

## Recent Advances in the Application of Plasma in Textile Finishing (A Review)

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THE TEXTILE industry is seeking innovative manufacturing technology to increase the quality of the fabric, and society needs modern environmental finishing techniques, such as using plasma Treatment as atmospheric-pressure dielectric barrier discharge (APDBD) corona discharge at atmospheric pressure (CDAP) which are gaining popularity in the textile industry due to their many advantages over traditional wet processing methods the textiles industry is gaining in popularity. The initiation of plasma by air or conventional industrial gases, such as hydrogen H<sub>2</sub>, N<sub>2</sub> and oxygen O<sub>2</sub> at ambient pressures, may be accomplished. Plasma introduces usable surface groups to provide properties such as antibacterial, UV, flame retardant and antistatic that are used in various fabrics such as cotton, linen, polyester, and surface fabrics after plasma therapy.

**Keywords:** plasma treatment, Environmental impact, Atmospheric Pressure, antibacterial, Flame retardant, UV protection, Antistatic.

### Introduction

Finishing processes are designed to increase the attractiveness or serviceability of the textile product. [1-17] Low-temperature plasma (LTP) treatment has been used to treat fabrics to improve their antibacterial, ultraviolet protection, flame retardant, antistatic properties. Theoretically, plasma treatment only affects the topmost surface of the substrate without having any effect on their internal structure and bulk characteristics. [18, 19] Not only the physical properties but also the treated substrate surface chemical properties can be altered, depending on the used plasma gas (or gases) and treatment parameters. [20] Plasma is a collection of particles that contain an equal number of positive ions and electrons, free radicals, UV radiation, and neutral species produced by a gas or vapor in electromagnetic or electrical fields. Plasma, being highly reactive, has been used to enhance surface adhesion, polymerization, sterilization, and surface modification materials. [18, 19] surface adhesion Plasma is a cluster of particles. [21] The triggered surface then integrates quickly with the excited gas species and

provides chemical reactive groups that are bound to the surface substrate covalently. The desired surface chemical can be obtained by choosing the gas, vapor, or mixture of gases. [22, 23]

Cotton is an excellent natural material, but it is easy for bacteria to grow on it. To a certain extent, this can generate an unpleasant odour, stains, and discoloration. The ideal antibacterial finishing should be non-toxic, washable, environmentally friendly, and durable. [21, 24] Textile fabrics protect our skin from toxic UV radiation. The ultraviolet protective factor (UPF) is widely used to determine the level of UV radiation protection to textile materials. UPF is the average ratio of effective ultraviolet irradiation for exposed skin to an average effective ultraviolet skin protected radiation. [25] The need to produce flame-retardant textiles may be assessed in terms of identifying the hazard to life and property which burning textiles using plasma atmospheric-pressure dielectric barrier discharge (APDBD) which applied to the cotton and polyester fabric. [21, 26] An antistatic agent's primary which are role to prevent the generation of electricity within

the various textiles as low temperature plasma (LTP) treatment increases the amount of oxygen-containing polar groups on the polyester fibre surface. All this finishing are presented in this review with details.

*Definition of plasma*

A plasma is a partially ionized gas consist of positive ions and free electrons and is sometimes referred to as the fourth state of matter. [27, 28] the gas matter becomes plasma with high heat and high pressure (see Fig. 1). [22, 29, 30] Apply an electric field to the gas plasma formed in the chamber at low pressure to maintain a steady state. Plasma, as a very reactive material, can be used to alter the surface of a certain substratum (usually known as plasma activation or plasma modifications), to store chemical matter (Plasma polymerization or plasma grafting), to convey the necessary properties, to extract substances previously stored on the substratum (plasma cleansing or plasma grafting) [22, 29, 30] Different gas types used with plasma, such as argon,

oxygen, nitrogen, fluorine, carbon dioxide, and water can produce specific surface characteristics for different applications. [31]

*Types of plasma*

Plasma systems have a wide variety of potential substance therapies. Industrial plasma technology uses two main forms of plasma (see Fig. 2): the first “thermal plasma” generated by direct and alternate (dc-ac) current or by microwave source at high-pressure (>10kPa). The devices produce plasmas with 1-2 eV electron and ion temperatures and very low gas ionization. Thermal plasma may be used to dissolve or produce anti-corrosion, thermal barriers, anti-wear coatings, solid, liquid, and gaseous radioactive halogenated and dangerous compounds.

