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Plasma: Unconventional Technology for Textile Wet Processing

C. R. Madhu
R C Technical Institute
Opp. Gujarat Highcourt, Sola
Ahmedabad

ABSTRACT

As per today's scenario, the world is transporting toward ecofriendly processes, in concern with green environment technology. Textile wet processing is one of the major, creating maximum effluent load by conventional wet processing. So many unconventional technologies have been introduced till today to reduce this load. Plasma is also one of them. Plasma process improved dyeability, finishing effect on textiles by decreasing effluent load. It also enhance the reduction in chemical consumption during chemical processing of textile substrates.

Keywords

Plasma, Textile Processing, Dyeing, Printing

INTRODUCTION

Textile industries are regularly in search of a technology; explore environmental friendly, less water consuming, replacement with special auxiliaries, known as unconventional technologies. The plasma application to textile is one of those unconventional technologies applied in textiles, improves fabric preparation, dyeing, printing and finishing of natural as well as synthetic fibre fabrics. It is a surface modification method, allows modification in the nm – range. Textile is placed in reaction chamber with gas and plasma is ignited, so generated particles reacts with surface and functionalised.

What is Plasma?

Plasma is fourth state of matter, after solids, liquids and gases, and this forth state was first introduced by Sir William Crooke in 1879 as a result of his experiments in the passage of electricity through gases. The word plasma comes originally from a Greek term, means something formed, fabricated and molded and was first used by Irving Langmuir.

High energy is supplied to gas, thus collision occurs between atoms and free electrons, excited molecules and molecular fragments are formed. Due to charge separation in electrons in plasma, magnetic fields and currents rise through system with neutrality.Plasma is also defined as ionised gas with positive and negative charges possessing same density. The term is also recognised as produced by electrical discharges through gas, containing the mixture of positive and negative ions, electrons, free radicals, ultraviolet radiation and many different electronically excited molecules.

Plasma processes divides in two main classes – low-density and high-density – according to their electron densities. In low-density, temperature of heavy particle and electron, radio frequency discharge, direct current are not at same level. It has neutrals and cold ions with hot electrons. High-density consist of the atmospheric plasma system, allows formation of uniform and homogeneous plasma at low temperatures using a broad range of inert and reactive gases. Plasma treatments have been used to improve surface modifications and bulk property of textile materials, from conventional fabrics to advance.

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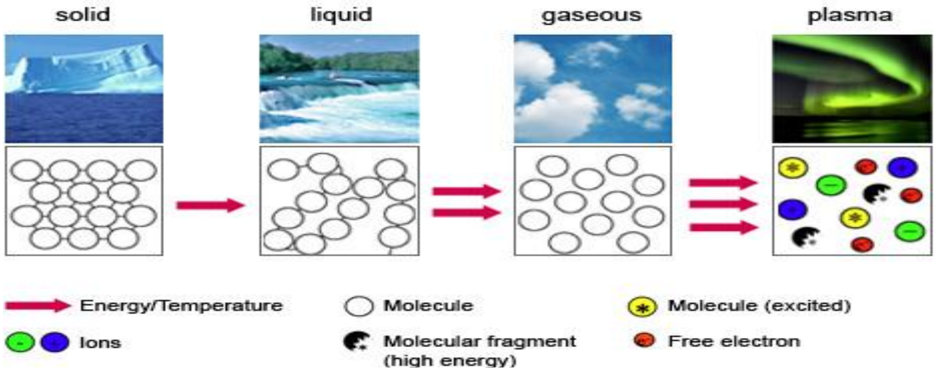

Figure 1.1 :- Understanding various states of matters

These treatments have been shown to enhance dyeing rates of textiles, improve colour fastness and wash resistance of fabrics, and change in surface energy of fibres and fabrics. Gases commonly used for plasma treatments are:

- Chemically inert (e.g. helium and argon).
- Reactive and non-polymerisable (e.g. ammonia, air, and nitrogen).
- Reactive and polymerisable (e.g. tetra fluoroethylene, hexamethyldisiloxane).

