low-pressure plasmas remain the most applied technology. Table 6.1 describes the application of plasma in textile dyeing processes by various researchers. Similarly, Table 6.2 and Table 6.3 describe the research studies on hydrophyllic and hydrophobic treatments of textile substrates, respectively.

6.3 Improving textiles hydrophilicity and hydrophobicity by plasma

Plasma technology is broadly used to improve surface wettability and/or hydrophilicity of numerous textile materials (Demir et al., 2011; Ren et al., 2008). The increase in hydrophilicity of numerous fibrous materials such as polyamide, polyester, polyethylene, polypropylene, silk, aramid, carbon fibers, wool, and cellulose has been

Table 6.1 Plasma application in textile dyeing processes.

Textile substrate	Carrier gas	Power (W)	Dye (C.I.)	References
Glow discharge (APGD)				
Polyester	Air	n.a.	Disperse Red 127	Gotoh and Yasukawa (2010)
Polyester	Air	n.a.	Disperse Yellow 211	Gotoh and Yasukawa (2010)
Polyester	Air	n.a.	Disperse Violet 57	Gotoh and Yasukawa (2010)
Wool	He	5000	Acid Red 13	Naebe et al. (2009)
Wool	He	5000	Reactive Red 84	Naebe et al. (2009)
Wool	He	5000	Natural Caspian	Ratnapandian et al. (2011)
Wool	He + N_2	5000	Natural Caspian	Ratnapandian et al. (2011)
Wool	He	5000	Natural Thar	Ratnapandian et al. (2011)
Wool	He + N_2	5000	Natural Thar	Ratnapandian et al. (2011)
Wool	Air + He	n.a.	Acid Blue 113	Cai and Qiu (2008)
Wool	O_2 + He	n.a.	Acid Blue 113	Cai and Qiu (2008)
Plasma corona				
Cotton	Air	380	Reactive Blue	Patiño et al. (2011)
Cotton	Air	660	Reactive Black 5	Nourbakhsh et al. (2008)
Cotton	Air	660	Reactive Red 158	Nourbakhsh et al. (2008)
Cotton	Air	1000	Direct Red 80	Carneiro et al. (2001)
Cotton	Air	1000	Direct Red 243	Carneiro et al. (2001)

Continued

Table 6.1 Continued

Textile substrate	Carrier gas	Power (W)	Dye (C.I.)	References
Cotton	Air	900	Disperse Red 73	Gorensek et al. (2009)
Cotton	Air	6000	Disperse Blue 79	Xu and Liu (2003)
Cotton	$O_2 + N_2$	2500	Acid Blue 158	Fakin et al. (2009)
Cotton	$O_2 + N_2$	2500	Acid Blue 113	Fakin et al. (2009)
Dielectric barrier discharge plasma (DBD)				
Cotton	Air + TETA	100	Acid Red 99	Karahan et al. (2008)
Cotton	Ar + TETA	100	Acid Red 99	Karahan et al. (2008)
Polyamide	Air	1000	Direct Orange 57	Oliveira et al. (2014)
Polyamide	Air	1000	Direct Orange 57	Souto et al. (2012)
Polyamide	Air	1500	Reactive Yellow 27	Souto et al. (2011)
Polyamide	Air	1500	Reactive Red 231	Souto et al. (2011)
Polyamide	Air	1500	Reactive Yellow 26	Souto et al. (2011)
Polyamide	Air	1500	Realan Red EHF®	Souto et al. (2011)
Polyamide	Air	1500	Realan Yellow EHF®	Souto et al. (2011)
Polyamide	Air	1500	Realan Blue EHF®	Souto et al. (2011)
Polyamide	Air	1500	Sirius Scarlet KCF®	Souto et al. (2011)
Polyamide	Air	1500	Direct Violet 47	Souto et al. (2011)
Polyamide	Air	1500	Direct Orange 57	Souto et al. (2011)
Polyamide	Air	1500	Telon Blue MGWL®	Souto et al. (2011)
Polyamide	Air	1500	Telon Red A2FR	Souto et al. (2011)
Polyamide	Air	1500	Telon Rot M-6BW	Souto et al. (2011)
Polyamide	Air	600	Reactive Yellow 125	Oliveira et al. (2010b)
Polyamide	Air	600	Acid yellow 240	Oliveira et al. (2010b)
Polyamide	Air	30	Disperse Blue 19	Kamel et al. (2011)