The second type of plasma, called cold or non-balance plasma, has a higher electron temperature than ion. It has been traditionally considered that low-pressure plasmas, working between 0.1 pa and 100 pa.[32] Cold plasmas may be used to modify the surfaces from simple topographical

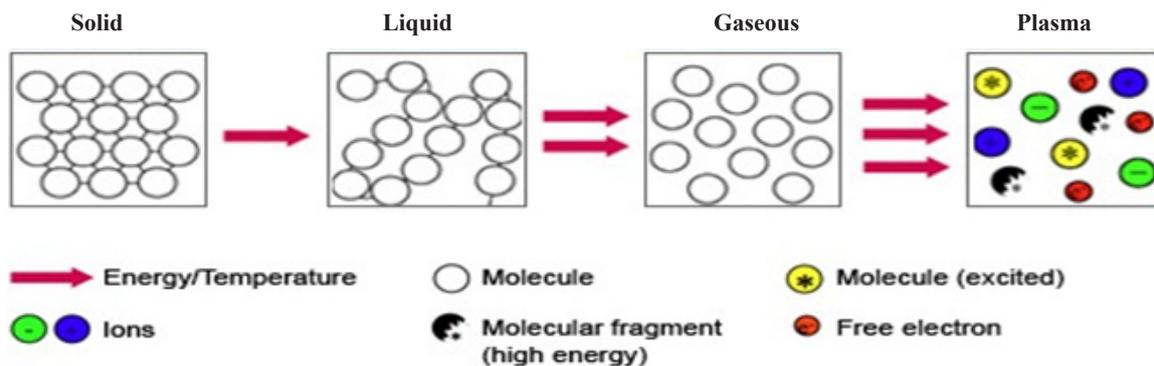


Fig. 1. States of matter.

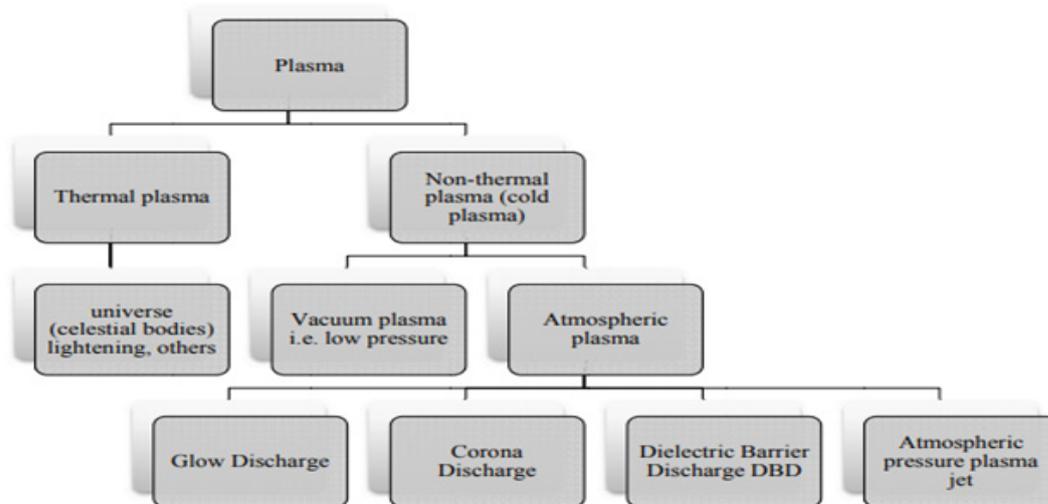


Fig. 2. Forms of industrial plasma technology uses two main forms of plasma

modifications to surface chemistry development and coverings that differ considerably from the bulk substance. [33]

In several various textile applications, non-thermal plasmas or cold plasmas are commonly used. Textile plasma operations are either under vacuum pressure or under pressure from the atmosphere. Plasmas are the most inimitably effective surface treatment tools. [34]

#### *Advantage of plasma for textile functionalisation*

The following properties make plasma so unique for textile functionalisation:

- plasma is applied at low temperatures and thus decreases the risk for fabric exposure.
- The ability in large thermal, physical, and chemical ranges to use plasma allows effective customization of the cloth surface therapy
- Continue to improve adhesion
- Sterilization properties
- Clean the fiber surface and remove thin films of organic impurities
- The hydrophobic features caused by plasma
- Plasma dry processes make it a friendly solution to the environment.

