### Plasma treatment in textile industry





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#### Introduction



Plasma treatment of textiles is considered as an eco-technology, since it is used in functionalizing different materials in a dry state without/with minimum added chemicals in relatively short time. Unlike conventional wet and chemical processing, plasma treatment does not require the use of solvents or water, and it is a non-destructive technology overall. By using different elements and gases, different functionalities can be acquired on the treated surfaces.

In the last decade, numerous types of plasma have been used to treat textile materials made from all kinds of fibers (natural, synthetic and regenerated), using a variety of gases and gas mixtures, to change the wettability and surface energy of textiles like wool, PET, cotton, silk, aramid, acrylic, carbon and PA6.

It was additionally used to increase fiber-matrix adhesion in composite materials (based on carbon especially), and to improve energy efficiency in flow batteries, through integration of new functional groups at these surfaces.

The important property of plasma is that it mainly affects the exposed surface, which guarantee maintained properties of the bulk material while modifying surface properties.

Hence, plasma treatment is an important technology to develop and upgrade the advanced manufacturing processes of textile materials, in step-forward towards sustainability and resource-efficient methods with added economical value.

#### Keywords

Plasma treatment, Textile, Surface modification, Dry technologies

#### Goals



Herein, we aim to provide a comprehensive yet summarized resource about the plasma technology to a wide variety of interested scholars with focus on main points such as: the nature of plasma and how it can occur naturally and be created artificially. Additionally, state of the art of this technology on both research and industrial scales is discussed, and how plasma is used in innovative and smart materials as well as in functional and decorative textiles via different systems that adopt to different materials and temperatures.

Furthermore, the potential of plasma as a dry method in surface modifications of textiles is highlighted. Since this technology is used nowadays in the production of high-quality textile materials that fits different purposes in our daily lives.

Finally, some of the applications of this Ecotechnology in textile innovation and advanced manufacturing are summarized with both the pros and cons of these treatments and the challenges that face the large-scale integration of plasma in textile industry.

#### Learning outcomes



This education resource was developed in efforts to facilitate and enrich the learning process of interested scholars from different educational levels.

The expected learning outcomes can be summarized:

- Understanding the nature of plasma and the methods used to create it in laboratory levels.
- The main systems of plasma in markets nowadays.
- The chemical and physical mechanisms of surface modification of textiles, that can be achieved by plasma treatment.
- How the different plasma gases can affect the outcome of the treatment
- The main fields of application of plasma in textile research and industry

#### Structure

- 1. Background
- 2. Main types of plasma systems
- 3. Plasma Characteristics
- 4. Plasma interactions with textile material
- 5. Advantages and disadvantages of plasma treatment
- 6. Applications of plasma treatment in textile industry and research

### 1. Background

- Plasma is the fourth state of matter
- It can be created by subjecting a gas or gas mixture to energy leading to ionized-gas state formation
- It can conduct electrical currents
- Plasma mainly consist of: free radicals, UV radiation, electrons and meta-stables
- It contains an equal amount of negative and positive particles



Figure: plasma main contents





Figure: States of matter

#### 1. Background

- Plasma is a surface treatment
- The properties of the bulk material are maintained after plasma treatment
- The main chemical reactions stimulated by plasma are:
- 1. Breaking the chemical chain
- 2. Free radical formation
- 3. Creation of double bonds
- 4. Degradation (etching)
- 5. Elimination of lateral bond
- 6. End-of-chain functionalization
- 7. Grafting of lateral group
- 8. Crosslinking



Figure: Modified zones via plasma



#### 2. Main types of plasma systems



There are different methods used to create artificial plasma

1- Subjecting gas to high frequency electromagnetic field **"Torch plasma"**  2- Excitation of gas between two electrodes

"Vacuum and atmospheric plasma" 3- Excitation of gas by electrodeless microwave discharge with high frequency

"Cold Remote Plasma"

These two types of plasma differ according to the material of electrodes

metallic electrodes like Corona,

electrodes are covered by dielectric barrier like ceramic or silicon that we can refer to it as Dielectric Barrier Discharge (DBD).

 Samal, Sneha. 2017. "Thermal Plasma Technology: The Prospective Future in Material Processing." Journal of Cleaner Production 142. Elsevier Ltd: 3131–50. doi:10.1016/j.jclepro.2016.10.154.
Interreg. 2017. "Atmospheric and Low Pressure Plasma Treatments : A Comparison Outline," 21.