Table 6.1 Continued

Textile substrate	Carrier gas	Power (W)	Dye (C.I.)	References
Polyamide	Air	30	Disperse Brown 1	Kamel et al. (2011)
Polyamide	N_2	30	Disperse Blue 19	Kamel et al. (2011)
Polyamide	N_2	30	Disperse Brown 1	Kamel et al. (2011)
Polyamide	O_2	30	Disperse Blue 19	Kamel et al. (2011)
Polyamide	O_2	30	Disperse Brown 1	Kamel et al. (2011)
Polyamide	Ar	30	Disperse Blue 19	Kamel et al. (2011)
Polyamide	Ar	30	Disperse Brown 1	Kamel et al. (2011)
Polyamide	Air	1000	Curcumin	Kerkeni et al. (2012)
Polypropylene	Ar	100	Vat Yellow 46	Yaman et al. (2011)
Polypropylene	Air	100	Vat Yellow 46	Yaman et al. (2011)
Polypropylene	Air	130	Basic Yellow 28	Yaman et al. (2013)
Polypropylene	Air	130	Basic Red 18	Yaman et al. (2013)
Polypropylene	Air	130	Basic Red 46	Yaman et al. (2013)
Polypropylene	Ar	200	Basic Blue 3	Yaman et al. (2009)
Polypropylene	Ar	200	Basic Red 18	Yaman et al. (2009)
Polypropylene	Ar	200	Basic Red 46	Yaman et al. (2009)
Polypropylene	Ar	200	Acid Blue 264	Yaman et al. (2009)
Polypropylene	Ar	200	Acid Violet 17	Yaman et al. (2009)

Continued

Table 6.1 Continued

Textile substrate	Carrier gas	Power (W)	Dye (C.I.)	References
Polypropylene	Air	600	Reactive Yellow 125	Oliveira et al. (2010b)
Polypropylene	Air	600	Acid yellow 240	Oliveira et al. (2010b)
Polypropylene	N_2	30	Acid Orange 19	El-Zawahry et al. (2006)
Polypropylene	N_2	30	Acid Green 9	El-Zawahry et al. (2006)
Polypropylene	N_2	30	Acid Red 249	El-Zawahry et al. (2006)
Polypropylene	N_2	30	Acid Blue 83	El-Zawahry et al. (2006)
Polypropylene	N_2	30	Acid Blue 25	El-Zawahry et al. (2006)
Polypropylene	N_2	30	Acid Green 27	El-Zawahry et al. (2006)
Polypropylene	N_2	30	Reactive Blue 19	El-Zawahry et al. (2006)
Polypropylene	N_2	30	Reactive Red 4	El-Zawahry et al. (2006)
Polypropylene	N_2	30	Reactive Red 194	El-Zawahry et al. (2006)
Polypropylene	N_2	30	Reactive Black 5	El-Zawahry et al. (2006)
Polypropylene	N_2	30	Reactive red 120	El-Zawahry et al. (2006)
Low-pressure plasma (LPP)				
Polypropylene	EDA	20	Reactive Black 5	Ozdogan et al. (2002)
Polypropylene	TETA	20	Reactive Black 5	Ozdogan et al. (2002)
Polypropylene	Ar + EDA bath	20	Reactive Black 5	Ozdogan et al. (2002)
Polypropylene	Ar + TETA bath	20	Reactive Black 5	Ozdogan et al. (2002)

