ECO-FRIENDLY TEXTILE DYEING AND FINISHING

Edited by **Melih Gunay**

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Preface

Initially the sole purpose of dyeing was to color textile substrates for fancy fabric appearances. Although, this was an impressive achievement at the time, the competitive challenges began to drive the development of highly functional fibers and substrates through advanced dyeing and finishing processes for higher added value in applications of; membrane filtration, coatings, composites, microelectronic devices, thin-film technology, super absorbency, antimicrobial materials, biocides and insecticides, flame reterdancy, improved reactivity and numerous others.

Polymeric fibers that are mechanically strong, chemically stable, and easy to process often have inert surfaces which makes them not suitable for these advanced applications. Consequently, there has been significant number of studies that focuses on enhancing the chemical, biological, physical, optical and dyeability properties of fibers without negatively effecting their mechanical and most desired properties. Among the techniques, perhaps the plasma treatment is one of the most investigated. Also, Cyclodextrins which can act as hosts and form inclusion compounds with various small molecules to provide certain desired attributes may be applied to textile substrates as reagent during the finishing processes. The majority of these studies often involve a) the embedding of novel nanoparticles for adding unique features to textiles, b) uniformly maximizing the loading capacity of textile substrates to improve nanoparticle adsorption for optimal surface property.

While for the purpose of coloration only natural dyes were used initially. Due to limitations in coloration and with the invent of synthetic fibers, natural dyes are mostly replaced with dyes themselves are either chemically hazardous or require auxiliary chemicals that are not good for the environment. At the beginning, we were not as concerned of the damage caused by dyeing to the environment. However over time as we come to understand that our being healthy and well being also depends on our environment, we have been increasingly paying attention to reduce our footprint on our ecosystem. In particular for dyeing of textiles, the efforts primarily focuses on reducing the water consumption, using of natural dyes or less harmful dyes and chemicals, right-first-time dyeing, the development of an effective degumming process based on enzymes as active agents , dyeing and energy optimization and development of advanced waste water treatment processes. In recent years, many attempts have also been made to improve various aspects of dyeing by the introduction and advancement of new technologies that used ultrasound, ultraviolet, ozone, plasma, microwave, gamma irradiation, laser, supercritical carbondioxide.

Consequently, as market forces demand unique and sophisticated products from the textile industry, recent research has been focused on the development of technologies for functional textiles some of which implemented advanced finishing and dyeing techniques. Meantime, the local governments and regulators also require the textile industry to become more environment friendly in their operations. Hence, this book aims to present the cutting edge research in both areas to advance the knowledge in this field.

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Advances in Dyeing Chemistry and Processes

Chapter 1

Multifunctional Textiles – Modification by Plasma, Dyeing and Nanoparticles

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1. Introduction

The textile industry in developed countries is confronting the world's marketing conditions and competitive challenges which are driving towards the development of advanced, highly functional textiles and textiles with higher added value. The conventional textile finishing techniques are wet chemical modifications where water and rather hazardous chemicals are used in large quantities and wastewaters need to be processed before discharging effluent, whereas the most problematic factor are ecological impacts to the environment and effects to human health. The increasing environmental concerns and demands for an environmentally friendly processing of textiles leads to the development of new technologies, the use of plasma being one of the suitable methods [1]. Plasma technology is an environmentally friendly technology and a step towards creating solid surfaces with new and improved properties that cannot be achieved by conventional processes [2]. Plasma is the fourth state of matter. It is a gas with a certain portion of ionized as well as other reactive particles, e.g. ions, electrons, photons, radicals and metastable excited particles. Several types of plasma are known; however, only non-equilibrium or cold plasma is used for the modification of physical and chemical properties of solid materials such as textiles. Chemically reactive particles produced at a low gas temperature are a unique property of cold plasma; hence, there is minimal thermal degradation of a textile substrate during the plasma processing [3]. Cold plasma is a partially ionized gas with the main characteristic of a very high temperature of free electrons (typically of the order of 10,000 K, often about 50,000 K) and a low kinetic temperature of all other species. The average energy of the excited molecules is usually far from the values calculated from the thermal equilibrium at room temperature. The rotational temperature, for instance, is often close to 1000 K, while the vibrational temperature can be as high as 10,000 K, although the kinetic (translation) temperature is close to room temperature. Furthermore, the dissociation fraction is often several percent, which is orders of magnitude larger than that calculated from thermal equilibrium at room temperature. This also applies to the ionization fraction; although this is often much lower than the dissociation fraction. Plasma with such characteristics readily interacts with solid surfaces, causing reactions that would otherwise occur only at elevated temperature of the solid material. For this reason, non-equilibrium plasma represents an extremely powerful medium for modification of the surface properties of solid materials. A medium of particular interest is weakly ionized highly dissociated oxidative plasma that can be sustained in high frequency discharges in oxygen, air, carbon dioxide, water vapor, and mixtures of these gases with a noble gas. Such plasma has been successfully utilized in an extremely wide range of applications from nanoscience to fusion reactors. Plasma is used for synthesis of nanostructures with interesting properties, removal of thin films of organic impurities, selective etching of composites, sterilization, passivation of metal, ashing of biological materials, etching of photoresists, functionalization of polymers, and conditioning of tokamaks with carbon walls [4-9].