The effect on fiber and polymers of plasma treatments results in chemical, structural changes, and change in the surface layers of textiles. There are typically four significant consequences. One influence is often present, but depending on the substrate surface and gas chemistry one will benefit the other. [31, 35]

#### *Effect of plasma on fibers and polymers*

Textiles subject to plasma undergo significant chemical and physical transformations, including (i) chemical modifications in surface layers, (ii) surface layer structure modifications, and (iii) alteration in surface layer physical properties. By disassociating molecules by electron collision and photochemical processes, plasmas produce a high density of free radicals. This allows the chemical connections in the surface of the fiber polymer to disrupt, contributing to the creation of new chemical species. Surface chemistry and surface topography are impacted, with major changes in the real surface area of fabric. [22]

Surface modified pathways for plasma involve excited and ionized electrons, photons, complex radicals. While they all have adequate energy to cause a chemical reaction of the surface on

polymers, their respective roles in the change of surface are distinct. [36]

Fiber and polymer surface plasma treatment leads to the formation of new functional groups, such as hydroxyl (-OH) and carboxyl (-COOH) which influence the weight of the fabric and enable graft polymerization, and hence the repellence of liquid products of the manufactured textiles and nonwovens. In the plasma treatment of fibers and polymers, the energetic particles and plasma photons intensely interact with the surface of the substratum, typically by free radical chemical techniques. There are usually four major effects on surfaces. All of them are often to some extent present, but depending on the substrates and the gas chemistry, reactor configuration, and operational parameters, one might be preferred over the other

Surface washing, ablation or etching, the linkage between near-surface molecules, and the changes in chemical surface structure are the four main effects:

- Plasma cleaning and etching: means exclusion from the exposed surface of the material (impurities or substrates)
- Plasma activation: The introduction to the treated surface is composed of new functional groups. The surface properties depend on the existence of the chemical groups.
- Plasma-assisted grafting is a two-stage mechanism in which plasma activation is accompanied by exposure to fluid or gas precursors such as monomer. In the monomer on the active surface, there is a traditional free radical polymerization.
- In plasma polymerization, A monomer is immediately injected into the plasma and the plasma itself is polymerized.[34, 37]

#### *Ways to Induce the Ionization of Gases*

##### *Glow-Discharge*

It is manufactured under lower pressure, meaning the plasma therapy is as uniform and flexible as possible. It consists of a pair of electrodes using a direct current and a microwave, a low frequency (50 Hz), or a radio frequency (40 kHz, 13,56 MHz). The microwave (GHz) power supply can also be used to discharge the vacuum glow. [38, 39]

##### *Corona Discharge*

It is generated by applying a low frequency or pulsed high voltage over an electrode pair which can be configured as one of many types at atmospheric pressure. The corona consists  
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of a small form of lightning discharge, their homogeneity, and the high degree of local energy make the traditional corona treatment of textiles in many cases difficult. [40]

#### *Dielectric-Barrier Discharge: (DBD) [41]*

It consists of applying a pulsed voltage over an electrode pair whose dielectric material at least one is protected by. While fluorescent forms are produced, a major benefit over corona substances is enhanced uniformity of textile treatment. [29, 42, 43].

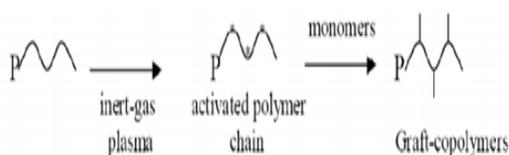
#### *Atmospheric pressure plasma jet (APPJ)*

As the name suggests, these systems process materials at atmospheric pressures thereby increasing the processing capabilities of the machine while reducing processing costs and loading times.