Table 6.1 Continued

Textile substrate	Carrier gas	Power (W)	Dye (C.I.)	References
Polypropylene	Air	40	Reactive Red 1	Bhat et al. (2011)
Polypropylene	Air	40	Direct Red 28	Bhat et al. (2011)
Polypropylene	Air	40	Natural Amazon	Bhat et al. (2011)
Polypropylene	O_2	120	Basic Blue 9	Malek and Holme (2003)
Polypropylene	Air	20	Direct Red 81	Malek and Holme (2003)
Polypropylene	O_2	70	Direct Red 81	Malek and Holme (2003)
Polypropylene	O_2	120	Direct Red 81	Malek and Holme (2003)
Polypropylene	O_2	300	Acid Red 330	Sun and Stylios (2004)
Polypropylene	Acrylic acid	10	Basic red 18	Oktem et al. (2000)
Polypropylene	Water	10	Basic red 18	Oktem et al. (2000)
Polypropylene	Ar	10	Basic red 18	Oktem et al. (2000)
Polypropylene	Air	10	Basic red 18	Oktem et al. (2000)
Polypropylene	O_2	10	Basic red 18	Oktem et al. (2000)
Polypropylene	Acrylic acid	10	Basic red 24	Ferrero et al. (2004)
Polypropylene	O_2 + acrylic acid bath	800	Acid dye	Liao et al. (2005)
Polypropylene	O_2 + HEMA bath	800	Acid dye	Liao et al. (2005)
Polypropylene	CF_4	100	Acid Blue 62	Yip et al. (2002)
Polypropylene	CF_4	100	Disperse Blue 56	Yip et al. (2002)
Polypropylene	Acrylic acid	20	Basic red 18	Oktem et al. (1999)
Polypropylene	Ar + acrylic acid bath	20	Basic red 18	Oktem et al. (1999)

Continued

Table 6.1 Continued

Textile substrate	Carrier gas	Power (W)	Dye (C.I.)	References
Polypropylene	N_2	n.a.	Disperse Red 60	Mirjalili and Karimi (2013)
Polypropylene	N_2	n.a.	Acid Red 138	Mirjalili and Karimi (2013)
Polypropylene	N_2	n.a.	Basic Violet 16	Mirjalili and Karimi (2013)
Polypropylene	O_2 + poly-DADMAC	600	Acid Red 18	Salem et al. (2011)
Polypropylene	O_2 + poly-DADMAC	600	Acid Blue 80	Salem et al. (2011)
Polypropylene	$NH_3 + C_2H_4$	600	Acid Blue 127	Hossain et al. (2007)
Polypropylene	Air	10	Direct Red 79	Lehocký and Mráček (2006)
Polypropylene	$NH_3 + C_2H_2$	475	Acid Blue 127	Hossain et al. (2009)
Polypropylene	Acrylic acid	10	Basic red 18	Oktem et al. (2000)
Polypropylene	Water	10	Basic red 18	Oktem et al. (2000)
Polypropylene	Ar	10	Basic red 18	Oktem et al. (2000)
Polypropylene	Air	10	Basic red 18	Oktem et al. (2000)
Polypropylene	O_2	10	Basic red 18	Oktem et al. (2000)
Polypropylene	Acrylic acid	25	Basic red 24	Ferrero et al. (2004)
Polypropylene	Air	120	Disperse Blue 94	Raffaele-Addamo et al. (2006)
Polypropylene	Ar	130	Disperse Blue 94	Raffaele-Addamo et al. (2006)
Polypropylene	$SiCl_4$	n.a.	Basic Blue	Sarmadi et al. (1996)

Table 6.1 Continued

Textile substrate	Carrier gas	Power (W)	Dye (C.I.)	References
PET/Cotton	Acrylic acid	10	Basic red 18	Oktem et al. (2002)
PET/Cotton	Water	10	Basic red 18	Oktem et al. (2002)
PET/Cotton	Acrylic acid	75	Basic red 24	Ferrero et al. (2004)
PET/Cotton	Ar + acrylonitrile	100	Basic dye	Sarmadi et al. (1993)
Silk	O_2	50	Reactive Black 5	Iriyama et al. (2002)
Silk	N_2	50	Reactive Black 5	Iriyama et al. (2002)
Silk	H_2	50	Reactive Black 5	Iriyama et al. (2002)
Silk	O_2	20	Acid Orange 19	Gawish et al. (2011)
Silk	O_2	20	Acid Violet 90	Gawish et al. (2011)
Silk	O_2	20	Reactive Red 194	Gawish et al. (2011)
Silk	Air	100	Acid Red 27	Jocic et al. (2005)
Silk	N_2	40	Acid Blue 83	El-Zawahry et al. (2006)
Silk	N_2	40	Acid Red 249	El-Zawahry et al. (2006)
Silk	N_2	50	Reactive Blue 50	Jin and Dai (2003)
Silk	O_2	300	Acid Red 330	Sun and Stylios (2004)

demonstrated (Riccardi et al., 2005; Masaeli et al., 2007; Li et al., 2009; Huang et al., 2013; Bessada et al., 2011; Šimor et al., 2010; Wang and Qiu, 2007; Vander Wielen et al., 2006). Plasma treatments in air or using different carrier gases are able to introduce hydrophilic functional groups such as −COOH, −OH, and $-NH_2$ on the fabric surface. The increase in wettability is attributed to the generation of these new

Table 6.2 Plasma technology in hydrophyllic treatment of textiles.