The choice of discharge parameters is determined by the requirements of each particular application. For selective plasma etching, for instance, extremely aggressive plasma is needed; thus, it is created with powerful generators at a moderate pressure (where the O density is the highest) in pure oxygen or in a mixture of oxygen and argon. For treatment of delicate organic materials, on the other hand, weak plasma performs better, since aggressive plasma would destroy organic material in a fraction of a second. Therefore, extremely delicate organic materials are rather treated in an afterglow or in plasma created at low pressure and with a low-power generator. Water vapor is sometimes used instead of oxygen. The advantages of using plasma are ecological and economical. Moreover, the textiles subjected to the treatment are modified without an alteration of the bulk properties. Unlike wet chemical processes, which penetrate deep into the fibers, plasma produces no more than a surface reaction, the properties given to the material being limited to the surface layer of a few nanometers [10]. The modification of textile substrates using plasma enables different effects on the textile surfaces from the surface activation to a thin film deposition via plasma polymerization. In the first stage of the treatment, plasma reacts with the substrate surface where active species and new functional groups are created, which can completely change the reactivity of the substrate [11]. The changes in the surface morphology of fibers can be induced by plasma etching process where the nano- or micro-roughness of fibers is formed [12]. The nanostructured textile surfaces have a higher specific surface area, which leads to new or improved properties of the treated surface, i.e. increased surface activity, hydrophilic or hydrophobic properties, and increased absorption capacity towards different materials, i.e. nanoparticles and nano-composites [13- 18].

When researching the deposition of nanoparticles onto different substrates, it is important to understand the adhesion of particles, which is dependent on the interaction mechanism with a material. The mechanism of nanoparticle adhesion has not been completely explained yet, since there are many different opinions among the theorists on the subject. Thus, it is generally considered that attractive forces and chemical bonds play an important role in the adhesion of particles [19]. The physical or mechanical adhesion of nanoparticles mostly occurs due to van der Walls or electrostatic forces, while the chemical adhesion of particles is a consequence of ionic, covalent, metallic and hydrogen bonds [20]. Moreover, the nanoparticles can penetrate into certain parts of the substrate, such as pores, holes and crevices, and they lock mechanically to the substrate. This adhesion mechanism, which is called mechanical interlocking, has been solved from the perspective of surface roughness effects [21]. Since plasma causes etching of the fibers and leads to an increase of the surface roughness higher adhesion properties towards metal or ceramic particles onto substrates can be achieved [22-30]. The adhesion of TiN (titanium nitride) onto PP (polypropylene) and PC (polycarbonate) was increased after a modification of substrates with argon low-pressure plasma [31]. The roughness after plasma treatment increased from 15 nm to 17 nm for PP and from 12 nm to 30 nm for PC. Consequently, contact angles decreased from 95° to 59° for PC and from 87° to 35° for PP. The surface modification of polyethylene terephthalate (PET) polymer was created by oxygen and nitrogen plasma at different treatment times [32]. The surface of PET polymer was modified in order to achieve improved attachment of fucoidan, which is a bioactive coating with antithrombogenic properties. The attachment of fucoidan was improved by oxygen plasma treatment, especially due to the surface roughening. The adhesion work, the surface energy and the surface polarity of PA6 (polyamide-6) fibers were improved by dielectric barrier discharge (DBD) treatment in helium at atmospheric pressure. Furthermore, a new structure was observed at the nanoscale, with an increased roughness and a larger surface area, favoring the adsorption [33]. The self-cleaning and UV protective properties of PET fibers were drastically improved after a modification of PET fibers with oxygen plasma and loading of TiO_2 prepared by an aqueous sol-gel process [34]. Cotton also showed self-cleaning properties after RF plasma and TiO_2 treatment [35]. TiO_2 on textile substrates is also used for a biomedical application to improve antimicrobial effectiveness of the fabric [36]. By using oxygen radiofrequency plasma at a higher power input, the roughness of fibers increased and likewise the adhesion of TiO_2 onto treated fabric. Treatment of PA and PET with corona plasma increased the adhesion of colloidal silver which affected the antifungal protection of the fabrics [37]. The quantity of silver on plasma-treated fabric was three times higher than on untreated fabric.