Principles of Plasma Treatment

The atmosphere of plasma contains free electrons, radicals, ions, UV – radiations and lot of different excited particles in dependence of the used gas. So the gas plasma treatment differs in nature to the specific gas or gases, e.g. air, ammonia, argon etc. the textile placed near the plasma gas containing mixture of species that can react with, can lead to a various surface modifications. Type and adduction of surface modification depends on (i) nature of the gas mixture, (ii) type of textile fibre, (iii) machine parameters such, (iv) treatment temperature and time, and (v) the frequency and power of the electrical supply.

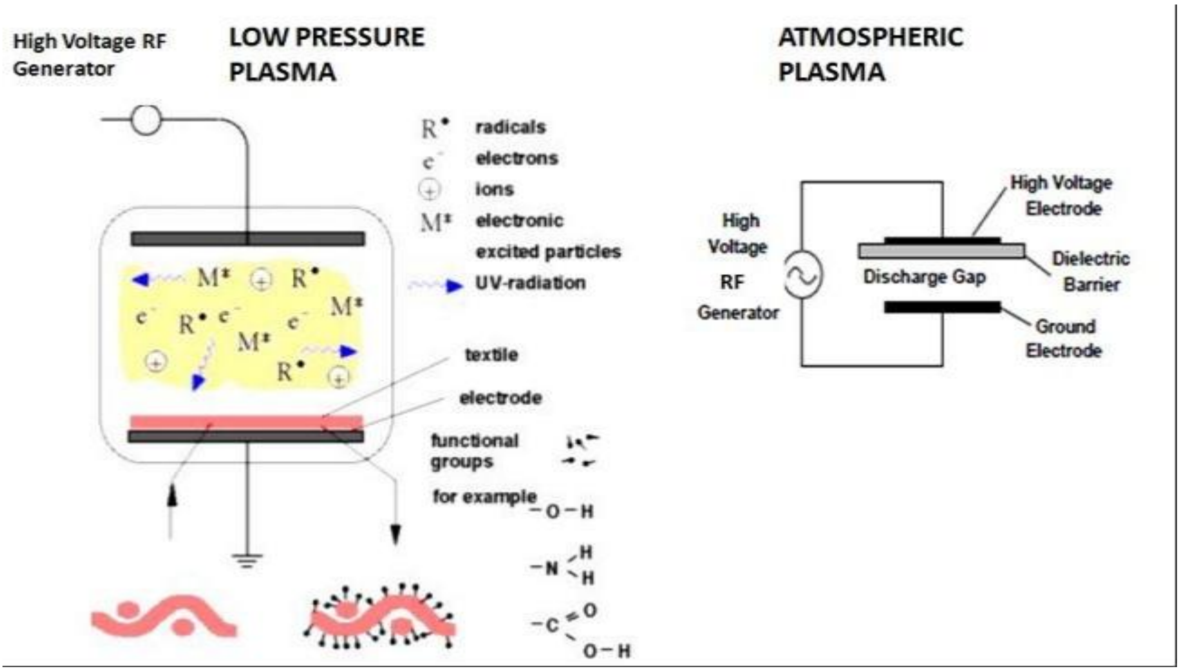

Figure 1.2 :- Principle of plasma production

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This plasma treatment can be done with different ways, viz., substrate can be treated directly in the plasma zone, substrate can be positioned outside the plasma (remote process), substrate can be achieved in the plasma followed by a subsequent grafting, substrate can be treated with a polymer solution of gas which will be fixed or polymerised by a subsequent plasma treatment. Different types of plasma are shown in table.

Table 1.1:- Types of Plasma

On the basis of pressure	Low pressure(0.01kpa) Atmospheric pressure(100 kpa)
On basis of the temperature of electrons and ions	Hot plasma(above 10000 degree) Cold plasma(below 100 degree)
On basis of frequency of power supply	Low frequency(40kHz) Radio frequency(13.56MHz) Microwave frequency(2.56GHz)

Plasma Processing Technology

Uncontrolled plasma treatment gives disadvantageous action on substrate, so it should be controlled carefully. Plasma technology, modifies the surface of substrate by various means of application, those are:-

(1) Low-pressure Cold Plasma Processing Technology
(2) Atmospheric-pressure Cold Plasma Processing Technology
(3) Corona and Dielectric barrier discharge Plasma Technology
(4) Nano-scale treatment using Plasma Technology

Low-pressure Cold Plasma Processing Technology

Low-pressure cold plasma processing technology is also known as vacuum plasma technology. In this technology, gas under sufficient low pressure and energy is provided to the gas for enhancing the plasma state. Under these conditions, the gas is ionised due to partial decomposition. The working gas pressure kept in 0.1 mbar range for the radiofrequency range (typically 40 kHz or 13.56 MHz), whereas for microwave sources, a working pressure between 0.5 to 1 mbar is often used. 0.01 mbar pressure needs for pure progress gas condition to reach sufficient plasma effect.