Textile substrate	Carrier gas	Power (W)	References
Glow discharge (APGD)			
Cotton	Air	200[a]	Temmerman and Leys (2005)
PA6	N_2, C_2H_2−He	850	Pappas et al. (2006)
PA6	He	50	Samanta et al. (2009)
PET	He	50	Samanta et al. (2009)
PET	Ar	0.3[a]	Kabajev and Prosycevas (2004)
PET	Air	0.3[a]	Kabajev and Prosycevas (2004)
PET	O_2	0.3[a]	Kabajev and Prosycevas (2004)
Polylinen®	O_2	460	Karthik et al. (2013)
PP	He	0.005[c]	Hwang et al. (2005)
Wool	Air	150	Binias et al. (2004)
Wool	$C_3H_4O_2$	40−100	Kutlu et al. (2010)
Atmospheric pressure plasma jet (APPJ)			
Cotton	O_2−He	40	Tian et al. (2011)
Cotton	O_2−He	40	Sun and Qiu (2012)
Cotton (hexane)	O_2−He	40	Tian et al. (2011)
PA	O_2−He	13.6[c]	Kan and Yuen (2013)
PET	Ar	14−20	Cheng et al. (2006)
PET	O_2−He	13.6[c]	Kan and Yuen (2013)
PET	O_2−He	100	Wang et al. (2008)
PET filament	Air	n.a.	Gotoh and Yasukawa (2010)
PET spun	Air	n.a.	Gotoh and Yasukawa (2010)
PP	Ar	14−20[b]	Cheng et al. (2006)
Wool	O_2−He	40	Wang and Qiu (2007)
Wool	O_2−He	40	Wang and Qiu (2012)
Wool	O_2−He	13.56[c]	Cheng et al. (2010)
Plasma corona			
Cotton	Air	530	Carneiro et al. (2001)
PA6	Air	n.a.	Ryu et al. (1991)
PET	Air	n.a.	Ryu et al. (1991)
PET	Air	7.1[a]	Pichal et al. (2004)
PET	Air	6000	Xu and Liu (2003)
Wool	Air	n.a.	Ryu et al. (1991)

Table 6.2 Continued

Textile substrate	Carrier gas	Power (W)	References
Dielectric barrier discharge plasma (DBD)			
Acryclic	Air	600	Oliveira et al. (2010b)
Aramid	Air	23.33[a]	Xi et al. (2008)
Aramid	Air	33.33[a]	Xi et al. (2008)
Aramid	Air	27.6[a]	Jia et al. (2011)
Carbon fibers	Air	0.008[c]	Li et al. (2009)
Cotton	Air	50	Karahan and Özdogan (2008)
Cotton	Air	100	Karahan and Özdogan (2008)
Cotton	Air	130	Karahan and Özdogan (2008)
Cotton	Ar	50	Karahan and Özdogan (2008)
Cotton	Ar	100	Karahan and Özdogan (2008)
Cotton	Ar	130	Karahan and Özdogan (2008)
Diacetate	Air	600	Oliveira et al. (2010b)
NCE	Air	5[b]	Borcia et al. (2006)
PA	Air	600	Oliveira et al. (2010b)
PA	Air	5[b]	Borcia et al. (2006)
PA12	Air	5.7[b]	Upadhyay et al. (2004)
PA6	Air	5.7[b]	Upadhyay et al. (2004)
PA6	$He-O_2$	1200	Pappas et al. (2008)
PA66	Air	2400[a]	Souto et al. (2011)
PA66	Air	500–1500	Bessada et al. (2011)
PE	Air	2[a]	Akishev et al. (2003)
PE	N_2	0.7[a]	Akishev et al. (2003)
PE	Ar	0.12[a]	Akishev et al. (2003)
PE	$He-O_2$	1200	Pappas et al. (2008)
PE	Air	6	De Geyter et al. (2008)
PET	Air	2[a]	Akishev et al. (2003)
PET	Ar	0.12[a]	Akishev et al. (2003)
PET	Air	600	Oliveira et al. (2010b)
PET	Air	5[b]	Borcia et al. (2006)
PET	Air	50[b]	Morent et al. (2007)

