Treatment of Metal and Textile Fabrics Surfaces Using Plasma

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This work was carried out in collaboration between the two authors. Author RM designed the study, wrote the protocol and wrote the first draft of the manuscript. Author AME managed the literature searches. Both authors read and approved the final manuscript.

ABSTRACT
In the next few years, the progresses in plasma technology will play an increasing role in our lives, providing new sources of energy. The studies conducted by scientists on plasma state not only accelerate technological developments, but also describe the characteristics and types of plasmas and improve the understanding of natural phenomena. Plasmas represent the recent fourth state of matter in addition to the three fundamental states namely solids, liquids and gases. Plasma is defined as a state of matter where the gas phase is energized until atomic electrons are no longer associated with any particular atomic nucleus or as a matter that exists as a mixture of neutral atoms, ions, electrons, molecular ions and molecules present in excited and ground states. Plasma is the result of the ionization of atoms and the level of ionization is mainly controlled by temperature, where an increase of temperature increases the degree of ionization. The term “plasma” introduced by the scientist Irving Langmuir (1928) and comes from a Greek word that means moldable or Jelly material. Plasma may be produced by either heating a gas at high temperature until it is ionized or by subjecting it to a strong electric or magnetic fields. Investigators categorized plasma as non-thermal and thermal plasma. In non-thermal plasma, the electrons are at a much higher temperature than the ions and neutral particles however, in thermal plasma, the
1. INTRODUCTION

One of the most important applications of plasma technology is that, it can be utilized to develop thin protective layers to surfaces, as surface pretreatment and cleaning are the most important operations of coating technologies [1-3]. Unique new surface technologies like plasma treatments with partially ionized (plasma) gases are used to clear away thick contaminant layers, greasy organic contaminants that commonly adhere to metallic surfaces, native oxide / hydroxide compound layers and corrosion products from surfaces [4,5]. There are two methods able to eliminate native oxide films and other impurities from metallic surfaces namely wet-chemical cleaning methods and progressive plasma technologies [6-8]. The latter is superior for accomplishing this treatment due to the following functional characteristics:- a) Most of the gases used have no toxicity. b) Processes are easily controllable through RF, DC or microwave power. c) Waste products are generally in gaseous form. d) No liquid wastes or residues remain [9]. Atmospheric plasma is very effective at activating and cleaning the surface of a material, increasing the adhesion characteristics and making it easier to bond, paint and glue [10, 11]. The aim of this review article is to provide a brief overview of surface treatments with plasma gases and its applications in surface treatment of metals and in textile industry.

2. IMPORTANCE OF PLASMA TREATMENT OF SURFACES

Surfaces treatment of metals can be carried out by different conventional methods namely, physical, chemical, mechanical, physicochemical and chemi-thermal methods [12]. In mechanical treatment, contamination removal is achieved by mechanical wiping, scraping, milling, exposure to air or water jet, physical treatment mechanism consists in dissolution of contaminants with the help of various solvents and in their subsequent removal from the work-piece surface [13,14]. Intensification of the treatment process is achieved by placing of ultrasonic vibration into the treatment area [15], physicochemical treatment consist in dissolution, emulsification and chemical destruction of contaminations, chemi-thermal method consists in chemical destruction of contaminations in flame or in alkaline melt at high temperatures (400-450°C) and mechanical treatment efficiency can be improved by optimization of alkaline melt composition and process automation [16,17]. The surface treatment of metals is now increasingly carried out by plasma treatment, which is very effective and environmentally friendly [18,19]. Plasma technology for the treatment of metals is used in the electrical industry, automotive industry, construction industry, the container industry, medical and adhesive technology [20]. The technology of plasma is mostly used for fine cleaning of metals from organic materials and oxides [21]. In case of organic impurities compressed air is used, whereas forming gas is used for oxide layers. Electrolyte-plasma technology provides productive surface cleaning of high quality and can remove almost any type of contamination: mineral and organic rust-preventing greases, residual galvanic-lacquer coatings and rust. When galvanic coating is applied with failure, electrolyte-plasma technology allows to take such coating off less than for 1 minute and the processing time depends mainly on the thickness and the type of galvanic coating [22,23].

The increase interest of textile end-users, scientists and manufacturers lead them to search for new methods to improve the surface properties of natural and man-made fibers, (such as adhesion, wettability, dyeability, printability and material shrinkage) [24,25]. Different methods have been evaluated including modifying fiber properties to make polypropylene (PP) dyeable, utilization of primers with low melt points to coat fabrics to promote heat-sealing ,ink adhesion and thermoforming performance and enhancing color-fastness properties for PP nonwovens because of its low cost, excellent chemical resistance, high melting point and

direct products from surfaces [4,5]. There are two methods able to eliminate native oxide films and other impurities from metallic surfaces namely wet-chemical cleaning methods and progressive plasma technologies [6-8]. The latter is superior for accomplishing this treatment due to the following functional characteristics:- a) Most of the gases used have no toxicity. b) Processes are easily controllable through RF, DC or microwave power. c) Waste products are generally in gaseous form. d) No liquid wastes or residues remain [9]. Atmospheric plasma is very effective at activating and cleaning the surface of a material, increasing the adhesion characteristics and making it easier to bond, paint and glue [10, 11]. The aim of this review article is to provide a brief overview of surface treatments with plasma gases and its applications in surface treatment of metals and in textile industry.

