J Fusion Energ (2014) 33:97–102
DOI 10.1007/s10894-013-9657-2

REVIEW ARTICLE

New Advances in Plasma Technology for Textile

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Published online: 25 December 2013
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Abstract Plasma processing technologies are of vital importance to several of the largest manufacturing industries in the world. Foremost among these industries is the electronics industry, in which plasma-based processes are indispensable for the manufacture of very large-scale integrated microelectronic circuits. Plasma processing of materials is also a critical technology in, for example, the aerospace, automotive, steel, biomedical, and toxic waste management industries. Most recently, plasma processing technology has been utilized increasingly in the emerging technologies of diamond film and superconducting film growth. The dominant role of plasma-treated surfaces in key industrial sectors, such as microelectronics, is well known, and plasmas, certainly experimentally and, in places, industrially, are being used to modify a huge range of material surfaces, including plastics, polymers and resins, paper and board, metals, ceramics and in organics, and biomaterials. In the textile field, significant research work has been going on since the early 1980s in many laboratories across the world dealing with low temperature plasma treatments of a variety of fibrous materials showing very promising results regarding the improvements in various functional properties in plasma-treated textiles. The growing environmental and energy-saving concerns will also lead to the gradual replacement of many traditional wet chemistry-based textile processing, using large amounts of water, energy and effluents, by various forms of low-liquor and dry-finishing processes. Plasma technology, when developed at a commercially viable level, has strong potential to offer in an attractive way achievement of new functionalities in textiles. The objective of this work is to give a comprehensive description and review of the science and technology related to plasmas, with particular emphasis on their potential use in the textile industry.

Keywords Plasma · Textile · Surface modification

Introduction

The textile industry manufactures fibers, yarns, and fabrics in various forms, all of which may be either natural or synthetic materials. Fibers can be twisted, spun into yarns, threads, cords, ropes, cables, etc. Fibers or yarns can be further converted into knitted, woven, and nonwoven fabrics by different processes. Textile materials have been widely used in making apparels, home upholstery, and daily-use articles. The development of textile industries and technologies offers the benefits of combining polymer, fabrics, and other materials to improve the performance properties of textiles for a wide range of applications ranging from geo textiles, hygienic and health care textiles to electronic textiles. In these applications, the functions of textile materials are associated with phenomena, such as wetting, biocompatibility, adsorption, and electrical conductivity. Wetting, biocompatibility, adhesion, and many other performance properties all begin at the surface. The properties of textile surfaces and interfaces play key roles in material processing and application technologies. In recent years, surface modification of textile materials by plasma treatment has opened up new possibilities in this field [1–9].

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Recent developments in the plasma treatment of textile materials has revealed its enormous potential as an alternate technology for the textile processing, due to its cost saving, water saving and eco friendliness. Wet processing of fabrics, such as scouring, desizing, bleaching, dyeing/printing, and finishing, consume enormous amounts of water, produce pollution through effluents, and consume large amount of energy. As a result, it has become necessary to look for 'green processes'. Plasma technology, when used effectively, can offer such 'greener' possibilities as it is a dry process, is energy efficient, needs a minimum amount of chemicals, and there is no down-stream pollution.

Plasma is a cluster of particles, including equal numbers of positive ions and electrons, free radicals, ultraviolet (UV) radiation, and neutral species created by exciting a gas or vapor in electromagnetic or electric fields. The free radicals and electrons collide with the exposed material surface, rupturing covalent bonds and creating free radicals. The activated material surface then readily combines with the excited gas species and provides chemically reactive groups that are covalently bonded to the substrate surface. By selecting the gas, vapor, or combination of gases, the desired surface chemistry can be obtained. The effect of plasma treatment on the structure and properties of cotton and dyeing behavior has been reported by many researchers. Researchers have used both non-polymer forming and polymer forming plasmas to improve appearance, texture, aesthetic appearance, and functional performance of fiber surfaces. The flexibility of plasma surface modification has opened up many possibilities for using it in textile processing as a stand-alone process or as a pre-treatment for improving the efficiency of the next process, also known as plasma-assisted processing [10–13].

A typical plasma system consists of a gas inlet, a reactor vessel, a vacuum pump, a matching network, and a power source. Various reactors have been used in plasma processing, for dc and low-frequency glow discharges, internal electrodes are necessary.