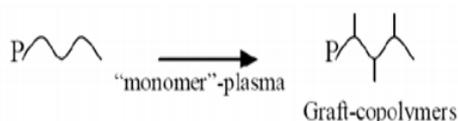
#### *Chemical Surface modification route using plasma*

a- Radical formation: Radical sites are formed by ionizing or raising the polymers

b- Grafting: commonly known as plasma graft copolymers with two mechanism



➤ The growth of active species on the polymer surface and interaction with the monomer



➤ Free radicals are formed as a result of inert on the polymer surface in this process Care of plasma gas. These radicals may either be grafted directly or Converted by oxidative gases into peroxide or hydro-peroxides.

➤ Direct polymer grafting with normal or unconventional monomers Conditions of "monomer".

a- Polymerization: Polymerization caused by plasma can be described as a phase of polymer Thin films are immediately placed on the surface without any substrate Manufacture

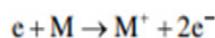
b- Cross-linking: Cross-linking occurs when two polymer molecules join to form one large molecule/network. This occurs when radical

sites are created in the polymer, resulting in the formation of H or Y-links. Can result in improved mechanical properties, decreased solubility, elimination of the melting point, and increased resistance to corrosive attack. [44]

#### *Plasma processes and mechanism of plasma on the substrate*

Plasma activation is a method of surface modification employing plasma processing. It is widely used in industrial processes to prepare surfaces for bonding, gluing, coating and painting. It improves surface adhesion properties of many materials including metals, glass, ceramics, a broad range of polymers and textiles, and even natural materials such as wood and seeds. Plasma activation can be performed at atmospheric pressure using air or typical industrial gases including hydrogen, nitrogen, and oxygen. Plasma functionalization also refers to the introduction of functional groups on the surface of exposed materials.

Plasma initiates a multitude of physical and chemical processes upon contact with the surface. It efficiently removes organic surface contaminants, reduces metal oxides, creates a mechanical microstructure on the surface, and deposits functional chemical groups. [34].

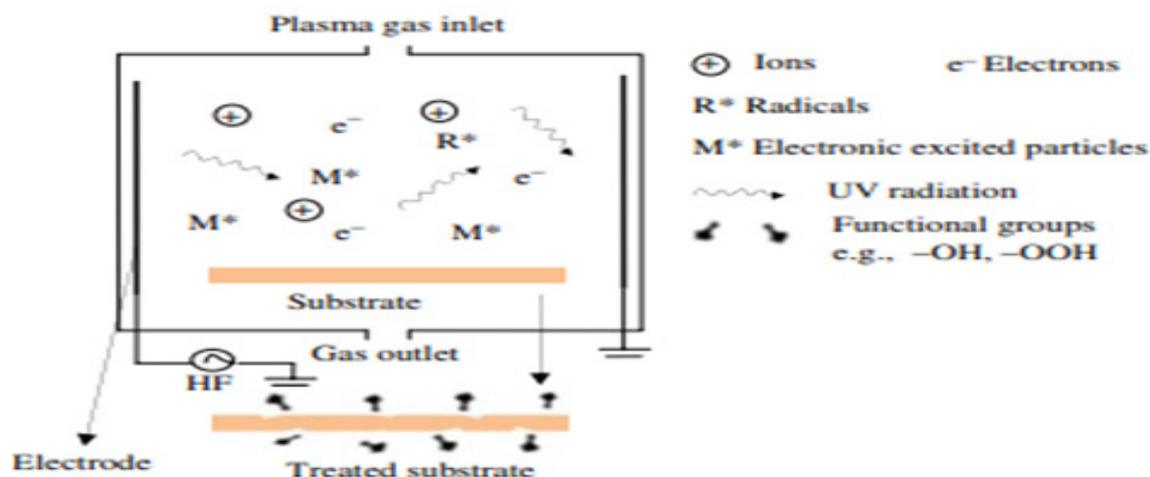


**Fig. 3** describes the principle of plasma treatment. Free electrons gain energy from the imposed radio-frequency (RF) electric field, colliding with neutral gas molecules and transferring energy dissociating the molecules to form numerous reactive species. The primary ion productions are shown as illustrated in Fig. 3.