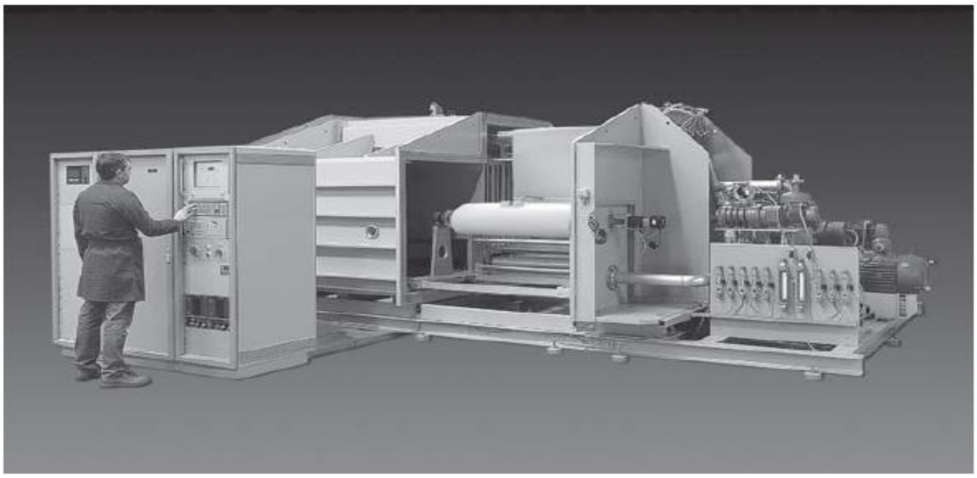

Figure:- Large industrial roll-to-roll vacuum plasma treatment machine

Atmospheric-pressure Cols Plasma Processing Technology

Low pressure plasma processing is incompatible with industrial mass production, has failed to make an impact in the textile. Low pressure plasma process is too much expensive, need closed vacuum system and not suitable for continuous production lines at a high speed. To overcome these limitations, Atmospheric Pressure Plasma Techniques are being developed. In this technique, plasma density is much higher (in the range of 1 to 5 x 10^{12} electrons cm^{-3}), substrate is treated at cold plasma, without damaging it with high energy or temperature. The Atmospheric Pressure Plasma is a unique, non-thermal, glow-discharge plasma operating at atmospheric pressure. The discharge uses a high-flow feed-gas consisting primarily of an inert carrier gas, like He, and small amount of additive to be activated, such as O_2, H_2O or CF_4.

APP can be achieved by three mean, those have relevance for textile treatment – the Corona Discharge, the Dielectric Barrier Discharge, the Atmospheric Pressure Glow Discharge.

The Corona Discharge:

Corona discharges are plasmas, generated via high electrical fields using electrically singularity, where high voltage is applied. This electric field is supplied by using needle of the wire, discharge like spray out from wire, and plasma id generated. Due the narrow discharge, fabric put in plasma for very short time, and cross section of wire is also very narrow responsible for limited power level. Accordingly, in its pure form, corona is far from an ideal textile surface processing medium.

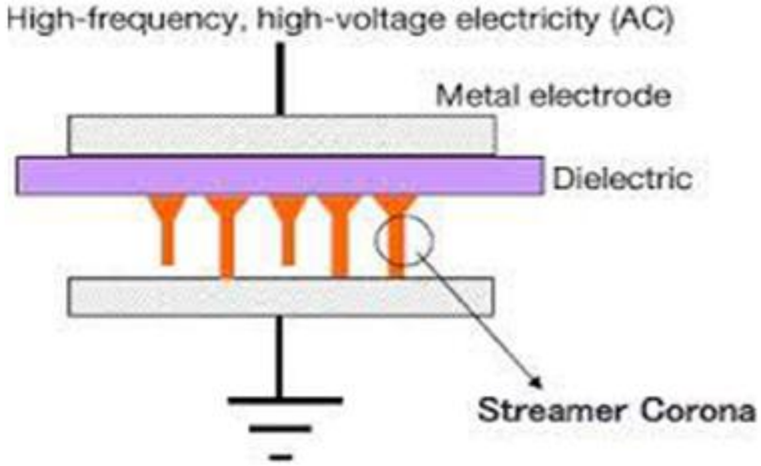

Figure: Corona discharge

Dielectric barrier discharge:

In contrast to corona system, which is asymmetrical, symmetrical electrode arrangement is set up arranged with two parallel conducting plates placed in opposition, with the gap of ~10 mm, and a high voltage, 1–20 kV is applied, is known as Dielectric barrier discharge. The gas passes between these two plates, so gas molecules are broken electronically and plasma discharge generated. In this treatment, arc of hot thermal plasma jumps from one electrode to other, this creates spot on the opposing electrode. This would do nothing except burn a hole in the fabric, so not useful for textile application. If, however, one or both of the electrode plates is covered by a dielectric such as ceramic or glass, the plasma finds it much more difficult to discharge as an arc and, instead, is forced to spread itself out over the area of the electrodes to carry the current it needs to survive. The DBD must be powered by AC and is typically driven by high voltage power supplies running at frequencies of 1 to 100 kHz. It is denser than the corona with a typical free electron density of about 10^{10} electrons/cm^3 but the free electrons are slightly cooler at temperatures of 20 000 to 50 000 K. This is a much more attractive candidate for textile processing than the pure corona.

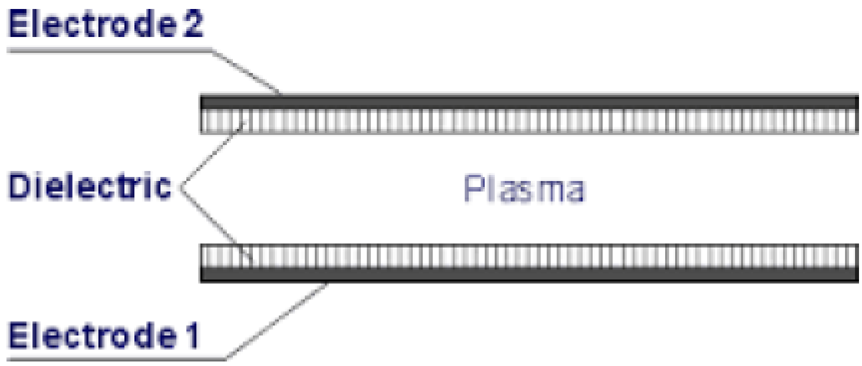

Figure:- Dielectric barrier discharge

The atmospheric pressure glow discharge:

Atmospheric Pressure Glow Discharge (APGD) is the third type of APP, capable of creating size and temperature required for textile processing. In this technology, low pressure glow discharge plasma is involved, that is the backbone of plasma industry as well as major industries related to this area. The APGD is generated by application of relatively low (~200 V) voltages across opposing symmetrical planar or curved electrodes, separated by mm at high frequency, or even very high frequency, radio frequencies 2–60 MHz, much higher than the other plasma types. The electrodes are not covered by dielectric but are bare metal, a feature that enables significantly higher power densities (up to 500 W/cm^3) to be coupled into the discharge than can be achieved with corona or DBD. The APGD is denser than the DBD, with typical free electron densities of 10^{11}–10^{12} $electrons/cm^3$, but the free electrons are slightly cooler at temperatures of 10 000 to 20 000 K.

Effect of plasma on textile surface

There are three major effects: surface activation, etching, and deposition.

Surface activation by plasma:

Surface activation by plasma is nothing but a chemical grafting. It always present with surface cleaning. In this phenomenon, plasma reacts with contamination present on substrate surface, loosely bound hydrocarbons. Both H and C will react with oxygen and will leave the substrate surface in the form of volatile H_2O and CO_2. This contaminated free surface is ready to react with oxygen for forming carbonyl-, carboxyl- or hydroxyl functional groups on the substrate surface. The effect of grafting carbonyl-groups onto a surface of PP, polyethylene (PE), or polyesters such as polyethyleneterephthalate (PET) or polybutyleneterephthalate (PBT) gives rise to an increase in surface energy to levels higher than 68 mN/m immediately after the plasma treatment. This effect has a certain shelf-life.