#### 2. Main types of plasma systems



Examples of Plasma technologies



Image: Torch Plasma



Image: Cold remote plasma



lmage: Corona



Image: Atmospheric pressure plasma

### 3. Plasma Characteristics



- Plasma can be characterized mainly by:
- 1. Plasma's potential: which indicates its equilibrium voltage
- 2. Plasma's density: referring to the concentration of electrons
- 3. Electron temperature: indicates the mean electron energy
- 4. Interactions between the species, indicating the main collisions between the charged particles
- The outcome of plasma treatment for a certain material depends on factors:
- 1. The electrical power
- 2. Frequency
- 3. Gap between electrodes
- 4. The gas used

### 3. Plasma Characteristics

#### How to create plasma in laboratory

- In order to create artificial plasma, certain equipment are required:
- 1. A holder to contain the material (textile)
- 2. A power source
- 3. A tool to inject the gas in a controlled manner
- 4. Coupling elements such as electrodes
- 5. If it is low pressure plasma, a vacuum chamber is required



Example: schematic of atmospheric pressure plasma system adopted from (Narendiran, Vitchuli Gangadharan, 2011)





- **Removing** effect includes: cleaning textile, desizing, etching to modify topography of the surface and sterilization from contamination.
- Adding effect includes: Activation of textile surface can be temporary effect to modify the surface energy
- **Functionalization** of textile surface: permanent effect and includes the introduction of new chemical groups of the surface
- **Deposition** and coating: to add materials as thin layers on the surface of textiles



#### Cleaning

- For cleaning surfaces using plasma, usually an inert gas (Ar, He) and oxygen plasmas are used.
- Contaminants on the surface and under the influence of ions, free radicals and electrons of the plasma undergo:
- 1. Abstraction of hydrogen with free radical formation
- 2. And repetitive chain scissions, until molecular weight is sufficiently low



Sparavigna, Amelia. 2002. "Plasma Treatments for Textiles: An Innovative Technology for Traditional and Technical Fabrics." http://arxiv.org/abs/0801.3727.
Šimončicová, Juliana, Svetlana Kryštofová, Veronika Medvecká, Kamila Ďurišová, and Barbora Kaliňáková. 2019. "Technical Applications of Plasma Treatments: Current State and Perspectives." Applied Microbiology and Biotechnology 103 (13): 5117–29. doi:10.1007/s00253-019-09877-x.



#### Activation

- Activation can happen when a textile surface is treated with a gas that does not contain carbon (such as  $O_2$ ,  $N_2$  or  $NO_3$  and others)
- Activation results in incorporation of different moieties of the gas used onto the

surface of the treated textile

- The activated surface contains functional groups such as carbonyl, carboxylic, hydroxyl, amino and amines
- Almost any fiber, textile, or polymeric surface may be activated to provide chemical functionality to improve compatibility with adhesives or coatings
- Examples of surface activation by substituting hydrogen in a polymeric chain with other groups such as COOH, NO<sub>3</sub>, NH<sub>2</sub>, O, OH, etc...



 Sparavigna, Amelia. 2002. "Plasma Treatments for Textiles: An Innovative Technology for Traditional and Technical Fabrics." http://arxiv.org/abs/0801.3727.
Šimončicová, Juliana, Svetlana Kryštofová, Veronika Medvecká, Kamila Ďurišová, and Barbora Kaliňáková. 2019. "Technical Applications of Plasma Treatments: Current State and Perspectives." Applied Microbiology and Biotechnology 103 (13): 5117–29. doi:10.1007/s00253-019-09877-x.



#### **Grafting polymers**

- Usually, an inert gas such as Argon is used as process gas for this purpose, and consequently, free radicals will be created on the material surface
- If a monomer, which is capable of reacting with those free radicals, is introduced into the treatment chamber, the monomer shall become grafted on the surface
- This procedure is suited for low-pressure plasma treatment. However, polymer grafting can be conducted using atmospheric plasma systems as well
- Typical monomers are acrylic acid, allyl amine and allyl alcohol



8. Sparavigna, Amelia. 2002. "Plasma Treatments for Textiles: An Innovative Technology for Traditional and Technical Fabrics." http://arxiv.org/abs/0801.3727. 9. Šimončicová, Juliana, Svetlana Kryštofová, Veronika Medvecká, Kamila Ďurišová, and Barbora Kaliňáková. 2019. "Technical Applications of Plasma Treatments: Current State and Perspectives." Applied Microbiology and Biotechnology 103 (13): 5117–29. doi:10.1007/s00253-019-09877-x.



