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PLASMA TECHNOLOGY & ITS APPLICATION IN TEXTILE WET PROCESSING

S. K. Chinta*, S. M. Landage and Sathish Kumar. M
D.K.T.E.Society's, Textile & Engineering Institute, Ichalkaranji, Maharashtra, India

Abstract

Plasma treatments are gaining popularity in the textile industry due to their numerous advantages over conventional wet processing techniques. The plasma treatment does not alter the bulk property. Plasma surface treatments show distinct advantages, because they are able to modify the surface properties of inert materials, sometimes with environment friendly devices. Application of "Plasma Technology" in chemical processing of textiles is one of the revolutionary ways to enhance the textile wet processing right from pretreatments to finishing. This paper deals with application of plasma technology for cotton pretreatment and finishing.

Key words: Cotton, Dyeing, Finishing, Pretreatments, Plasma Technology

1. Introduction

Textiles have undergone chemical processing since time immemorial. The textile industry is searching for innovative production techniques to improve the product quality, as well as society requires new

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finishing techniques working in environmental respect. Over recent years, physicochemical techniques have become more commercially attractive and have begun to overcome conventional wet chemical methods for property modification. The importance of surface modification of textile materials extends over a wide range of alterations or embedded selective additions, to provide desired single or multi features for various applications. It is a highly focused area of research in which alterations to physical and/or chemical properties lead to new textile products that provide new applications or satisfy specific needs. These processes, however, can involve numerous chemicals, some of which are toxic to humans and hazardous to the environment. Additional problems also arise due to degradation and/or weakening of the treated material. Alternative techniques have been investigated over the past two decades to decrease or eliminate dependency on chemical treatments. One recent alternative, involving non-aqueous processing, is plasma treatment of textile materials. Appropriate choice of gas and control of plasma operation conditions provide a variety of effects on textiles (improvement of dyeability, printability and colour fastness, improvement of adhesion properties of coated fabrics, increase in hydrophobicity and water resistance, etc.). Surface modification via plasma treatment not only eliminates the need for wet processing, but also yields unique surface characteristics. Several modifications include, but are not limited to: hydrophilicity/ hydrophobicity alterations, surface roughening, grafting, flame retardant, antimicrobial, insect repellant, stain resistant, and single or multiple surface functionalisation. An ideal plasma treatment for textile applications is a plasma system that can be

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introduced into the production line without major changes or system interruption, allowing for high speed and continuous processing.

"Plasma" derived from the *Greek* and referring to "something molded or fabricated". A literature review of plasma technology reveals considerable interest of the scientific community in this field since the fifties. Several studies proved that surface properties of different polymeric materials can be easily modified with high energy irradiating sources. Plasma can be considered as *a gaseous condition that contains several excited species such ions, free electrons and a large amount of visible, UV and IR radiations*. The plasma state can be generated by:

- Electrical energy
- Nuclear energy
- Thermal energy
- Mechanical energy
- Radiant energy

The differentiation between plasmas can be made based on his main characteristics, namely by the charged particle density, temperature, pressure and the presence/absence of electrical and/or magnetic fields.

1.1 *Types of Plasma*

Plasma is generally classified as thermal or non-thermal. In thermal plasma, temperature of several thousand degrees is reached which is of a destructive

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nature and no material can stand their action. Contrary to thermal plasmas, non-thermal plasmas are 'cold' plasmas where the chemically active environment is achieved at nearly room temperature and this one is used for surface modification of textiles. There are two types of cold plasma which can be used for application on textiles, namely vacuum pressure and atmospheric pressure. Since plasma cannot be generated in a complete vacuum the name vacuum pressure is somewhat misleading and only refers to the low working pressures of such systems. Many authors, however, choose to classify vacuum pressure plasmas into sub categories of low and medium pressures. The table below gives an idea of the working pressures of vacuum and atmospheric plasmas.

This text, due to very little difference between the sub classes of vacuum plasma will not differentiate between the two forms and discuss two main classes of plasma which are (near) vacuum pressure plasmas and atmospheric pressure plasmas. Both these forms are suitable for application on textiles and progress continues to determine their effect on textiles. More work has, however, been documented on characterization of vacuum pressure plasmas as compared to atmospheric pressure plasmas.

The coupling of electromagnetic power into a process gas volume generates the plasma medium comprising a dynamic mix of ions, electrons, neutrons, photons, free radicals, meta-stable excited species and molecular and polymeric fragments, the system overall being at room temperature. This allows the surface functionalisation of fibres and textiles without affecting their bulk properties. These species move under electromagnetic fields, diffusion

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gradients, etc. on the textile substrates placed in or passed through the plasma. This enables a variety of generic surface processes including surface activation by bond breaking to create reactive sites, grafting of chemical moieties and functional groups, material volatilization and removal (etching), dissociation of surface contaminants/layers (cleaning/scouring) and deposition of conformal coatings. In all these processes a highly surface specific region of the material (<1000 A) is given new, desirable properties without negatively affecting the bulk properties of the constituent fibres.