Plasma activation is being used in several fabric and nonwoven applications in the textile industry:

- Fabrics for automotive and medical applications
- Pre-treatment before dyeing
- Activation of transportation textile before application of flame-retardant chemistry

Etching by plasma:

Direct plasma is used to create an efficient etching process. The substrate is bombarded with charged particles (ions and electrons) and apart from a purely chemical effect; the substrate is subjected also to a physical sputtering effect. In the case of textiles and nonwovens, this effect of plasma treatment is not often used. A plasma etching enhances a controlled Nano- or micro-roughness, increasing diffuse reflectance and minimising the specular component.

Thin film deposition by plasma polymerisation:

A very important usage of low-pressure vacuum plasma technology is thin film coating deposition by plasma polymerisation. In this technique, gases are polymerising on the surface of substrate. The precursor gases are broken into radicals that react with each other on the substrate surface. The nature of the precursor gases will very much determine the properties of the deposited coating. Coating thickness is normally in the 10–50 nm range (5–30 molecular layers).

Application of plasma technology in Textile

Plasma technology can improve surface modification for enhancing various textile wet processes, viz., fabric preparation, colouration, finishing. Table reports summery of some of the properties that plasma treatments can impart to material textiles.

Table:- Some properties of textile materials that can be modified by plasma Treatment

Property	Material	Treatment
Wettability	Synthetic fibres	Oxygen, air, NH_3
Hydrophobicity	Cellulosic fibres, wool, silk, Polyester	Fluorocarbon, SF_6, Siloxanes
Dyeability	Synthetic fibres, wool, silk	Oxygen, air, nitrogen, argon, SF_6, acrylates
Flame retardance	Cellulosic fibres, synthetic fibres	Phosphorus compounds
Softness	Cellulosic fibres	Oxygen
Wrinkle resistance	Wool, silk, cellulosic fibres	Nitrogen, siloxanes
Antistaticity	Synthetic fibres	Chloromethylsilanes, acrylates
Adhesiveness	Synthetic fibres, cellulosic fibres	Air, oxygen, nitrogen, argon, acrylates
Bleaching	Wool	Oxygen
Antifelting	Wool	Oxygen, air

Desizing of cotton fabric:

sizing material like PVA from cotton can be remove by using plasma technology. In conventional desizing process we use chemicals and hot water to remove size. But desizing with plasma technology we can use either O_2/He plasma or Air/He plasma. This treatment break downs chains of PVA making them more soluble. Of the two gas mixtures that were studied, the results also indicate that O2/He plasma has a greater effect on PVA surface chemical changes than Air/He plasma.

Dyeing

Several studies have shown that colouration of textiles can be markedly improved by plasma treatments.

Dyeability of Natural Fibres:

It has been reported that plasma treatment on cotton in presence of air or argon gas increases its water absorbency which in turn increase both the rate of dyeing and the direct dye uptake in the absence of electrolyte in the dye bath. This happens due to, the change of the fabric surface area per unit, the etching effect of the plasma effect, the chemical changes in the cotton fibre surface. The dye exhaustion rate of plasma treated wool has been shown to increase by nearly 50%. It has been shown that O_2 plasma treatment increases the wetability of wool fabric thus leading to a dramatic increase in its wicking properties.

Dyeability of Synthetic Fibres:

In the synthetic fibres, plasma causes etching of the fibre and the introduction of polar groups leading to improvement in dyeability. The researchers believe that this technique can lead to a continuous flow system, low energy consumption, and more environmentally friendly consumption, low temperature dyeing technology on polyester substrates. Polyamide (nylon6) fabrics have been treated with tetrafluoromethane low temperature plasma and then dyed with commercially available acid and dispersed dyes. Dyeing results showed that the plasma treatment slows down the rate of exhaustion but does not reduce the amount of absorption of acid dyes. The dyeing properties of disperse dyes on plasma treated nylon fabric charged markedly when compared with untreated fabric. A slight improvement in colorfastness was seen with the treated sample.

Textile finishing:

Plasma technology leads to produce various types of functional textiles. Various finishing applications of plasma in textiles are given in table.