A typical reactor is a bell jar with circular or square electrodes. As the frequency increases, electrodes maybe placed outside the reactor vessel. Plasma treatment has been used to improve print ability, wettablility, bond ability, biocompatibility, surface hardness, and surface heat resistance. It is also a means of cleaning polymer and textile surfaces without a solvent and of introducing cross-linking at the surface. The different types of gas or mixtures of gases that can be used for plasma treatment of textiles include argon, helium, hydrogen, nitrogen, ammonia, nitrous oxide, oxygen, carbon dioxide, sulfur dioxide, water, and tetrafluoromethane. Oxygen and oxygen-containing plasmas are the most frequently and are very effective at increasing the surface energy of textiles. Nitrogen and nitrogen-containing plasmas are used to produce nitrogen functionality such as amino groups on polymer surfaces. Fluorine and fluorine-containing plasma are used to decrease the surface energy and to increase the hydrophobicity of polymer surfaces. Each gas produces a unique modified surface. In oxygen plasma two processes occur simultaneously: etching of polymer and textile surface through the reaction of atomic oxygen with the surface carbon atoms, giving volatile reaction products; and the formation of oxygen functional groups at the textile and polymer surface through the reactions between the active species from the plasma and the surface atoms. The balance of these two processes depends on the operation parameters of a given experiment. Many parameters such as the nature of textile substrate, the temperature of the substrate, electrode materials, pressure, power level, and gas flow rate play a significant role in affecting the outcome of a plasma treatment [14–16].

The present paper reports findings of plasma treatments on fabrics using a variety of gases and its effects on different properties of textile, such as wetting and dyeing ability properties, etc.

Effect of Plasma on Textiles

Textile materials subjected to plasma treatments undergo major chemical and physical transformations including (1) Chemical changes in surface layers, (2) Changes in surface layer structure, and (3) 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 fiber 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 fibers is significantly increased. Plasma treatment on fiber 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 fibers 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.

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 [14, 17].

Application of Plasma in Textile Industry

In the textile field, significant research work has been going on since the early 1980s in many laboratories across the world dealing with low-pressure plasma treatments of a variety of fibrous materials showing very promising results regarding the improvements in various functional properties in plasma-treated textiles. A variety of commercial low-pressure plasma machines, mostly in prototype form, have been offered for batch/in-line processing of textiles for more than 15 years. 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.

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.

Some application of plasma technology for textiles pretreatment and finishing has been done previously and describe below.

Improvement the Antibacterial Activity on Fabric

Antibacterial activities of cellulose fabrics were easily achieved with a DC magnetron sputtering device, by coating copper on the surface of a fabric, without any chemical or wet process. In addition, the duration of the process is much shorter than the time needed for the conventional process (more than 100 min) using a detergent, metallic salts, and at least three washing baths. The antibacterial activity of the fabrics remained even after laundering at least 30 cycles [18].

Effects of using low temperature plasma pretreatment on silver particle adsorption by cotton fabrics were also investigated in previous works. The results showed that the absorption of silver particles by cotton can be increased strongly with nitrogen plasma treatment.

This can be attributed to the formation of cationic groups on cotton fabrics because of the change of surface charge of the cellulose fibers. This study clearly confirms that plasma treatment has good potential for removing and recovering heavy metal ions from aqueous media. Thus, cationic modification by plasma can be used for modification of cellulose fibers to increase silver particle absorption on their surfaces and thus demonstrates a stronger antibacterial activity [19].

Plasma treatment can be used for modification of PP fibers for increasing copper particle adhesion on their surfaces and producing stronger antibacterial activity [20].

Decolorization of Denim Fabrics

Decolorizing of denim fabrics by means of Argon Low Temperature Plasma procedure has been investigated. The comparison between treated and untreated denim samples shows that plasma technique has some advantages in comparison with washing. This method leaves a good varnish and smooth surface on the denim, without damaging the strength of the fibers. In addition, the duration of the process (about 15 min) is much shorter than the time needed for stonewashing (more than 90 min). There is also no need for expensive pumice stones and for special enzymes which are essential in the stonewash technique [21].

Also, results obtained in decolorizing of denim, when different gases such as Argon or Oxygen have been used in a DC magnetron sputtering device was compared. The results show better decolorized output for Argon rather than Oxygen when being treated for 15 min. However, after washing the treated denims, the O_2 treated samples look better than those treated by Argon due to the removing of all oxided dyestuffs produced during the plasma treatment [22].

Improving Dyeability of Fabrics

Dye-ability of Polypropylene Fabrics is improved by using low temperature plasma treatment. The dye-ability of PP fabrics which treated by LTP of N_2 is increased with anionic dyes, and by creating OH and C=O groups on the surface of the fabrics with O_2 LTP treatment, the dye exhaustion for cationic dye increases noticeably. So PP can dyes with O_2 LTP treatments with cationic dyes easily. And new usage of PP fabrics as textile garments developed. The present examples show that plasma technology performed under reduced pressure, leads to variety to processes to modify fiber or textile materials to fulfill additional highly desirable requirements. It is to be expected that, this technology, which has been known for a long time and is being used in different branches of industry, in the near future will conquer textile as well [23–25].

Effect of plasma sputtering treatment on the natural dyeing properties of wool and the possibility of substituting this technique for mordant treatment was also studied. The results show that, the sputtering has improved the natural dying properties of wool fabrics. It has also improved the wool resistance to washing and light. The dyed treated samples have also gained very good antibacterial properties [26, 27].