Preparation of metal nanoparticles also enables the development of new biocides. Due to their large surface area and ability to detain moisture, the textile materials are an excellent environment for a microorganism growth. Microorganisms can cause milder, aesthetic unpleasantness to serious health related problems. Textile materials with an antimicrobial effectiveness are used for medical, military and technical textiles, textiles for sports and leisure and bedding. At nanotechnology researches in textiles, different forms of silver were used, such as metal silver nanoparticles, silver chloride (AgCl) and composite particles of silver and titanium dioxide (Ag-TiO_2) [3, 24, 25, 27, 38-47]. In the case of antimicrobial efficiency, the surface coating of nanosilver on titanium dioxide maximizes the number of particles per unit area in comparison with the use of an equal mass fraction of pure silver [48,49]. Different methods have been used for the deposition and loading of silver nanoparticles onto synthetic and natural textiles, i.e. sonochemical coating, sol-gel process, dip-coating, pad-batch and exhaustion method, the use of nanoporous structure of cellulose fibers as a nanoreactor for *in situ* synthesis of nanoparticles and plasma sputtering process [3, 27, 48-54]. The possibility of loading nanoparticles using exhaustion method started recently [55]. The exhaustion method is the best process for uniform distribution of nanoparticles and is especially appropriate to be used when the simultaneous application of nanoparicles and dye onto fabric is performed, and dyed and antimicrobial effective fabric is achieved at the same time [3, 24, 25, 27]. Depending on the desirable functionality of a functionalized fabric, a treating bath may contain only dye, dye and silver nanoparticles or silver nanoparticles alone. An exhaustion method for loading of silver nanoparticles onto textile substrate was also used on silk fibers [54]. In that research, different concentrations of colloidal silver were used (10, 25, 50 and 100 ppm) and the effect of medium pH on the silver nanoparticles uptake on the fibers was studied. The antimicrobial effectiveness of functionalized fibers was better for samples with higher silver concentration and for samples treated in a medium with a lower pH. Also the use of salt (NaCl) improved a uniform distribution of silver particles on the fibers' surface which consequently improved antimicrobial effectiveness of fabrics. A difference between pad-dry-cure and exhaustion method on adhesion and antimicrobial activity of fabrics was performed with commercial silver nanoparticles and a reactive organic-inorganic binder [45]. Results revealed that using the same initial concentration of silver, the pad-dry-cure method resulted in a much lower quantity of adsorbed silver nanoparticles in comparison to the exhaust method. Another possible method for applying silver onto textiles is plasma polymerization method where surface of textile is functionalized with nanostructured silver film by magnetron sputtering [56].