#### Material deposition (coating)

- A complex molecule is employed as the plasma gas for this purpose
- Plasma-enhanced chemical-vapour deposition (PECVD) may result in fragmentations of gas during plasma treatment, reacting with itself to produce a thin layer of polymer
- PECVD process permanently alters surface properties of textiles, including plasma-assisted crosslinking



Sparavigna, Amelia. 2002. "Plasma Treatments for Textiles: An Innovative Technology for Traditional and Technical Fabrics." http://arxiv.org/abs/0801.3727.
Šimončicová, Juliana, Svetlana Kryštofová, Veronika Medvecká, Kamila Ďurišová, and Barbora Kaliňáková. 2019. "Technical Applications of Plasma Treatments: Current State and Perspectives." Applied Microbiology and Biotechnology 103 (13): 5117–29. doi:10.1007/s00253-019-09877-x.



#### What gas does what?

- Each gas produces a unique plasma composition and results in different surface properties
- Gases, or mixtures of gases used for plasma treatment of textiles can include  $O_2$ , air, Ar, He,  $CO_2$ ,  $N_2$ ,  $H_2$ , Tetrafluoromethane, water vapor, methane, or ammonia



9. Šimončicová, Juliana, Svetlana Kryštofová, Veronika Medvecká, Kamila Ďurišová, and Barbora Kaliňáková. 2019. "Technical Applications of Plasma Treatments: Current State and Perspectives." Applied Microbiology and Biotechnology 103 (13): 5117–29. doi:10.1007/s00253-019-09877-x. 10. https://www.textilesphere.com/2019/08/plasma-technolgy-in-textiles.html

# 5. Advantages and disadvantages of plasma treatment of totols

#### ✓ Advantages

- Saving water, since it is a dry method
- Production of meta-stable surfaces and materials
- It is adaptable for polymer treatment since it is low-temperature treatment (except few types)
- Resource-efficient process using less energy and low concentrations of gasses and monomers
- Treatment for the surface and does not alter the properties of bulk material
- It is a clean process without waste generation
- The consumption of chemicals is very low
- It is simple process which could be easily automated to control the parameters

11. Sarmadi, Majid. 2013. "Advantages and Disadvantages of Plasma Treatment of Textile Materials." International Symposium on Plasma Chemistry, no. August: 7–10. https://www.semanticscholar.org/paper/Advantages-and-Disadvantages-of-Plasma-Treatment-of-Sarmadi/19e75834ff72a047f546d6b86b599690c3539e01.



#### X Disadvantages

- The plasma treatment tends to produce harmful gasses such as ozone and nitrogen oxides during operation. It is therefore recommended to install the plasma treatment systems in well-ventilated areas
- Scaling up could present some technical challenges, along with converting batch mode to continuous mode
- In some cases, effects of plasma treatment can be only temporary, this can be prevented by proper storgae

11. Sarmadi, Majid. 2013. "Advantages and Disadvantages of Plasma Treatment of Textile Materials." International Symposium on Plasma Chemistry, no. August: 7–10. https://www.semanticscholar.org/paper/Advantages-and-Disadvantages-of-Plasma-Treatment-of-Sarmadi/19e75834ff72a047f546d6b86b599690c3539e01.



### 1. Surface wetting changes for natural and synthetic textiles

- After plasma treatment the surface energy changes depending on the gas used
- Improvement of surface wetting in polymers such as PA, PE, PP, PET PTFE

(treatment by O<sub>2</sub>, air, NH<sub>3</sub>-plasma)

• Hydrophobic finishing of cotton and cotton/PET blends

(treatment by siloxane or perfluorocarbon plasma)

• Oleophobic finish for cotton/ PET

(grafting of perfluoroacrylat by plasma)



