

Textile Strategy for Innovative Higher Education

e-book

Edited by Rimvydas Milašius

Co-editors:

Daiva Mikučionienė

Aileni Maria Raluca

Sofia Papakonstantinou

Desiree Scalia



ERASMUS+ project

Textile Strategy for Innovative Higher Education

Partners:

INCDTP, Romania
AEI TEXTILS, Spain
CIAPE, Italy
CRETHIDEV, Greece
ITTI, Italy
KTU, Lithuania
MCI, Italy
TUIASI, Romania
UMINHO, Portugal
UNIWA, Greece



**Funded by the
Erasmus+ Programme
of the European Union**

Programme - Strategic Partnership, Project Nr: 2017-1-RO01-KA203-037289

This project has been funded with support from the European Commission. This publication reflects the views only of the author, and the Commission cannot be held responsible for any use which may be made of the information contained therein.

2.5. Plasma Treatments

Andrea Zille, Antonio P. Souto, Universidade do Minho, Portugal

Fernando R. Oliviera, Federal University of Santa Catarina (UFSC), Brazil

Introduction

In recent years, plasma technology has assumed a great importance among all available textile surface modifications processes. It is a dry, environmentally- and worker-friendly method to achieve surface alteration without modifies the bulk properties of different materials. The plasma state also known as the fourth state of matter, is an electrically neutral ionized gas composed of neutral energy species, ions, photons and excited species not bound to an atom or molecule. More than 99% of the known universe is in the plasma state, except for the celestial cold bodies and planetary systems. The most used plasma classification divide plasmas in two categories: thermal plasma, when species are in thermal equilibrium, and cold plasma, when species are not in thermal equilibrium. Thermal plasmas are characterized by very high temperatures of electrons and heavy particles close to high ionization level. Temperatures can range from 4000 K, where species such as Cesium is easily ionized, to 20000K for species of difficult ionization, such as helium. Thermal equilibrium implies that the temperature of all species (electrons, ions, neutral species) must be the same. Some examples are: electric arcs, plasma jets from rocket motors and thermonuclear plasma-generating reactions. Thermal plasma is obtained at high gas pressures, which implies many collisions in the plasma since the average free path of the species is small. In this way, the energy exchange between the species of the plasma is efficient maintaining equal temperatures among the species. Cold plasma, also called non-thermal plasma, is composed of low-temperature particles (charged and neutral molecules and atomic species) and relatively high electron temperatures that are associated with low ionization. For cold plasmas, low pressure is used, which results in a few collisions of the plasma species, since the average free path is long. Consequently inefficiencies occur in the energy transfer, caused in the different temperatures of the plasma species. Cold plasmas are particularly appropriate for textile surface modification and processing because most fiber-based materials are heat sensitive polymers. Cold plasma treatments can be used to improve 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. Such forms of discharge have the major advantage of inducing significant surface chemical and morphological modifications improving hydrophilicity and making fibers more accessible to various chemical species without altering the bulk properties of the materials. Cold plasmas may be divided

into atmospheric pressure plasmas and vacuum or low-pressure plasmas (Figure 2.5.1).

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 the best results, especially for disperse dyes. However, low-pressure plasma treatments require expensive vacuum systems, therefore making it difficult to upscale and obtain continuous processing.

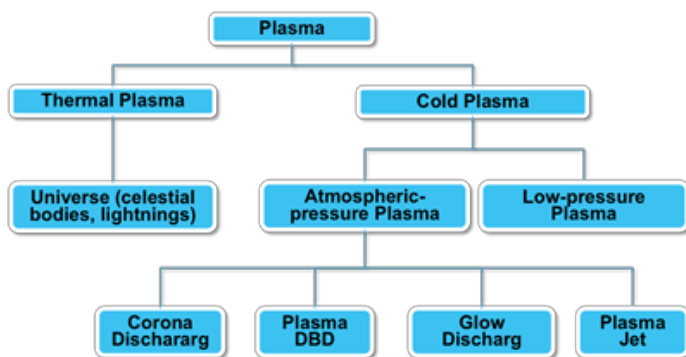


Figure 2.5.1. Plasma classification

Atmospheric plasma is an 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 fibers surfaces. The dielectric barrier discharge technology (DBD) is one of the most effective non-thermal atmospheric plasma sources and has been attracting increasing interest for industrial textile applications. Recently, both surface activation and deposition of thin functional coating by means of DBD atmospheric pressure plasma have been investigated in order to confer to textiles various properties (Figure 2.5.2), such as affinity for painting and dyeing, stain-resistance, antibacterial, no-shrinking and no-felting character. At this purpose different feeding gas mixtures have been used, from non-polymerizing ones (air, Ar, He, N₂, O₂), to hydrocarbon, fluorocarbon and organosilicon precursors.