Table:- Various application of plasma in textile finishing

APPLICATION	MATERIAL	TREATMENT
Hydrophilic finish	PP, PET, PE	Oxygen plasma, Air plasma
Hydrophobic finish	Cotton, P-C blend	Siloxane plasma
Antistatic finish	Rayon, PET	Plasma consisting of dimethyl silane
Reduced felting	Wool	Oxygen plasma
Crease resistance	Wool, cotton	Nitrogen plasma
Improved capillarity	Wool, cotton	Oxygen plasma
UV protection	Cotton/PET	HMDSO plasma
Flame retardancy	PAN, Cotton, Rayon	Plasma containing phosphorus

Bio-Medical Applications:

Plasma treatments of biomedical textiles suggest a numbers of advantages. A few examples are shown in table.

Table: Textile in biomedical application

APPLICATION	MATERIAL
Polyester	Sutures, cardiovascular implants, artificial tendons and ligaments, orthopaedic bandages, artificial kidneys
Nylon	Wound dressing, compression bandages, sutures, surgical hosiery
Polypropylene	Orthopaedic bandages, sutures, mechanical lungs
Cotton	Wound dressing, bandages
Viscose	Wound dressing, bandages, artificial kidneys and livers
Silk	Wound dressing, sutures, artificial tendons

Antifelting of wool:

In regular conventional processes, wool tends to shrink, can be cover up by oxidation using a suitable plasma treatment. Surface oxidation induces by plasma prior to wool coating by plasma polymerisation reduces, wool fibre shrinkage and consequent felting. But plasma deposited on wool fibre reduces the wetablity of surface, which reduces the dye uptake.

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Water repellent fabric:

Cotton or hemp fabric usually absorbs water immediately. Applying a low-pressure plasma process, the fibre's surface can be altered to make it repel water. After the treatment, drops run freely over the surface while mechanical properties, the visual appearance, and the permeability for water vapour remain unchanged. The surface modification is limited to a very thin layer. A treatment as short as 2 seconds can be sufficient to achieve this effect in a batch process. Continuous treatments with a speed of more than 20 m/min are conceivable. The stability of the modification can be seen in intermitted washing cycles of fluorocarbon treated cotton fabric.

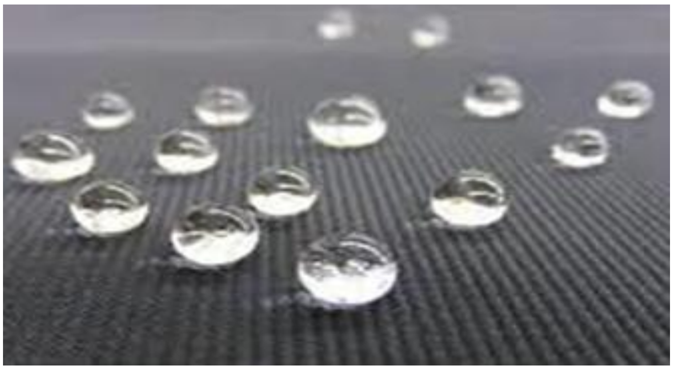

Figure:- Water repellence of fabric

Flame retardant fabric:

Currently, halogen-containing flame retardants are being banned for ecological reasons. The new kinds of flame-retardant chemistry, e.g. based on organic phosphonate derivatives, are much more expensive. Therefore, their usage should be limited to the absolute minimum. It has been shown that, in the case of plasma-activated fabrics consisting of both natural fibres and polymers, the concentration of flame-retardant chemicals can be reduced considerably without influencing the flame-retardant properties of the treated web. This again leads to considerable cost savings.

Hydrophobation of nonwovens for filtration applications:

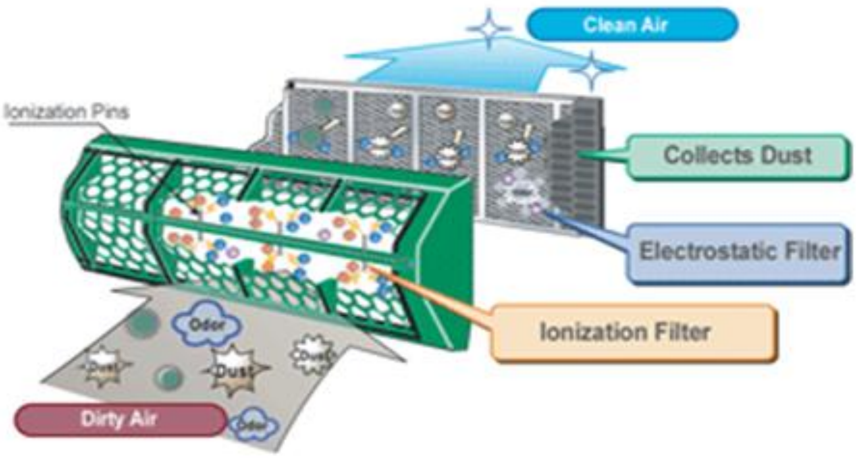

Figure:- Hydrophobation of nonwovens for filtration applications

It is mainly plasma polymerisation for coating deposition that has found its way into the filtration industry. A first example of plasma coating can be found in air filter media both for respirator masks and for filters used in HVAC systems. Such filters consist of several layers of meltblown nonwoven PP, which are electrically charged (electrets). Filtration efficiency for oily particles can be greatly improved by applying a hydrophobic/oleophobic coating prior to electrical charging.

Ink Jet Printing

Inkjet printing is becoming increasingly widespread for the printing of textiles. Ink jet printed fabrics have demonstrated improved properties over the traditional textile printing methods, such as roller, screen and transfer printing. It displays excellent pattern quality, considerably little pollution, and especially a faster response to the frequent fashion changes. An atmospheric plasma surface pre-treatment of PET fabrics with air and argon for pigment printing, the results showed better colour yield and drawing sharpness on the pre-treated polyester fabrics. Others plasmas types, such as radio frequency and DBD discharge have been employed for the pre-treatment of PET fabric before printing with pigment showing superior wettability in final properties of the printed polyester. A wool/polyester blended fabric (45/55) pre-treated with an atmospheric DBD plasma has been printed using two different dye mixtures. The experimental results indicated that the wettability and colour strength of treated fabrics are enhanced. Moreover, changes in surface morphology of treated samples are also observed. The quality of a digitally printed polypropylene fabrics pre-treated with low-temperature plasma discharge, Polypropylene is known as very hard-to-print and hard-to-dye material. It is clear that plasma pre-treatment is able to provide added value to inkjet printing on polypropylene.

Figure:- (Left) Inkjet Printing on PP before Washing &
(Right) Inkjet Printing on PP after two washing Cycle.

Traditional textile processing vs. plasma technology

Table is showing the advantages of plasma technology over textile wet processing.

Table: Traditional textile processing vs. plasma technology:

	Plasma processing	**Traditional wet processing**
Medium	No wet chemistry involved. Water-based Treatment by excited gas phase	Water – based
Energy	Electricity – only free electrons heated (<1% of system mass)	Heat – entire system mass temperature raised
Reaction type	Complex and multifunctional; many simultaneous processes	Simpler, well established
Reaction locality	Highly surface specific, no effect on bulk properties	Bulk of the material generally affected
Potential of new processes	Great potential, field in state of rapid development	Very low; technology Static
Equipment	Experimental, laboratory and industrial prototypes; rapid industrial developments	Mature, slow evolution
Energy consumption	Low	High
Water consumption	Negligible	High
Handling and storage of bulk Chemicals	No	Yes
Mixing of chemicals, formulation of baths	No	Yes
Raw materials consumption	High	Low
Drying ovens and curing operations	No	Yes
Need for solvents, surfactants, acid	No	Yes
Number of process steps	Single	Multiple
Waste disposal/recycling needs	Negligible	High
Environmentally costly	No	Yes
Innovation potential	Very high	Moderate

Conclusion

- ⇨ Plasma is a versatile technology to chemically and physically modify the surface of materials.
- ⇨ Plasma technology is used to achieve new or improved properties to textiles. It is an alternative environmentally friendly technology to complement or substitute several conventional textile processes.
- ⇨ Research and development of plasma treatments applied to textiles are still globally increasing. Different studies have been done on natural, artificial and synthetic fibers.
- ⇨ Sputtering, etching, chemical functionalization, free-radicals generation and UV radiation are some of the most important effects conferred by plasma treatments to textiles.
- ⇨ Plasma treatments are increasing their presence in the textile industry for several applications.

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