Free radicals may also be generated by electron impact, thermal effect, and photolysis. The impact with a monomer can lead to its excitation and dissociation, generation of free radicals. It is the interaction of these exciting species with solid surfaces placed in the reactor that results in the chemical and physical modification of the material surface. [20]

#### *Environmental benefits of using plasma treatment*

A high degree of water consumption and electrical resources, high demand for oxygen for many inputs, and vast quantities of high demand for chemical oxygen (COD), excessive dye,



**Fig. 3. Mechanism of the surface treatment of substrate**

where  $e$  is the electron,  $M$  is the plasma gas molecule, and  $h\beta$  is the energy of photons

pH, and toxicity are the first explanations why textiles production impacts the environment. The major causes of contamination from effluent are usually desizing, dyeing, cleaning, and finishing. Dry treatment is the biggest benefit of plasma production. It is also a very clean and energy-efficient operation.

Generally, plasma therapy should summarise the environmental benefits:

- Reduced chemical quantity available in traditional processing
- Better depletion of bath chemicals
- Effluent Lowering BOD/COD
- Wet production time reduction
- Reduce the appropriate temperature for wet processing
- decreases production costs owing to energy savings and reduction of processing times. [21, 26, 34, 45]

*Application of using plasma in finishing some fabrics*

#### *Antibacterial Finishing Processes with Plasma*

Textiles with enhanced resistance against microorganisms (antibacterial, antimicrobial, antifungal textiles, etc.) [24, 36] are becoming increasingly desirable for textile manufacturers. In general, antibacterial properties can be imparted to the textile materials by chemically or physically incorporating functional agents into the fibers of the fabrics. [24, 46]

Cotton is one of the excellent natural materials, but it is easy for bacteria to grow on it. As a hydrophilic fabric textile, cotton easily provides suitable conditions, such as humidity, adequate temperature, and nutrition, for the growth of microorganisms. To a certain extent, this can generate an unpleasant odour, stains, and discoloration in the fabric. Therefore, it becomes necessary to apply an antibacterial finishing on cotton fabrics. Furthermore, the ideal antibacterial finishing should be non-toxic, washable, environmentally friendly, and durable. [24, 46]

- Important enhancement of antibacterial function and resilience of multiple cellulosic substrates. Pre-surface modification using  $N_2$  or  $O_2$  plasma was performed to produce cotton, linen, viscose, and lyocell with antibacterial properties
- new active and binding sites,  $NH_2$  groups, and the resulting modification on fabric surfaces. Packing of silver nanoparticles biosynthesized (AgNPs) in conjunction with certain antibiotics. The Ag-content as well as a remarkable improvement in the antimicrobial activity of the treated material. Enhancement of the abovementioned properties reflects the positive impact  $O_2$ -plasma pre-treatment had on surface modification and activation of the treated substrates using exhaustion method can discuss in terms of surface morphology, cellulose content, amorphous/crystalline areas, fabrics weight, and extent of surface changing and functionalization, which in turn affected the extent of AgNPs retention and antibacterial

efficacy. [34, 47] The noticeable enhance the antibacterial efficacy of plasma-treatment, AgNPs loaded fabric samples, even after 15 washing cycles, is a direct consequence of improved bonding of AgNPs via the plasma-generated polar groups, i.e. –COOH groups. The remarkable decrease in the antibacterial activity of Ag-NP treated fabric samples that were not plasma pre-treated is attributed to the physically adhered Ag-NPs onto the fabric structure, resulting in a lower extent of fixation and easier removability compared with plasma-treated samples. [48-51]

- The surface of cellulose substrates was pre-treated with O<sub>2</sub> plasma followed by acrylic acid (AAc) as a monomer in the plasma polymerization process. Results indicate that the surface of the cotton fibers was cleaner and smooth with micro-fibrils visible along to fiber axis after treatment with AAc. [52]
- The effect on comfort and antibacterial properties of polyester fabric was explored by the variables in argon plasma therapy. In terms of water vapor permeability, coagulability, and antibacterial behavior relative to untreated fiber, the plasma-treated polyester materials showed improved fabric properties. Using the program Design-Expert the ideal operational power conditions were 600 W, treatment time 30 S and the gap between electrodes of 2.8 mm. [53] the efficiency of the process depends on the intensity of the treatment, intensity of corona discharge at atmospheric pressure (CDAP ) is a function of the discharge power and exposure times.