Continued

Table 6.2 Continued

Textile substrate	Carrier gas	Power (W)	References
PET	He	50[b]	Morent et al. (2007)
PET	Ar	50[b]	Morent et al. (2007)
PET	Air	n.a.	Klenko et al. (2006)
PET	Air	500−1500	Bessada et al. (2011)
PET	Air	500[b]	Leroux et al. (2009)
PI	He−O_2	1200	Pappas et al. (2008)
PP	Air	2[a]	Akishev et al. (2003)
PP	N_2	0.7[a]	Akishev et al. (2003)
PP	Ar	0.12[a]	Akishev et al. (2003)
PP	Air	200[b]	Morent et al. (2007)
PP	He	200[b]	Morent et al. (2007)
PP	Ar	200[b]	Morent et al. (2007)
PP	N_2	0.5[b]	Rahel' et al. (2003)
PTFE	He−O_2	1200	Pappas et al. (2008)
Wool	Air	600	Oliveira et al. (2010b)
Wool	Air	5[b]	Borcia et al. (2006)
Low-pressure plasma (LPP)			
Aramid	Ar	n.a.	Freitas et al. (2006)
Aramid	N_2	n.a.	Freitas et al. (2006)
Aramid	O_2	n.a.	Freitas et al. (2006)
Aramid	O_2	0.38[a]	Verschuren (2005)
Cotton	O_2	0.64[a]	Poll et al. (2001)
Cotton	O_2	300	Sun and Stylios (2004)
Lyocell®	O_2	500	Persin et al. (2012)
Modal®	O_2	500	Persin et al. (2012)
PA6	N_2	60	Canal et al. (2007)
PA6	O_2	60	Canal et al. (2007)
PE	Ar	40	Huang et al. (2013)
PET	$SiCl_4$	150	Negulescu et al. (2000)
PET	O_2, N_2, H	n.a.	Costa et al. (2006)
PET	O_2, N_2	0.4[b]	Vatuňa et al. (2004)
PET	Air	7.7[b]	Riccardi et al. (2003)

Table 6.2 Continued

Textile substrate	Carrier gas	Power (W)	References
PET	O_2	0.38[a]	Verschuren (2005)
PP	O_2	300	Wei et al. (2005)
PP	O_2	500	Masaeli et al. (2007)
Viscose	O_2	500	Persin et al. (2012)
Wool	O_2	300	Sun and Stylios (2004)
Wool	N_2	60	Canal et al. (2007)
Wool	O_2–N_2	60	Canal et al. (2007)
Wool	O_2	60	Canal et al. (2007)

n.a., not available.
[a]Power density (W cm^{-2}).
[b]Power (W).
[c]Frequency (MHz).

chemical groups and/or to the reduction/elimination of polymeric layers on the fabric surface. The wettability of a textile material is directly related to its surface energy and defines surface and interfacial phenomena including chemical reactivity, adsorption, desorption, wet processing, and adhesion (Kale and Desai, 2011).

The use of plasma discharge to improve various properties in low surface energy textile materials (e.g., polyethylene, polypropylene, and polyester) today is a deep-rooted technology (De Geyter et al., 2008; Samanta et al., 2009; Leroux et al., 2009; Thurston et al., 2007; Aouinti et al., 2003; Kabajev and Prosycevas, 2004). The increase in surface wettability is certainly one of the simplest studied properties to identify surface modification of plasma-treated textile materials. However, plasma-surface interactions are not yet fully comprehended because they are influenced by complex factors such as the chemistry of plasma gases, the nature of the substrate, and the operating parameters. Moreover, the energy or power density is one of the most important parameters to calculate plasma treatment costs and benefits, and at the same time it is also the most omitted parameters in literature (Abd Jelil et al., 2013) (Table 6.2).

The most commonly used methodologies to hydrophobize a textile substrate can be divided into three categories: (1) plasma treatment, (2) plasma etching (or ablation), and (3) plasma polymerization (Roth, 2001; Bahners et al., 2008). Plasma treatment uses inert gases such as argon (Ar), helium (He), nitrogen (N_2), and chemically active molecules such as oxygen (O_2) or ammonia (NH_3), as well as fluorinated gases such as carbon tetrafluoride (CF_4), hexafluoroethane (C_2F_6), perflutren (C_3F_8), perfluoroisobutylene (C_4F_8), decafluorocyclopentane (C_5F_{10}), trifluoromethane (CHF_3), sulfur hexafluoride (SF_6), and other (larger size) fluorine-containing molecules such as perfluoroalkyl acrylates (Zille et al., 2015; Morent et al., 2008; Yim et al., 2013; Gotoh et al., 2017; Vietro et al., 2015; Tendero et al., 2006;

Table 6.3 List of most important input chemical monomers used in plasma hydrophobization treatment of textiles.