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adaptable to many fabrication methods. It is well known that polypropylene (PP) a non-polar fiber cannot be easily dyed because of its highly crystalline. In this case and in order to overcome restriction of dyeability, functional groups may be introduced onto fiber surface using gas plasma treatments, thus creating a polar layer on the fiber surface and improving fiber bulk properties without affecting fiber properties [26].

3. APPLICATION OF PLASMA

Plasmas represent the recent fourth state of matter in addition to the three fundamental states namely solids, liquids and gases. The generation of a technical plasma starts by giving the high-frequency electromagnetic transmitter energy to the less inactive electrons rather than ions, followed by collisions between electrons and ions which cause transferring of electron energy on to the ions. On the other hand, due to the great mass difference, this energy transfer is small and a numbers of collisions are necessary to achieve a balance between ion and electron temperatures. The number of collisions depends also upon the pressure [27]. The number of collisions increased by increasing the pressure and vice versa. The thermal equalization also plays an important role in the maintenance of the charge carriers and finally a mixture of electrons and ions tend to form neutral ions. This recombination leads to the two free charge carriers becoming a neutral atom which reflects causing the plasma some of its conductivity. When equilibrium exists between ionization and recombination, the plasma will burn in a stable manner [28]. Minimum ionization energy of an electron is required to ionize an atom and if energy transfer due to the impact is less than the ionization energy, then the struck atom is excited [29].

4. SURFACE TREATMENT OF METALS WITH PLASMA TECHNOLOGY

There is a wide variety of conventional techniques for finishing the surfaces of metal products to protect them from corrosion and to look better such as electroplating, electrolytic polishing, galvanizing, enamels and glazing, metalizing, heat treatment, phosphating, etching and plastics coatings [30]. Generally, any type of surface treatment or modification can be implemented by means of plasma treatment; the plasma process is able to ensure accuracy practically to the atomic layer and to act also in the narrowest cracks and cavities. Another major benefit of plasma treatment is the complete absence of toxic chemicals and their problematic handling [31]. Surface treatment of metals is already firmly implemented in many industrial sectors by conventional methods. The main objective of surface treatment is oxide reduction, cleaning and pre-treatment of the metal under treatment in order to optimize adhesion and achieve wettability [24]. Metals such as stainless steel, silver alloys, aluminium-magnesium alloys and copper alloys can be clean, reduce and pretreated using atmospheric plasma technology [32]. By treating these surfaces by this technique they achieved more effective cleaning and microscopic roughening of the functional surface by transferring the electric arc to the grounded metal substrate [33,34]. The latter leads to a larger surface and to a better adhesion of adhesive, sealing or potting compounds. The removal of oxide layers is also made possible with this process that can replace the use of costly and environmentally harmful chemical baths.

4.1 Reduction of Metal Surfaces Using Atmospheric Plasma

Atmospheric plasma is an excellent method for cleaning and reducing a broad variety of metal surfaces [35]. Metallurgical conventional processes can be achieved at high temperatures. On the other hand, the reduction of metals is known to be possible at relatively low temperatures if the hydrogen offered has previously been dissociated by a plasma process. Atomic hydrogen is known to play a role in reducing oxides [36]. The reduction process starts from the surface and is characterized by the diffusion of atomic hydrogen into the material’s lattice structure. The desorption kinetics of the water generated are equally important for effective depth penetration [37]. The speed of conversion accelerates with rising temperatures and with a higher concentration of hydrogen atoms offered [38,39]. This process leads to surface reduction using atmospheric hydrogen plasma rich in excited atomic hydrogen. Applied plasma system for the technical-scale reduction of metal surfaces should be adjusted to the requirements of the processing steps. This application is quite suitable especially when organic residue needs to be removed via oxidation. The plasma system makes it possible to oxidize, clean and reduce a surface in a series of sequential steps, and in order to prevent post-oxidation, the final process step can be carried out in a protective gas atmosphere [40].
5. PLASMA SURFACES TREATMENT IN TEXTILE INDUSTRY