Due to the intrinsic sterility of the treated surface, plasma processes are also attractive for applications in biology and medicine. In medical, food and textile fields, bacterial adhesion and subsequent surface growth is a persistent problem that leads to infection and biomaterial failure. Medical textiles are used in a range of applications from bandages, dressings, suture and surgical clothing to implants

such as scaffolds, stents and meshes. Infections associated with these devices are responsible for at least 2-7% of post-operational complications increasing mortality and healthcare costs. In the last decade, due to operation at atmospheric pressure and mild conditions, and to its ability to ignite plasma in small volumes, several efforts are being exerted to develop the dielectric barrier discharges (DBD) plasma processes for biomedical applications such as environmentally friendly non-fouling and antibacterial coatings. Several strategies using DBD plasma have been employed to impart antimicrobial properties to textiles materials (Figure 2.5.3). Silver (Ag) or Ag ion and quaternary ammonium salt are the most investigated antimicrobial agents. There is increasing interest in use of metals, especially silver and copper in a form of ions and especially nanoparticles as antimicrobial finishing agents, because of their pronounced oligodynamic and biocidal activity.

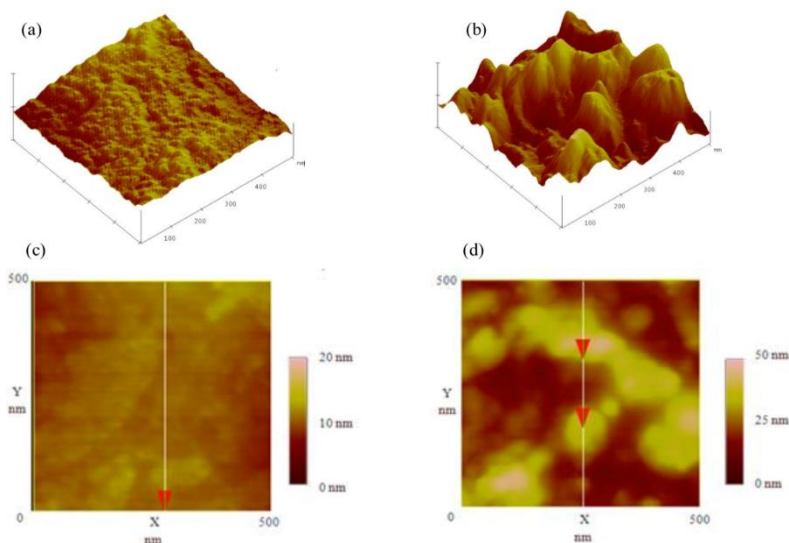


Figure 2.5.2. Example of a polyester fiber before (a,c) and after (b, d) DBD plasma treatment

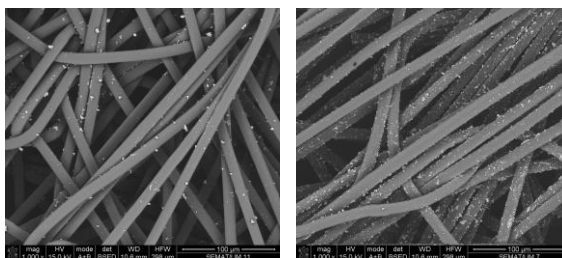


Figure 2.5.3. Example of AgNPs on polyester fiber before and after DBD plasma treatment