Plasmas are acknowledged to be uniquely effective surface engineering tools due to:

- Their unparalleled physical, chemical and thermal range, allowing the tailoring of surface properties to extraordinary precision.
- Their low temperature, thus avoiding sample destruction.
- Their non-equilibrium nature, offering new material and new research areas.
- Their dry, environmentally friendly nature.

1.2 *Plasma reactors*

Different types of power supply to generate the plasma are:

- Low-frequency (LF, 50–450 kHz)
- Radio-frequency (RF, 13.56 or 27.12 MHz)
- Microwave (MW, 915 MHz or 2.45 GHz)

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The power required ranges from 10 to 5000 watts, depending on the size of the reactor and the desired treatment.

1.3 *Effect of plasma on fibers and polymers*

Textile materials subjected to plasma treatments undergo major chemical and physical transformations including (i) Chemical changes in surface layers, (ii) Changes in surface layer structure, and (iii) Changes in physical properties of surface layers. Plasmas create a high density of free radicals by disassociating molecules through electron collisions and photochemical processes. This causes disruption of the chemical bonds in the fibre polymer surface which results in formation of new chemical species. Both the surface chemistry and surface topography are affected and the specific surface area of fibres is significantly increased. Plasma treatment on fibre and polymer surfaces results in the formation of new functional groups such as -OH, -COOH which affect fabric wettability as well as facilitate graft polymerization which, in turn, affects liquid repellence of treated textiles and nonwovens.

In the plasma treatment of fibres and polymers, energetic particles and photons generated in the plasma interact strongly with the substrate surface, usually via free-radical chemistry. Four major effects on surfaces are normally observed. Each is always present to some degree, but one may be favored over the others, depending on the substrate and the gas chemistry, the reactor design, and the operating parameters. The four major effects are surface cleaning, ablation or etching, cross-linking of near-surface molecules and modification of surface-chemical structure.

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- ***Plasma cleaning*** and etching means a removal of material (impurities or substrate material) from the exposed surface.
- ***Plasma activation*** consists of the introduction of new functional groups onto the treated surface. Properties of the surface then depend on the nature of the chemical groups.
- Plasma-assisted ***grafting*** is a two-step process in which the plasma activation is followed by the exposure to a liquid or gaseous precursor, e.g. a monomer. The monomer then undergoes a conventional free radical polymerization on the activated surface.
- In ***plasma polymerization***, a monomer is introduced directly into the plasma and the polymerization occurs in the plasma itself.

1.4 *Environmental benefits*

The complexity of textile processing environmental impact starts with high water and energy consumption, high oxygen demand of several input materials being used as well as a generation of huge amounts of effluents with high chemical oxygen demand (COD), excessive colour, pH and toxicity. In general, desizing, dyeing, washing and finishing are the main sources of effluent pollution. The main advantage of plasma processing is that it is a *dry treatment*. Additionally, it is a very energy efficient and clean process. In general, the environmental benefits of plasma treatment can be summarized as:

- Reduced amount of chemicals needed in conventional processing

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- Better exhaustion of chemicals from the bath
- reduced BOD/COD of effluents
- shortening of the wet processing time
- Decrease in needed wet processing temperature
- Energy savings.

2. Application of Plasma in Textile Processing

2.1 *Desizing*

Atmospheric pressure plasma treatment on cotton grey fabric (sized by standard sizing recipe containing starch) with air and He gas mixture alters the surface morphology, gave rise to desizing effect and enhance the wettability and wicking action. The hitting of ions gave rise to loosening of the surfaces that were removed in subsequent process of washing. The surface roughness as well as formation of (-C=O, -OH or C-N) bonds created functional groups are responsible for improved hydrophilic properties. The loss of weight in desizing process was more for plasma treated fabric that too in initial part of treatment. These higher rates of desizing plasma pre treated fabric can save time, energy and water. [1]

Atmospheric plasma treatments are applied to Desizing the cotton (PVA were used for sizing) using air/He and air/He/O_2 combinations. These treatments removed some PVA film and significantly improved PDR (percent desizing ratio) by washing, especially by cold water washing. The tensile strengths of cotton fabrics treated with atmospheric pressure plasma were the same as for the unsized fabric. Results of the plasma treated PVA films revealed surface chemical changes such as *chain scission* and formation of polar groups, which promoted the

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solubility of PVA in cold water. *Air/He/O_2 plasma is more effective than air/He plasma* on PVA desizing (because of oxidation is more for Air/He/O_2 plasma) [2].