Atmospheric plasma **Refs: (Yim et al., 2013); (Gotoh et al., 2017); (Tendero et al., 2006); (Zille et al., 2015); (Sparavigna, 2008); (Morent et al., 2008)**	**Low pressure plasma** **Refs: (Vietro et al., 2015); (Zille et al., 2015); (Sparavigna, 2008); (Morent et al., 2008); (Jafari et al., 2013); (Hochart et al., 2003b); (Hegemann, 2006)**
$C_{11}H_7F_{13}O_2$	CF_4
$C_{13}H_7F_{17}O_2/C_{15}H_7F_{21}O_2$	C_2F_4
Unidyne TG-571®	C_3F_6
CF_4	C_2F_6
CF_3CHF_2	C_3F_8
CHF_3	C_4F_{10}
C_3F_6	C_6F_{14}
C_2F_6	C_4F_8
$C_8F_{17}CH_2CH_2OCOCH{=}CH_2$	CF_3CHF_2
C_3F_8	SF_6
$C_{13}H_7F_{17}O_2$	CF_3SO_3H (co-monomer)
SF_6	C_2ClF_3 (co-monomer)
$H_2C{=}CHCO_2CH_2CH_2(CF_2)_7CF_3$	C_6F_6 (co-monomer)
$C_6H_{13}F_3O_3Si$ (FAS-3)	HC_6F_5 (co-monomer)
C6F5Si(OC2H5)3 (FAS-5)	$CF_3(CF_2)_7CH{=}CH_2$
$C_{13}H_{13}F_{17}O_3Si$ (FAS-17)	1,1,2,2, tetrahydroperfluorodecyl acrylate

Sparavigna, 2008; Jafari et al., 2013). The plasma-activated gases introduce chemical functionalities or create and deposit free radicals onto the target surface that can be subsequently used to cross-link or surface-graft other molecules to attain specific surface properties (very often more hydrophilic surfaces).

Another method consists of the immersion of the fabric in a fluid of hydrophobic fluorinated prepolymer with added initiators followed by a plasma treatment leading to the grafting on the surface of the fabric. Plasma etching occurs when the substrate is bombarded with ions from the plasma to clean, sterilize, or enhance surface adhesion of the fabrics. For example, dry plasma etching can be accomplished by using CF_4 in a plasma discharge to create active species capable of reacting chemically with the layer to be etched (Sigurdsson and Shishoo, 1997).

Plasma polymerization is a process where a monomer in vapor phase such as CF_4, C_2F_6, C_3F_8, or larger fluorinated molecules such as fluorodecylacrylate is converted into reactive fragments, which polymerize at the surface (plasma-induced

polymerization) or combine with polymers in the gas phase (plasma-state polymerization) to be deposited on the substrate (Sigurdsson and Shishoo, 1997; Li and Jinjin, 2007; Artus et al., 2012; Sun and Stylios, 2006). The deposition can occur while the plasma is excited or in a two-step process: (i) creation of radicals on the fiber surface by plasma in inert gas (e.g., argon) and (ii) reaction of these radicals with unsaturated monomers (Morent et al., 2008).

Numerous studies with different plasma discharges were conducted with the objective of increasing the hydrophobicity of various textile fibers such as polyesters, polyacrylonitrile, polypropylene, cotton, and silk. (Sigurdsson and Shishoo, 1997; Hegemann, 2005; Ji et al., 2008; Leroux et al., 2008; Hochart et al., 2003a; Höcker, 2002; Mattheus, 2005; Kim et al., 2006; Caschera et al., 2013; Vasiljević et al., 2012; Suanpoot et al., 2008). Nowadays, fluorocarbons are used to reduce the fiber friction due to their low frictional coefficients and hydrophobic properties. Despite the price of these fibers remains high, fluorocarbon fibers remain the most efficient solution to provide effective anti-stain to both water and oil at the same time (Bertaux et al., 2009).