#### *Ultraviolet protection Finishing Processes with Plasma*

There is a growing demand in the marketplace for textile apparel that offers comfort and protection from the harmful effects of ultraviolet (UV) radiation [54]. Sun protective clothing is one of the most effective ways to protect against skin cancer. Such fabrics are specifically designed for sun protection by covering a maximum amount of skin and made from a fabric rated for its level of UV protection. Throwing on a protective shirt with an ultraviolet protection factor (UPF) of 30+ is a proactive decision, which can simply help to live a healthier life. [47]

Raw cotton fabrics have been exposed to low-pressure non-equilibrium gaseous plasma to improve the adsorption of natural dyes as well as

ultraviolet (UV) protection facto Plasma created in a glass tube by an electrodeless radiofrequency (RF) discharge was created either in oxygen<sub>02</sub> or ammonia NH<sub>3</sub> at the pressure of 50 Pa to stimulate the formation of oxygen and nitrogen groups. The color yield for curcumin dye was improved significantly for samples treated with ammonia plasma. The ultraviolet protection factor (UPF) was over 50 indicating excellent protection due to improved absorption of the dye on the ammonia plasma-treated samples. [55, 56]

Plasma sputtered/naturally dyed wool samples have UPF values of more than 25 offer very good UV protection. For Fe plasma sputtering wool samples, UPF was increased. [57]

UPF values calculated to fabric samples with this equation

$$UPF = \frac{\sum_{290}^{400} E_{\lambda} S_{\lambda} \Delta_{\lambda}}{\sum_{290}^{400} E_{\lambda} S_{\lambda} T_{\lambda} \Delta_{\lambda}}$$

where  $E_{\lambda}$  is the qualified erythemal spectral effectiveness,  $S_{\lambda}$  is the solar UVR spectral irradiance,  $T_{\lambda}$  is the measured spectral transmission of the fabric,  $\Delta_{\lambda}$  is the bandwidth in millimetre and  $\lambda$  is the wavelength in nanometre.

#### *Flame retardant Finishing Processes with Plasma for some fabrics*

The need to produce flame-retardant textiles may be assessed in terms of identifying the hazard to life and property which burning textiles create. [58]

To protect the fiber from quick-fire is considered a fire retardant fiber It's a chemical and finishing property. The cloth does not influence the properties of the material, hue or shadow, feel, treat or irritate the skin. The finish should be cleaned easily, lightly, and washed. The flammable testing mechanism is to decrease fiber oxygen and/or increase fiber's moisture content. Flame proofing can be carried out by precipitating insoluble metal (or) metallic salts. [59-62]

Permanent fireproofing of textiles of natural origin such as cotton is still challenging because only a surface treatment can be applied. To be resistant to washing or harsh weather conditions the flame retardant must be fixed strongly to the surface, most efficiently achieved via covalent bonds. The simultaneous grafting and polymerization of fire-retardant monomers on

cotton fabric induced by argon plasma have been investigated. The good flame-retardant properties of two new phosphoramidate monomers are attributed to the presence of nitrogen which causes a synergistic enhancement in the efficiency of phosphorus-based flame retardants. [63]

Plasma atmospheric-pressure dielectric barrier discharge (APDBD) was applied to the cotton fabric, which then was treated by flame retardants (FR) using the pad-dry-cure method. The purpose of using plasma was to have a flame-retardant cotton fabric (limiting oxygen index (LOI)  $\geq 25$ ) and a mechanical loss of the treated fabric owing to the curing step as low as possible. The vertical flammability characteristics, LOI value, and tensile strength of the treated fabrics were measured. It was predicted that the optimum temperature and time-to-treatment to achieve LOI of 25 was at 160°C for 90 s, while the flame-retardant treatment process without plasma pre-treatment, was at 180°C and 114 s. [64]

A low-frequency oxygen plasma treatment at low temperature was carried out before padding the polyester fabrics with alkyl-phosphonate structured flame retardant agents. Hydrophilic characteristics of the Polyester fabrics were also tested after the plasma treatment. According to the results, the hydrophilic properties of the polyester fabrics improved after oxygen Plasma treatment. However, the chemical amount consumed was half of the maximum concentration without the LOI test changing significantly. The plasma treatment allowed the reduction of the flame retarder concentration to 50 g/L in the padding system. [65]

#### *Anti-static Finishing Processes with Plasma for some fabrics.*

An antistatic agent's primary role is to prevent the generation of electricity within the various textiles. In general, these inequalities may be generated either by separating or friction of two materials or by induction processes in particular due to the contact of ionized air because of extra electron or by a lack of an electron. During processing, static electricity can be produced; also in final use, the textile material is used in transport and manipulation. [66]

For many textile products, safety requirements include anti-static limitations to defined relative moisture (mostly ranging from 65 to 25 percent).