Notwithstanding the clear advantages of plasma technology application, its use in textile industry is limited. This is due to four main reasons: i) The traditional and not open to novelty of the textile industry sector; (ii) The contaminations or different surface conditions of the textile can influence negatively the surface cleanliness because plasma treatment only influences the top layer of the materials; (iii) The porous and 3D structure of textiles difficult the penetration of the plasma species deep into fabric structure as the wet processes; (iv) Textile materials have a large surface area, usually one order of magnitude larger than flat films. Despite that limitation, in the last decade due to constant technological and scientific developments, plasma technology is today used for several specific applications in technical textile industry and its use in improved devices for wider application is near to breakthrough. In the textile industry vacuum plasma technology is more advanced than atmospheric-pressure plasma technology because it is easier to control concentration, large volume of plasma, composition and process chemistry of the gas atmosphere in a closed system under vacuum. Several low-pressure plasmas company already commercialize equipment for the textile industry: the Italian (HTP Unitex, SAATI), Belgian (Europlasma), English (P2i) 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. Other European plasma equipment providers also develop low-pressure plasma products for the textile market such as Grinp, Softal, Iplas, Ahlbrandt Systems, and Arioli. 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 € m⁻². On the other hand, the costs of plasma coating at low pressure are higher (0.05 € m⁻²) because of the lower web speed and the more expensive process gases. 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 advantage in textile process that operate at higher processing speeds, for treat full width textiles (2 meter or wider) in continuous on-line mode allowing the easy integration in the conventional textile finishing lines. Some example of commercial atmospheric-pressure plasma technologies based on corona, DBD, Glow Discharge and new atmospheric devices are available: i) an industrial prototype 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 2.5.4). 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 € kg⁻¹) resulted higher than DBD (0.013 € kg⁻¹) [22]; ii) The company Softal, claims a payback time of only 9 months single-shift operation for its Aldyne plasma adhesion primer system versus conventional liquid priming; iii) The Swiss compay Sefar

AG/Switzerland uses the world largest atmospheric pressure plasma systems for industrial applications in the production of high-performance filtration solutions; iv) APJET (USA) company commercialize a proprietary all-dry APPJ technology to produce textile fabrics repelling oil and water on the outside, while retaining its original qualities and comfort on the inside; v) The Green Theme Technologies LLC company (USA) designed a so called ChemStik technology to be compatible with a 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; vi) the atmospheric pressure non-equilibrium plasma (APNEP) developed by EA Technology Ltd. in conjunction with the University of Surrey. 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.

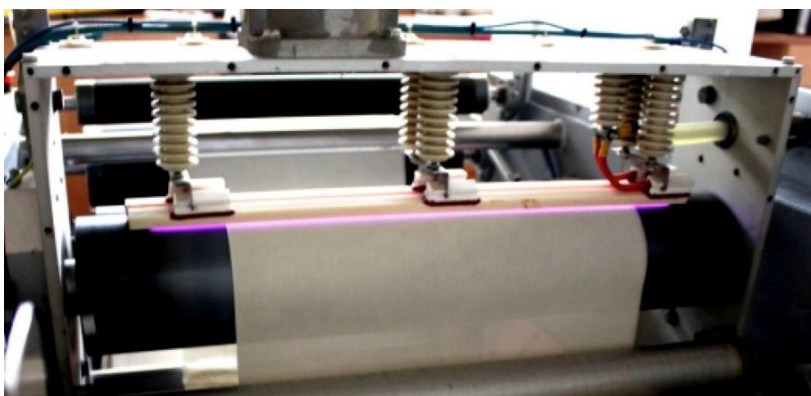


Figure 2.5.4. Semi-industrial prototype installed at the University of Minho

References

1. Fridman, A. Plasma chemistry, Cambridge University Press, New York 2008.
2. Vandecasteele, N., Reniers, F., J. Electron Spectrosc. Related Phenomena 2010, 178–179, 394.
3. Xi, M., Li, Y.-L., Shang, S.-y., Li, D.-H., Yin, Y.-X., Dai, X.-Y. Surf. Coat. Technol. 2008, 202, 6029.
4. Gleizes, A., Gonzalez, J. J., Freton, P. J. Phys. D: Appl. Phys. 2005, 38, R153.
5. Morent, R., De Geyter, N., Verschuren, J., De Clerck, K., Kiekens, P., Leys, C., Surf. Coat. Technol. 2008, 202, 3427.
6. Borgia, G., Dumitrascu, N., Popa, G. J. Optoelectron Adv. M 2005, 7, 2535.
7. Zille, A., Oliveira, F. R., & Souto, A. P. Plasma treatment in textile industry. Plasma processes and Polymers, 2015, 12(2), 98-131.
8. Denes, F., Macromolecular plasma-chemistry: an emerging field of polymer science. Progress in Polymer Science, 2004. 29(8): p. 815-885.