The majority of plasma-based textile treatment processes for the production of hydrophobic and oleophobic surfaces (but also for some polymer coating, flame retardant, and medical antimicrobial fabrics) reported in the technical literature are based on nonthermal plasmas generated at low pressure (between 1 mTorr and 1 Torr) and in few cases at atmospheric pressure (Table 6.3). However, atmospheric plasma source designs based on corona discharges, glow discharges, dielectric barrier discharges (DBDs), plasma jet, capacitive or inductive coupled discharges, and radio frequency− or microwave-induced discharges have been intensively studied (Zille et al., 2015; Morent et al., 2008; Gotoh et al., 2017; Vietro et al., 2015; Tendero et al., 2006; Sparavigna, 2008; Jafari et al., 2013; Sigurdsson and Shishoo, 1997). Most of these technologies are still at an emerging stage although some of the manufacturers have developed commercial scale machinery and applications for specialized textiles that are currently being implemented at industrial scale.

6.4 Other applications and barriers

Compared with the traditional finishing processes, plasma technology has several advantages of improving the surface functionality, enhancing the interaction between fibers and reducing the usage of chemicals and energy, hence, cost saving. Plasma technology can be applied to fibers, yarns, fabrics, and garments; nonwovens; coated fabrics; and composites to enhance surface functionality. Plasma technology has the potential to be applied in a range of areas which includes antimicrobial treatment, UV resistant finish, self-cleaning, and flame retardant finish. Textiles with higher durability and fastness properties can be achieved with this technology without changing the textile bulk properties. The other areas of plasma application includes:

* Removing surface hairiness of textile materials.
* Scouring of cellulosic materials and synthetic materials such as polyester and nylon.
* Enhancing the electrical conductivity of yarns by plasma deposition.

* Antishrink treatment of textiles.
* Improved adhesion between various textile substrates.
* Desizing of textile materials.
* Producing stain-resistant finishing in the fabrics.
* Silicone coating on textile substrates such as airbags.
* Reducing color variation of textile materials.

Plasma technology has some barriers that need to be addressed in order to make this technology successful. The major problem is the availability of commercial machinery for industrial applications, gaps in the applied research to commercialize the technology, slow development in industrial system, and less transparency of the results achieved. Although the cost of running the machinery is low in plasma technology, the initial invest will be high, which restricts the plasma application of textiles. Furthermore, the whole procedure and components must be carefully selected and monitored during the processing. Continuous processing of some plasma treatment can cause technical problems, which also needs to be addressed. Some low-pressure plasma systems are available in the European market. However, in many other countries, there are not many manufacturers of industrial machinery.

6.5 Conclusions

The application of plasma technology into fashion and textiles is gaining impetus due to its eco-friendliness. Plasma technology is a dry, nonpolluting and worker-friendly method to achieve surface functionality of fashion and textile materials without modifying the bulk properties of the materials. For textile applications, atmospheric nonthermal plasma application is best suited as most textile materials are heat-sensitive polymers. In the last decade or so, plasma technology has become a very active, high growth research field, due to its great potential for the surface modification of textile substrates in the textile industry.

The introduction of plasma treatment in textile industry has improved the sustainability factor, since plasma technology helps to reduce the use of water and chemicals, which are essential in traditional processes. It is very effective with many properties modification without affecting bulk properties of the textiles. Moreover, economy-wise, plasma treatment gains huge advantages over conventional wet methods with reduction in cost and energy. On the other hand, initial purchases of the system, especially the vacuum pumps are fairly expensive and it must go through meticulous inspections for optimal outcome. With all the benefits plasma technology convey, its potential in the future is very promising.

Several research studies have been done in the last couple of decades on the low-pressure plasma applications to achieve various functionalities. A range of fibrous materials including plastics, polymers, resins, metals, ceramics, bio- and inorganic materials have been intensively researched and produced promising results. The surface modification include hydrophilicity, hydrophobicity, adhesion, sterilization, chemical resistivity, and inertness. Plasma technology has a promising future to achieve technical results economically.

Despite the high potential advantages and the environmentally friendly approach, the application possibilities of plasma technology in textile industry is still limited due to potential problems. The major problem is the availability of commercial machinery or industrial application systems, gaps in the applied research, and less transparency of the results achieved. In future, the textile and fashion manufacturers in developing countries will adopt this technology when these problems are overcome.

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