When dealing with modification of textiles by silver it is important to know how the functionalization will affect the color change of fabric. A reflectance (UV/VIS) spectrophotometry is one of the methods to be used when detecting or controlling the presence of silver nanoparticles in a solution or on a textile substrate. It is a direct measure that the abundance of silver is in the topmost layer of the textile fabric [30]. The instrument analyzes the light being reflected from the sample and produces an absorption spectrum. Some of the electrons in the nanoparticles are not bound to the selected atom of silver, but are forming an electronic cloud. Light falling on these electrons excite the collective oscillations, called surface plasmons. The resonance condition is established when the frequency of light photons matches the natural frequency of surface electrons oscillating against the restoring force of positive nuclei. Surface plasmon resonance is the basis of many standard tools for measuring adsorption of material onto planar metal (typically gold and silver) surfaces or onto the surface of metal nanoparticles. It is the fundamental principle behind many color-based biosensor applications. As a result of the particles growth, an intense absorption band at 400 nm to 415 nm caused by collective excitation of all free electrons in the particles was observed [57]. Increase in diameters of the nanoparticles from 1 to 100 nm induces a shift of the surface plasmon absorption band to higher wavelength [50, 57-59]. That means that the size of nanoparticles is defined by their optical response, therefore by that the color that can be seen [50, 60]. Loading of colloidal silver nanoparticles onto bleached cotton fabric caused yellowish coloring of fabric with absorption maximum at 370 nm [24, 30]. The evaluation of color changes of textiles modified by silver nanoparticles was also determined in CIELAB color space [60]. Loading of colloidal silver nanoparticles in concentration of 10 ppm induced very small, eye insensitive, color change ($\Delta E^* < 1$) to the fabric. When colloidal silver nanoparticles in concentration of 50 ppm were loaded, the color change of fabric was obvious ($\Delta E^* = 15.09$). Loading of silver onto textiles before or after dyeing also causes color changes; however the changes are not as extensive as with the white fabric. When colloidal silver was loaded before dyeing, the color change was $\Delta E^* = 1.44$ and when loaded after dyeing, the color change was $\Delta E^* = 2.73$. Color changes of textiles can be also induced by plasma treatment. When plasma is used for a modification of cotton to improve its hydrophilicity, then cotton has a better dyeability and consequently deeper coloration [61]. Also, a raw cotton fabric can be bleached by using ozone plasma [62]. The whiteness index (CIE WI) of fabric was even higher after plasma treatment than after peroxide bleaching (CIE WI $O_3 = 95.3$; CIE WI $H_2O_2 = 94.5$).

Since the modification of substrates by plasma improves the adhesion of metal nanoparticles onto substrates than it is no surprise that plasma modification of textiles has a special significance when applying silver nanoparticles. The chapter presents the influence of plasma treatment on loading capacity of cotton toward different forms of nanosilver. Exhaust dyeing process was used for loading of nanosilver onto plasma-treated cotton, which represents a new approach to textile finishing in achieving multifunctional textile properties.

2. Experimental setup and methodology

Low-pressure plasma of different working gases and air atmospheric corona plasma were used for a modification of textiles. Untreated and plasma-treated textile substrates were additionally modified by loading of silver nanoparticles during dyeing process. Morphological, chemical and physical properties of plasma-treated textile substrates were studied using microscopy (SEM), spectroscopy (XPS) and measuring of the breaking strength and elongation of textiles. The quantity of adsorbed silver was determined using mass spectrometry (ICP-MS), while the antibacterial efficiency of functionalized textiles was determined using microbiological tests.

2.1. Plasma modification of textiles

Cotton substrates were modified using different plasma systems, i.e. atmospheric air corona plasma [63-65] and low-pressure inductively coupled radiofrequency (ICRF) discharge plasma of different working gases, water vapor [3, 26, 66, 67] and tetrafluoromethane [27], respectively. ICRF plasma is particularly suitable for treatment of delicate materials with a large surface for the following reasons: the neutral gas kinetic temperature remains close to the room temperature; the plasma-to-floating potential difference is small; the density of neutral reactive particles is large; and extremely high treatment uniformity is achieved. The use of low-pressure plasma is a contemporary technological process, not yet fully applied in textile industry due to its discontinuous process. For a continuous, on-line processing interfaced to a conventional production line the use of corona atmospheric pressure plasma is recommended. Furthermore, the corona plasma treatment also introduces new functional groups onto fibers surfaces, produces surface cleaning and etching effect of treated textiles. The comparative research of corona plasma treatment of polyester was presented as well [24].

2.1.1. *Low-pressure plasma treatment*

A RF generator with a nominal power of 5 kW and a frequency of 27.12 MHz was applied. The power absorbed by plasma, however, was much smaller due to poor matching and was estimated to about 500 W. The discharge chamber was a cylindrical Pyrex tube with a diameter of 27 cm and a length of 30 cm. Cotton fabric was put onto a glass holder mounted in the center of the discharge chamber. After closing the chamber the desired pressure of 0.4 mbar was achieved by a two-stage rotary pump with a nominal pumping speed of 65 m^3/h. The pressure was fairly stable during the experiment. Although the ultimate pressure of the rotary pump was below 1 Pa, the pressure remained much higher at 40 Pa. The source of water vapor was the cotton fabric itself. When tetrafluoromethane was used as a working gas, it was leaked into the chamber in order to obtain a pressure of about 100 Pa, the pressure where plasma is most reactive. By switching on the RF generator, the gas in the discharge chamber was partially ionized and dissociated, starting the plasma treatment of the fabric. The plasma treatment time was 10 s in both cases. The schematic diagram of low-pressure RF plasma reactor is presented in Fig. 1.