Image: water droplets on fabrics





### 2. Improved adhesion between textiles and coatings

- Adhesion can be increased via plasma treatment through several mechanisms
- Plasma is particularly efficient in composites and Laminates production
- Good adhesion depends on the interactions between the layers at the interface
- Fiber's surface energy can be modified with plasma treatments to improve the compatibility with resins and coatings via functional groups or electrostatic bonds
- Surface topography of the textile or fiber can be modified through plasma-etching to improve the mechanical interlocking at the interface



#### Adhesion enhancement mechanisms via plasma

- 1) Chemical bonding (functional groups)
- 2) Mechanical interlocking (etching)
- 3) Electrostatic interaction

Figure: Plasma effects on adhesion

13. Yu, Hang, Yiyuan Zhang, Anita Wong, Igor M. De Rosa, Han S. Chueh, Misha Grigoriev, Thomas S. Williams, Tommy Hsu, and Robert F. Hicks. 2014. "Atmospheric and Vacuum Plasma Treatments of Polymer Surfaces for Enhanced Adhesion in Microelectronics Packaging." Adhesion in Microelectronics 9781118831335: 137–72. doi:10.1002/9781118831373.ch4.

14. Awaja, Firas, Michael Gilbert, Georgina Kelly, Bronwyn Fox, and Paul J. Pigram. 2009. "Adhesion of Polymers." Progress in Polymer Science (Oxford) 34 (9): 948–68. doi:10.1016/j.progpolymsci.2009.04.007.



# 3. Changes in physical properties

- Softening of cotton / cellulose-based polymers (treatment by oxygen plasma)
- Reduced felting and shrinkage of wool (treatment by oxygen plasma)

#### 4. Changes in electrical Properties

• Antistatic finish of rayon (with chloromethyl dimethylsilane in plasma)

# 5. Dyeing and printing

- Capillary uptake improvement in wool (treatment by oxygen plasma)
- Improved dyeing for polyamide (treatment with Ar plasma)

Sparavigna, Amelia. 2002. "Plasma Treatments for Textiles: An Innovative Technology for Traditional and Technical Fabrics." http://arxiv.org/abs/0801.3727.
Šimončicová, Juliana, Svetlana Kryštofová, Veronika Medvecká, Kamila Ďurišová, and Barbora Kaliňáková. 2019. "Technical Applications of Plasma Treatments: Current State and Perspectives." Applied Microbiology and Biotechnology 103 (13): 5117–29. doi:10.1007/s00253-019-09877-x.
Abdelbagi, Hasabo, and Mohamed Ahmed. 2018. "Plasma Treatment in Textile Substrates - A Review Journal of Engineered Fibers and Fabrics Plasma Treatment in Textile Substrates - A Review Journal of Engineered Fibers and Fabrics Plasma Treatment in Textile Substrates - A Review." no. March.



# 6. Flame-retardant feature

• Adding flame retardancy for cotton, rayon and polyacrylonitrile (treatment by plasma with phosphorus containing monomers)

# 7. Other applications

- Fabrics favoring/ preventing overgrowth of bacteria in biology and medicine (treatment by plasma to modify functional groups on the surface)
- Electrically charged and bipolar membranes for separation applications (treatment with plasma to modify the electrostatic charge on the surface of membrane)

9. Šimončicová, Juliana, Svetlana Kryštofová, Veronika Medvecká, Kamila Ďurišová, and Barbora Kaliňáková. 2019. "Technical Applications of Plasma Treatments: Current State and Perspectives." Applied Microbiology and Biotechnology 103 (13): 5117–29. doi:10.1007/s00253-019-09877-x. 16. Ahmed, D, and U Rehman. 2010. "An Update on the Technology and Application of Plasma Treatment for Textiles."



#### Cotton plasma processing

- A helium/oxygen plasma improves desizing of starch from cotton fabrics
- Plasma technology can be used to remove PVA sizing from cotton fibers as well (O<sub>2</sub>/He plasma or air/He plasma)
- Modification of the mechanical properties of cotton fiber can be obtained by oxygen plasma (and adding wettability)
- Hydrophobic effect of cotton after CF<sub>4</sub> and C<sub>3</sub>F<sub>6</sub> plasma treatment, -CFx chemical groups were obtained after reaction between surface molecules and fluorinated gases
- $CF_4$  and  $C_3F_6$  are used on cotton denim fabrics with

a low-pressure low-temperature plasma system to

increase hydrophobic properties of the surface



Image: Hydrophobic effect on cotton

17. Cornelius, Carrie, Marian McCord, Mohamed Bourham, and Peter Hauser. 2017. "Desizing of Starch Sized Cotton Fabrics with Atmospheric Pressure Plasma." Cellulose 24 (12). Springer Netherlands: 5685–95. doi:10.1007/s10570-017-1509-1.