Several techniques have now become available which can be used to produce uniform films of functional materials on textiles which can offer functionalities. Conventional methods of finish application to textile, such as pad-dry-cure or coating that are currently being used to impart antimicrobial, anti UV and self cleaning, are often accompanied by excessive poor durability to washing, loss of mechanical strength and most importantly reduced comfort to wearer. Functional coating methods provide a flexible alternative to conventional finishing methods in that they are independent of fabric type, require low quantities of additives and allow combinations of different functionalities in a simple way. Enzymatic immobilization processes provide an effective, non polluting alternative to conventional chemical finishing treatments because they operate under mild conditions, are substrate specific, non toxic, biodegradable and do not produce any harmful byproducts. The most commonly used conventional methods of immobilization of enzymes are adsorption, covalent bonding, entrapment, encapsulation and cross-linking. Nano Coatings films to fabrics and fibers allow a much larger surface area to be created with improved functionality and durability [41]. Recently there is an increasing interest in plasma for textile materials processing. Plasmas offer the possibility to obtain typical textile finishes without changing the key textile properties. Textile materials have intrinsic properties and are excellent material for imparting additional functionalities such as hydrophobic, oleophobic or antibacterial. Plasma is a dry processing technique and provides a solution to reduce the use of large amount of water, chemicals and energy in the traditional wet methods. A very large range of possible plasma applications including different textile finishes are cited in the literature. The most common applications are imparting antimicrobial agents [42], hydrophilic properties, hydrophobic, oleophobic [43], anti-shrink treatment of wool [44] and fire retardant agents [45], in addition to other properties such as desizing of cotton [46], sterilization of fabric surfaces [47], changing the electrical conductance [48], influence printability and dyeability [49].

Plasma technology offers many interesting possibilities for the production of high-quality, functional textiles. Many types of plasma gases such as oxygen, nitrogen, argon, hydrogen etc. are used to impart surface modification by abstraction of hydrogen atom from the polymer chain of the fibre surface creating free radicals. These free radicals get further oxidized into oxygenated polar groups (C=O, OH, COOH) on exposure to air. This treatment may lead to the improvement of surface fibre properties such as surface texture gloss, dyeability and interfacial shear strength. The selection of gas depends on the surface effect desired. Plasmas are applied by applying an electric field to a gas at particular pressure in order to accelerate free electrons which are supplied by an electron emitting cathode. Plasma process on a given fibre substrate is controlled by gas pressure flow rate [50,51].

The surface of textile materials at nano-level can be modified by the atmospheric pressure plasma treatment. This modification is closely associated with surface structure and fabric weave construction. Different types of plasmas encountered in surface treatment processing techniques which are mainly formed by partially ionizing a gas at a pressure below that of the atmosphere [40,52]. Since these systems are run at low pressures, pumps and vacuum chambers are needed to create these plasma processes. The atmospheric plasma treatment process treats and functionalizes material surfaces in the same way as the vacuum plasma treatment process on a wide range of materials and has unique advantages over other treatment processes [53]. These materials include polypropylene (PP), polyethylene (PE) nonwovens, nylon, wool, polyester fiber, textile yarn, and other films such as PE teraphthalate (PET), poly-tetrafluoro-ethylene and oriented PP films. By applying plasma treatments, the surface energies of these treated materials increased substantially and consequently enhancing adhesion, wettability and printability properties [54]. Basic research performed in technical textiles recently has resulted in an increasing knowledge of the possibilities of this process regarding demands as dye ability, printability, wet-ability, shrinkage resistance of wool, coating and wash ability of conventional and technical textile. Plasma treatments have been used to induce both surface and bulk property enhancements to textile materials leading in improving conventional fabrics and composites properties. In addition, to improve color fastness and wash resistance of fabrics, enhance dyeing rates of polymers, and change the surface energy of fibers and fabrics [55]. The research conducted in various thermoplastic fibers has
shown improvements of shrink resistance, toughness and tenacity [56].

5.1 Plasma Spraying Process

In this method, the surface being coated is sprayed with droplets and the film material in plasma spraying is not liquid, and must first be melted by a high-energy heat source and then sprayed onto the cold surface of the fabric. When the droplets hit the surface they are flattened and cool off due to heat transfer to the base material. The particles solidify and shrink. The films adhere primarily due to mechanical adhesion and locally due to chemical bonding forces of different types [57,58]. In order to achieve a strong film adhesion, the cleaned surfaces are roughened by sandblasting. This gives good adhesion, because the particles penetrate into the surface roughness and shrink onto the peaks. An electric arc in a nozzle is used as a heat source to heat up a flow of argon, nitrogen or helium gas to very high temperatures. Due to high temperatures, there is an increase in the volume of the gas plasma which flows of the nozzle at high speed. By this method different oxide coatings can be applied such as, chromium oxide, aluminum oxide coatings, tungsten carbide cobalt coatings and pure tungsten coatings [59].

6. CONCLUSION

- Plasma science and plasma processing are applied in different interdisciplinary fields. Therefore, collaboration among the existing groups of scientists is of importance to focus on the new emerging technologies through seminar series and research programs.
- Plasma processing should capitalize on its tradition of excellence in basic research without competing with industrial application researches.
- Establishment and maintain contact with plasma processing scientists through collaborations with industry, universities, and other laboratories.
- Governmental funds should be allocated specifically to stimulate focused research in plasma processing, both for basic and applied plasma sciences.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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