9. Ragoubi, M., et al., Impact of corona treated hemp fibres onto mechanical properties of polypropylene composites made thereof. *Industrial Crops and Products*, 2010. 31(2): p. 344-349.
10. Morent, R., et al., Non-thermal plasma treatment of textiles. *Surface & Coatings Technology*, 2008. 202(14): p. 3427-3449.
11. Borcia, G., C.A. Anderson, and N.M.D. Brown, Surface treatment of natural and synthetic textiles using a dielectric barrier discharge. *Surface & Coatings Technology*, 2006. 201(6): p. 3074-3081.
12. D'sa, R.A. and B.J. Meenan, Chemical Grafting of Poly(ethylene glycol) Methyl Ether Methacrylate onto Polymer Surfaces by Atmospheric Pressure Plasma Processing. *Langmuir*, 2010. 26(3): p. 1894-1903.
13. Leroux, F., et al., Fluorocarbon nano-coating of polyester fabrics by atmospheric air plasma with aerosol. *Applied Surface Science*, 2008. 254(13): p. 3902-3908.
14. Radetić, M., Functionalization of textile materials with silver nanoparticles, *Journal of Materials Science* 2012, 48, 95.
15. Sarghini, S., S. Paulussen, and H. Terryn, Atmospheric Pressure Plasma Technology: a Straightforward Deposition of Antibacterial Coatings. *Plasma Processes and Polymers*, 2011. 8(1): p. 59-69.
16. Da Ponte, G., et al., Trends in surface engineering of biomaterials: atmospheric pressure plasma deposition of coatings for biomedical applications. *European Physical Journal-Applied Physics*, 2011. 56(2).
17. Sophonvachiraporn, P., et al., Surface Characterization and Antimicrobial Activity of Chitosan-Deposited DBD Plasma-Modified Woven PET Surface. *Plasma Chemistry and Plasma Processing*. 2011, 31(1): p. 233-249.
18. Mattheus, S. R. Plasma Aided Finishing of Textile Materials. North Carolina State University, 2005.
19. Roth, J. R., Nourgostar, S., Bonds, T. A., *IEEE Trans. Plasma Sci.* 2007, 35, 233.
20. Mohammad, H., Dirk, H., Substrate Independent Dyeing of Synthetic Textiles Treated with Low-Pressure Plasmas. in P. P. Hauser, Ed., *Textile Dyeing*. InTech Europe, Rijeka, Croatia 2011.
21. Souto, A. P., Os processos corona aplicados aos tratamentos de preparação e acabamentos de materiais têxteis, tese de doutoramento, Universidade do Minho, Guimarães. Os processos corona aplicados aos tratamentos de preparação e acabamentos de materiais têxteis. Universidade do Minho, 2003.
22. Shishoo, R. *Plasma Technologies for Textiles*, Woodhead Publishing Limited, Cambridge, England, 2007.
23. Gadri, R. B., Roth, J. R., Montie, T. C., Kelly-Wintenberg, K., Tsai, P. P. Y., Helfritsch, D. J., Feldman, P., Sherman, D. M., Karakaya, F., Chen, Z., *Surf. Coat. Technol.* 2000, 131, 528.
24. Castro, F. A., Chabreck, P., Hany, R., & Nüesch, F. Transparent, flexible and low-resistive precision fabric electrode for organic solar cells. *physica status solidi (RRL)*—Rapid Research Letters, 2019, 3(9), 278-280
25. Chirokov, A., Khot, S. N., Gangoli, S. P., Fridman, A., Henderson, P., Gutsol, A. F., Dolgopolsky, A. Numerical and experimental investigation of the stability of radio-frequency (RF) discharges at atmospheric pressure. *Plasma Sources Science and Technology*, 2009, 18(2), 025025.