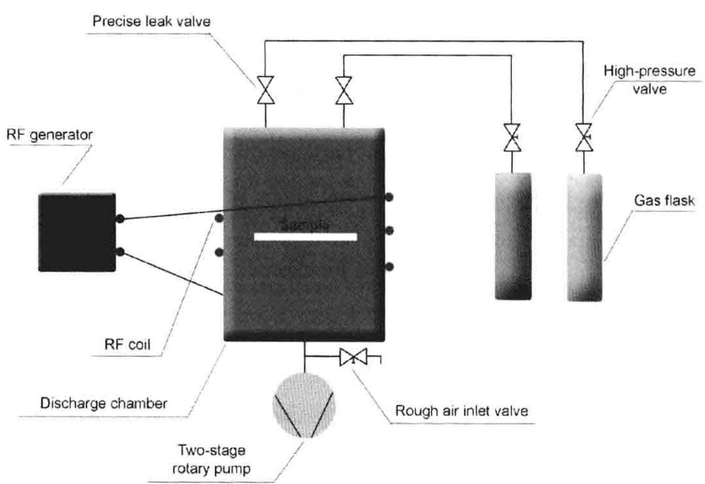

Figure 1. Schematic diagram of low-pressure RF plasma reactor

2.1.2. *Atmospheric plasma treatment*

Textile samples were treated in a commercial device, Corona-Plus CP-Lab MKII (Vetaphone, Denmark) (Fig. 2). Samples (270 × 500 mm^2) were placed on a backing roller (the electrode roll covered with silicon coating), rotating at a working speed of 4 m/min. The distance be-

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tween electrodes was adjusted with air gap adjusters at both sides of the electrode to 2 mm. Corona discharge was generated within the air gap between the electrode and backing roller. The power was 900 W and the number of passages was set to 30.

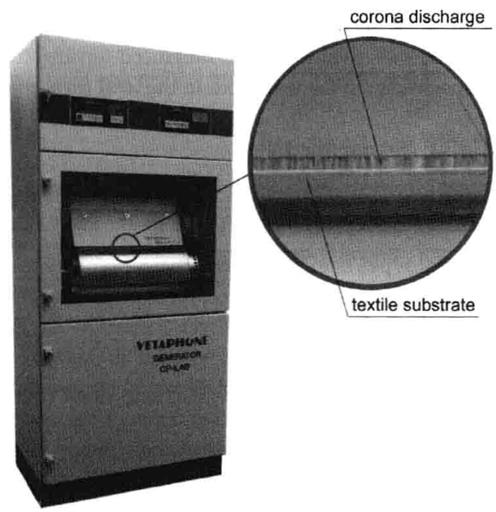

Figure 2. Picture of atmospheric corona plasma reactor and a detail of treating area shown in a red circle

2.2. Morphological, chemical and physical properties of untreated and plasma-treated textiles

2.2.1. X-ray photoelectron (XPS) analysis

Information on the chemical composition and chemical bonds of surface atoms of untreated and plasma-treated textile samples was obtained with XPS analysis. During the XPS analysis, a sample is illuminated with monochromatic X-ray light in an XPS spectrometer and the energy of emitted photoelectrons from the sample surface is analyzed. In the photoelectron spectrum, which represents the distribution of emitted photoelectrons as a function of their binding energy, peaks can be observed that may correspond to the elements present on the sample surface up to about 6 nm in depth. From the shape and binding energy of the peaks within XPS spectra, the chemical bonding of surface elements was inferred with the help of data from the literature.

2.2.2. Scanning Electron Microscopy (SEM)

The morphological surface properties of fibers and their changes after plasma treatment were studied using scanning electron microscopy (JEOL SEM type JSM-6060LV). All samples were coated with carbon and a 90% Au/10% Pd alloy layer.