Improving the Hydrophilic Properties of Fabrics

Surface of wool samples were changed both physically and chemically by using LTP treatment. The situation of wool samples in LTP reactor is very important factor. By putting samples on the cathode and using oxygen as a working gas, the wet ability and dye ability of wool samples were increased [28].

Improving Water Repellent Properties of Fabrics

By coating aluminium and copper on the surface of fabrics, with low temperature plasma treatment, the interstices between the warp and weft yarn are blocked and water will not pass through the treated fabrics. After the treatment, drops run freely over the surface while mechanical properties, the visual appearance, and the physical properties of the fabrics are unchanged. Crystallization structure of fabrics confirms that LTP doesn't change the strength of fabrics [29].

Properties (especially water repellency) of cotton coated by a thin layer of aluminum have been studied. The process has been performed in a low temperature plasma medium, using a magnetron sputtering device. Effect of different gases such as argon and oxygen as the discharge medium on the properties of the obtained samples has also been investigated. The results which are exposure time dependent show a good repellent property for 30 min of treating in argon medium under the condition of experiment. However, when O_2 is used in the system, the cotton property changes to become hydrophilic of which the factor decreases as we increase the time of treating [30].

Anti Felting Properties of Wool

Surface of wool could be changed both physically and chemically by LTP treatment. The results show that not only the topography of the surface is modified but also the chemical composition of the surface. The effect of exposing the samples when they are on cathode or anode and their response to different gases such as Argon, O_2 and N_2 as the discharge medium, were also investigated. Shrinkage has significantly decreased after the LTP treatment. From the results, it can be seen, the type of gas used and the position of samples inside the plasma reactor have an important role in shrink-resist properties of the wool samples. For Ar, O_2 and N_2-cathode plasma treated samples we had a marked improvement in shrink resistance, whereas, this improvement for the O_2 and N_2-anode plasma treated samples did not happen.

Also the wettability and dye ability of the wool could be increased under proper condition. The decrease of water absorption time and increase of dye ability of wool samples are attributed to the destruction of the scale structure due to plasma etching on a wool surface and the introduction of more polar groups such as carboxyl groups due to plasma chemical modification. Also, the LTP treatment could impose significant shrink-resistant and anti-felting effects to the wool fabrics [31].

Improving the Flame Retardant Properties of Fabric

Effects of using low temperature plasma pretreatment on metal salt adsorption by cotton fabrics and flame retardant properties of the treated samples before and after dyeing were investigated. Titanium dioxide (TiO_2), zinc sulfate ($ZnSO_4$), Lead(II) acetate ($Pb(C_2H_3O_2)_2$), Aluminium sulfate ($Al_2(SO_4)_3$) and Silver Nitrate ($AgNo_3$) were used as metallic salts and applied to cotton fabrics. Some analysis including char yield and LOI has been studied in order to evaluate flame retardant property of treated samples. The increased amount of char yield contributes to greater LOI values of the plasma pretreated/metal salt loaded fabrics. The results indicate that the inoculated the plasma pretreated cotton fabrics have good flame retardant properties. Inoculated in a 0.01 M solution of Silver Nitrate ($AgNo_3$) shows the increase of the LOI value from 18.6 to 23.3. From the results, it can be concluded that the FR property of treated fabrics can withstand against after dyeing and dyeing the inoculated cotton fabrics does not have any negative effect on flame retardancy of cotton fabric [32].

Nanoclay is an effective flame retardant for cotton fabrics. In the other research work, Cotton fabrics were treated with low temperature plasma to improve their adsorption capacity. After plasma treatments nanoclay was used as the flame-retardant finishing agent for cotton fabrics. Char yield of the untreated sample before treatment was 1.9 %, and for the treated samples increased greatly. The char yield of the sample which was treated with nanoclay is 10.20 % which is 5 times more than untreated sample. Also the results show that, N2 plasma treatment causes increase the flame retardant properties of cotton sample. It is observed that, Nitrogen plasma has synergistic effect on nanocaly for flame retardant properties. Char yield value for N2 plasma/nanoclay treated cotton increase to 12 %. Also the same results for LOI values have been achieved. By plasma pretreatment and nanoclay exhaustion, the LOI values increase up to 23.5 %. The improvement of flame retardancy of the treated samples is attributed to the earlier decomposition of nanoclay to drive the char formation, which could inhibit the transmission of heat, energy and O2 between flame and cotton fabrics. Presence of nanoclay leads to the formation of a barrier layer that limits the propagation of fire inside the material but increases the flame-spread rate over the surface of the specimen. The treated cotton fabrics have shorter afterglow time and no after-flame during the vertical burning test [33].

Conclusion

Plasma treatment can have profound effects on the properties of textile materials. Different gas plasma treatments have different effects on the surfaces of textiles. Plasma treatments provide great potential for the modification and functionalization of textile materials.

Plasma technology is slow, but steady in the industrial revolution. Plasma treatment of textiles 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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