2.2 *Scouring*

Low temperature plasma treatment modified the surface of cotton fabrics. The contact angles between the liquid (scouring bath) and the low temperature plasma treated cotton fabric surfaces decreased significantly. Furthermore, the O_2 plasma treatment by changing the surface properties dramatically increased the wicking rate of cotton fabrics, making them more absorbent. The results for scourability revealed that low temperature plasma treatment increased the scouring rate of cotton fabrics. O_2 plasma caused changes in the oil, fat, and wax contents by etching where the topmost of the layer of the substrate is stripped off. This increased rate means that a shorter time have been chosen for scouring, the process was more environmentally friendly, and energy consumption decreased because less time was needed to reach the desirable state. For the scouring process, 25 minutes have been used for plasma treated instead of 40 minutes needed for scouring cotton fabrics [3].

2.3 *Dyeing*

The O_2 plasma treatment dramatically increases the wicking rate of cotton fabrics, making them more absorbent hence increase the dyeing rate of cotton fabrics. Holes were visible on the O_2 plasma treated cotton fabric surfaces, which were caused by the ablation effect of this nonpolymerizing reactive plasma gas. These holes provided a new pathway for

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the dye to enter the fiber and hence increased the dyeing rate. For the dyeing process 50 minutes have been chosen after plasma treatment instead of 90 minutes needed for dyeing untreated cotton fabrics. [3]

The Modification of the Cuticle and Primary Wall of Cotton by Corona Treatment was studied in which the effects of corona treatment were limited to the cuticle and primary wall of cotton, although one or two experiments (radiation sensitivity, bundle strength) suggested possibility for deeper penetration through to the secondary wall. Some disturbance of the wax on cotton was indicated in air chlorine corona treatments, and both the wax and cellulose reacted with chlorine in an air chlorine corona to produce C-Cl covalent bonds. Air-chlorine corona treatments have greater effect than the air corona treatments and air-chlorine corona treated fabrics are more wettable. A possible practical application of these results was to reduce the scouring or kier boiling required achieving a given dyeing level or dyeing uniformity [4].

The effect of low pressure plasma treatment on bleached and mercerized cotton fabrics was investigated with water vapour as working gas. Though bleached and mercerized cotton fabrics were hydrophilic, the change in hydrophilicity after plasma treatment has been tested and higher concentration of oxygen was founded on the surface of water vapour plasma treated surface. These higher oxygen concentrated surfaces gained higher hydrophilic properties. An increase in hydrophilicity revealed deeper dyeability of plasma treated fabrics [5].

2.4 *Finishing*

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2.4.1 Hydrophobization

Plasma treatment is used to achieve the hydrophobic effect by varying the application gasses. Plasma Treatment of cotton fabric with hexamethyldisiloxane gas has been used to smoothen the surface of the fibers and has capable of increasing the contact angle on the fiber till up to 130^{o}. Similarly, by using hexaflouroethane plasma, a strong effect of hydrophobization has been achieved by introducing fluorine groups on the surface of the fibers. It produces very good water repellent effect on its treated fabrics. Neither of these methods reduces the water vapor transmission ability of cotton [6].

Plasma treatment also has been used to achieve the lotus effect on cotton fabrics. The underlying principle is etching of the fiber to create nano sized peaks and then covering them with a hydrophobic layer using an appropriate gas such as hexafluoroethane.

Fig. 1: The lotus effect

2.4.2. Antimicrobial activity

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The crosslinked cotton fabrics with the combined dimethyloldihydroxyethyleneurea (DMDHEU) and acrylic acid crosslinking agent under the pad-dry-plasma-cure process were determined to study antibacterial properties of the treated fabrics. The plasma treatment increased the surface distribution of crosslinking agents and lets the metal ion stay on the surface of the treated fabrics. Such crosslinks, increased the antibacterial property of the pad-dry-plasma-cure and pad-dry-plasma-cure with copper after-treatment fabrics compared to that of pad-dry-cure and pad-dry-cure with copper after-treatment fabrics [7].

The microwave induced plasma technique was used to modify the cotton fabric to study the effect of onion skin & onion pulp extractions' grafting reaction for cotton dyeing and compare the washing fastness and anti microbial S.*aureus* ability of differtially treated cotton fabric. It was observed that the cotton fabric with direct grafting of onion skin or onion pulp extractions shows negative results , on the contrary cotton fabric with microwave O_2 plasma pretreatment provides more polar functional groups on the cotton surface and makes onion skin or onion pulp grafting reaction with anti microbial S.*aureus* ability. Cotton fabric with longer onion grafting time does not show bigger anti microbial S.*aureus* inhibition zone. It might be so because some anti microbial S.*aureus* components of onion are not stable under long high temperature reaction [8].