The Polyester fabric's half-life decay period

was perfect after the low-temperature plasma treatment with oxygen. Decreased proofs that polyester's anti-static property Substance has been greatly changed. The perfect condition of plasma treatment at the low-temperature appropriate improvement of the polyester fabric's anti-static property calculated as (i) release power = 200 W, (ii) device pressure = 25 Pa, and (iii) processing time = 3 min and the improvement antistatic property on polyester fabric depended on low-temperature plasma treatment and antistatic finishing agent had a different antistatic mechanism. It is now recognized that low-temperature plasma change of the fibers results in oxidation and degradation (voids and pores creation) of the fiber surfaces. [67]

The oxidation creates oxidized functionalities, which lead to an increase in surface energy, while the degradation mainly modifications surface morphology of the fibers

As low-temperature plasma treatment increases the amount of oxygen-containing polar groups on the polyester fiber surface. These polar groups will include moisture through hydrogen bonding and help moisture penetration and binding on the fiber surface.

The water molecule can produce ionization of these polar groups and proceed to a systemic electricity conduction layer Fiber surface, which increases the dissipation of electrostatic material. Consequently, the fiber half-life reduces Plasma treatment after low temperature. [68]

#### *Summary*

Plasma treatment which used to finish different fabric improving the properties of antibacterial finishing as Plasma treatments created new active sites can act as an anchor for the biosynthesized AgNPs as well as AgNPs/antibiotic hybrid in the post-treatment step. Which remarked improvement in the imparted antibacterial, Water vapor plasma treatment of cotton increased the concentration of oxygen on the surface of sample UV protection. Plasma sputtered/naturally dyed wool samples have UPF values of more than 25 offer very good UV protection. For Fe plasma sputtering wool samples, UPF increased to 32.45 and 36.63 for madder and weld. Plasma atmospheric-pressure dielectric barrier discharge (APDBD) was applied to the cotton fabric, which then was treated by flame retardants using the pad-dry-cure method.

The purpose of using plasma was to have a limiting oxygen index (LOI) of 25 and mechanical loss of the treated fabric owing to the curing step as low as possible. The plasma treatment allowed the reduction of the flame retarder concentration to 50 g/L in the padding system in polyester fabric. Low-temperature plasma change of the fibers results in oxidation and degradation (voids and pores creation) of the fiber surfaces. As low-temperature plasma treatment increases the amount of oxygen-containing polar groups on the polyester fiber surface. These polar groups will include moisture through hydrogen bonding and help moisture penetration and binding.

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### التطورات الحديثة في تطبيق البلازما في تجهيز المنسوجات

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تسعى صناعة النسيج إلى تكنولوجيا تصنيع مبتكرة لزيادة جودة النسيج، حيث يحتاج المجتمع إلى تقنيات تجهيز بيئية حديثة مثل استخدام معالجة البلازما مثل استخدام معالجه البلازما بحاجز التفريغ العازل «التفريغ الكهربائي بين قطبين يفصل بينهما حاجز عازل» (APDBD) عند الضغط الجوي (CDAP) التي تكسب صناعة المنسوجات شعبية كبيرة نظرًا لمزاياها العديدة مقارنة بطرق المعالجة الرطبة التقليدية. يمكن بدء المعالجة بالبلازما عن طريق الهواء أو الغازات الصناعية التقليدية، مثل الهيدروجين و النيتروجين والأكسجين عند الضغوط المحيطة. تكسب المعالجة بالبلازما سطح الخامه مجموعات سطحية قابلة للاستخدام لتوفير خصائص مثل مضادات البكتيريا والأشعة فوق البنفسجية ومثبطات اللهب والمضادة للكهرباء الساكنة التي تستخدم في الأقمشة المختلفة مثل القطن والكتان والبوليستر والأقمشة السطحية بعد المعالجه بالبلازما.