#### Polyamide 6 plasma processing

- Plasma treatment on polyamide focuses mainly on dyeability, wettability and surface properties modification, since it is a hydrophobic polymer
- Air and O<sub>2</sub> plasma are used to increase wettability and dyeability
- On polyamide 6, an air plasma treatment was performed on industrial scale to increase of bonding with other fibers in blends
- Plasma treatment with NH<sub>3</sub> increases N-functionalities, such as amino (-N
  - (-CH=NH), and cyano (-C≡N) groups
- In addition, oxygen-containing groups are increased after

this type of treatment due to post-plasma atmospheric

oxidation on the surface of the fibers



Image: improved dyeing process pf PA6



#### Wool plasma processing

- Shrink-resist treatment of wool can be achieved by plasma with a simultaneously improved dyeing and printing
- The hydrophobic lipid layer on the surface of wool is oxidized via plasma and partially removed. Thus disulfide crosslinking bridges are reduced and the shrinkage is decreased.
- As the surface is oxidized via plasma, the hydrophobic property is changed to become increasingly hydrophilic.
- This improves dyeing kinetics, depth of shade of wool,

and reduces dye waste in effluents



Image: Shrink-resisting of wool

18. Shahidi, S., A. Rashidi, M. Ghoranneviss, A. Anvari, and J. Wiener. 2010. "Plasma Effects on Anti-Felting Properties of Wool Fabrics." Surface and Coatings Technology 205 (SUPPL. 1). Elsevier B.V.: S349–54. doi:10.1016/j.surfcoat.2010.08.003.



#### Carbon fiber plasma processing

- Carbon fiber is hydrophobic, which hinders its use in many applications
- Plasma improve wettability, adhesion of fiber-matrix interface in composite materials, and efficiency in flow batteries
- Plasma treatment is used on different carbon materials (fillers and graphene-based fibers) to improve supercapacitive properties to be used in electrical applications (low-temperature and atmospheric plasma)
- Improved biocompatibility with enzymes and bacterial

consortium is achieved by plasma treatment on

carbon textiles



Image: hydrophobic carbon nonwoven structure

19. Kahoush, May, Nemeshwaree Behary, Aurélie Cayla, Brigitte Mutel, Jinping Guan, and Vincent Nierstrasz. 2019. "Surface Modification of Carbon Felt by Cold Remote Plasma for Glucose Oxidase Enzyme Immobilization." Applied Surface Science 476 (August 2018). Elsevier: 1016–24. doi:10.1016/j.apsusc.2019.01.155.



#### PP, PE, PET and PTFE plasma processing

- Oxidative plasma treatment with a short treatment time can greatly improve wettability of these hydrophobic polymers
- Air-, O<sub>2</sub>- and NH<sub>3</sub>-plasma are usually performed with atmospheric or low-temperature systems
- These treatments are able to increase adhesion of these materials in composites
- Improve adhesion and stability in polymer-metal systems (anti-bacterial
- Improve biocompatibility with living culture and enzymes



Image: antibacterial effect of plasma treated textiles

#### Conclusions



- Plasma technology is a dry treatment that possesses a great potential in advanced manufacturing of textiles.
- This treatment showed to be efficient in modifying the surfaces of textiles from different sources such as wool, cotton, silk, and polymer-based fibers.
- The modifications after plasma treatment can be divided into physical (etching) and chemical (new functions) modifications.
- Modifying surface energy is considered one of the main benefits of plasma treatment, with the capacity of increasing/decreasing the wettability of textiles, as well as improving the adhesion between textiles and coatings.
- New applications for plasma treatment of textiles and membranes showed its benefits in customizing the compatibility between the treated surfaces and the bio-materials/ microorganisms.
- Reducing the added chemicals, reducing the power consumption, while creating no-waste are great advantages of plasma treatment.
- The integration of these systems in advanced textile processing is expected to increase added value without compromising the sustainability of resources.



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