2.4.3. Flash fire resistance

Flame-retardant textiles are designed to reduce the ease of ignition and also reduce the flame propagation rates. Conventional textiles can be

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rendered flame retardant by chemical after-treatments as co-monomers in their structures or use of FR additives during extrusion. High performance fibers inherently have high levels of flame and heat resistance with the synthesis of all aromatic structures.

Flash-fires generated from improvised explosive devices (IED) incident upon the target for up to 3 s (sec). Clothing with moderate levels of flame retardancy, while shielding the wearer from heat radiation, can ignite under such flash-fire conditions causing burn injuries even when the underlying garments have some level of flame retardancy. It is therefore necessary to provide flash-fire resistance to underlying garments including protective clothing for up to 3–8 s. flame retartend textiles with flash fire resistance help in avoiding the injuries in such cases. Nanoceramic surface treatment offer flash fire resistance, where the plasma treatment offers possibility of selective modification of the surface by keeping the bulk characteristics unchanged. A. R. Horrocks et al studied that plasma treatment of fabric (flame retardant cotton) surfaces in the presence of functionalized clay produced an inorganic or even a micro ceramic coating having reduced flammability at the high heat fluxes and it was an indicative of increased resistance to flash-fire ignition. [9]

2.4.4. Crease recovery finishing

The pad – dry – plasma – cure process with argon as working gas increased the cross linking effect between cross linking agent and cellulose molecules. The cross linking agent was a mixture of Dimethylol dihydroxy ethylene urea (DMDHEU) and acrylic acid (AA). The increased cross linking effect

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improved the physical properties of finished fabrics. The DCRA- dry crease recovery angle, WCRA- wet crease recovery angle and TSR- tensile strength retention values of pad – dry – plasma – cure finished fabrics are higher than pad – dry – cure finished fabrics at same value of nitrogen content and CL/AGU – number of cross linking per anhydrous glucose unit. Vinyl group of AA excited at Ar plasma treatment and grafted to cellulose fiber and DMDHEU under cure treatment increased the physical properties [13].

2.4.5. Biostoning

The influence of corona (COR) and RF low-pressure plasma (LPP) parameters on the decolorization of indigo-dyed denim fabric were examined. Low-pressure plasma and corona treatments could be a viable alternative to conventional biostoning for obtaining the 'worn out' look of indigo-dyed denim fabric. This could be associated with the production of chemically active molecules and radicals in gas mixtures containing oxygen, which consequently leads to an oxidation of dyes. In addition to satisfactory color change effects, the main advantages of these treatments are the lack of water consumption and shorter process duration [10].

2.4.6. Other Applications

Spinnability/ surface roughness

"Frictionizing" textile fibers by corona treatment produces larger effects than conventional chemical methods. Cotton roving cohesiveness is increased initially by chlorine-corona treatment to four times its

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original value. The residual cohesiveness increases cotton yarn tensile strength by 24%. It appears that the very high cohesiveness of cotton roving occur immediately after corona treatment, it improved further spinning process [11].

Cotton Spinnability, yarn and fabric strength, and abrasion resistance are increased by corona treatment. Injection of dilute chlorine gas into the corona cell during corona treatment increases the effects achieved, particularly at about 95^{o}C .Since fiber tensile strength is unaffected by this treatment, the improvements probably largely result from the increased fiber cohesiveness. The marked improvement in Spinnability attained suggested a possible significant improvement in cotton processing economy [12].

Mechanical property

Mechanical properties of plasma (water vapour – working gas) treated bleached and mercerized cotton fabrics were studied by determining the measurements of breaking stress and breaking elongation. Low pressure water vapour plasma treatment (10 s) did not affect the bulk property of cotton fibers. Tensile stress and elongation of the warp and weft of fabrics remain unaltered [5].

3. Conclusion

Plasma technology with all its challenges and opportunities is an unavoidable part of our future. The possibilities with plasma technology are immense and numerous. It can rightly be said that plasma technology is slow, but steady in the industrial revolution. The substantial shortcoming of plasma treatment of textiles is that it cannot replace all wet processes, but it can be a viable pretreatment, which can provide plenty of environmental and economical benefits. Therefore, textile industry should consider the concept of higher initial investments in equipment that will be paid off quickly with respect to environment related savings and the profit of the sale of high value added products.

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*Address for correspondence :
Prof. (Dr.) S.K. Chinta
D.K.T.E.Society's, Textile & Engineering Institute,
Ichalkaranji, Maharashtra, India

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