

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



## Pretreatments of Textiles Prior to Dyeing: Plasma Processing

R. R. Deshmukh<sup>1</sup> and N. V. Bhat<sup>2</sup>

<sup>1</sup>*Physics Department, Institute of Chemical Technology,  
N. Parekh Marg, Matunga, Mumbai,*

<sup>2</sup>*Bombay Textile Research Association,  
LBS Marg, Ghatkopar (w), Mumbai,  
India*

### 1. Introduction

Synthetic fibres have acquired an important part of the current textile industry. A great disadvantage of some of the synthetic fibres is their low surface energy. This causes poor wettability and dyeability. Surface modification techniques are mainly carried out to remove loosely bound materials, foreign particles/impurities and to improve hydrophilic nature and thereby improving dyeability. Manipulation of surface characteristics of textile materials is of fundamental importance in the production of advanced functional textiles. Textile fibres can be classified in two main groups: Natural and Synthetic. Natural fibres are of animal origin or plant origin such as silk, wool, hair, jute, cotton, cellulose etc. whereas there are a number of manmade/synthetic fibres such as viscose, polyester, polypropylene, nylon, PLA fibres, polyamide and acrylic fibres. Natural fibres are limited and are not sufficient and not always suitable for many applications. Hence synthetic fibres have acquired greater importance in the present era. Synthetic fibres form an important part of the textile industry, with the production of polyester alone surpassing that of cotton. Improving the surface properties suitably is a very important aspect of the textile processing. Low surface energy of the synthetic fibres affects the processing of the fibres, especially during wet treatments. The surfaces are not easily wetted, thus impeding the application of finishing compound and colouring agents. In addition, a hydrophobic polymer hinders water from penetrating into the pores of the fabric. For a number of applications it is necessary to modify surface properties of textiles from hydrophobic to hydrophilic and vice versa. Plasma processing has a potential to render and change such surface properties. Recent advances in textile chemistry have resulted in imparting various functional properties such as decreased skin irritations, enhancing antimicrobial activity and fragrance to the textile material. The surface composition and structure of a textile material plays an important role in the textile's performance in specific applications. E.g. The surface of apparel / textile garment that is in contact with human skin could be modified to absorb the body moisture while the outside surface could be modified to repel water. Several studies showed that properties of polymeric substrates could be altered through surface modification (Deshmukh and Bhat, 2003 (a); Deshmukh and Shetty, 2007; Jahagirdar and Tiwari, 2004; Navaneetha P., et al., 2009; Yen et al., 2006).

In the history of dyeing, right from early days, when natural dyes derived from extracts of trees, leaves, roots and flowers were used till the modern concept with the use of several synthetic dyes, it can be seen that each one has its own peculiarities. An efficient dyeing process needs good adhesion and penetration of dye molecule into the fibre structure. Thus the structure of the fibre – both Physical and Chemical – becomes important. If not found to be suitable, these need to be modified. Various pretreatments such as chemical, enzymes, plasma, irradiation have been tried.

Textile technology deals with several processes such as desizing, scouring, bleaching, calendaring, singeing, dyeing, printing etc. During each of these stages the structure, properties and behavior of fibres undergo many changes. The assembly of the fibres and fabrics as well as bulk of each fibre undergoes transformations. Of these changes, the surface modifications of the fibres is of profound importance as it improves properties such as softness, adhesion, wettability, dyeability, printability etc. Apart from clothing, textiles find use in a variety of applications such as furnishing, carpets, medical, automobile, geo-textile etc. Each of these can benefit from specially designed characteristics which are governed by surface properties. Wettability, adhesion, friction, biocompatibility, absorption, all begin at surface and thus surface composition is more important than bulk. The properties depend on surface chemical and physical structures which vary according to types of fibres, polymers and the assemblies. The surfaces offer a platform for functional modifications to meet specific needs. The surface modification can be achieved by various techniques such as traditional wet solution treatment, physical treatment, biological approach etc. New technologies using high energy beam process, vapour deposition, nano-particles etc. can have potential for modification of surfaces.

Textile industry is one of the most pollutant industries because of the various processes involved such as singeing, desizing, scouring, bleaching, mercerization, dyeing etc. These processes pollute the environment and water resources. Economical and ecological pressure on textile industry requires the development of economic and environment friendly “green” processes. So one has to select a proper pretreatment for the modification of surfaces amongst the available processes.

## 2. Surface modification techniques

Wettability and adhesion of polymers / films can be controlled by using surface modification techniques such as exposure to plasma, flame, chemicals, enzymes etc. Wettability can also be regulated by changing chemical composition of the surface. In addition surface roughness can be an important factor for enhancing the adhesion and wettability. Wettability is governed by molecular interaction of the outermost surface layer of a few angstrom units. Therefore the forces dictating the wetting behavior of organic substances do not originate from the organic molecule as a whole, but rather from the outermost surface group. Further interfacial energy minimization needs molecules to arrange themselves in such a way that only the low energy portions come in contact with surrounding phase. As a result wettability depends on the chemical nature of energetically favoured functional groups and the extent to which these are exposed. Several surface modification techniques have been developed to improve wetting, adhesion, dyeing, feel and other properties of textile surfaces by introducing a variety of reactive functional groups. Few important techniques are described below.

### 2.1 Wet chemical processing

In this surface modification technique, the textile surface is treated with liquid reagent to generate reactive functional groups onto the surface. Chemical agent penetrates in the textile material / substrate, thereby damaging the bulk property. The commonly used chemical processing agents are chromic acid and potassium permanganate which introduce oxygen containing functional groups on synthetic fibres such as PET, PP, Nylon and PE. The degree of functionalization is therefore not repeatable between the polymers of different molecular weight and crystallinity. The another disadvantage is that it can lead to the generation of hazardous chemical waste and can cause skin irritation, even with very small amount of residual on the textile material. The effect of pretreatment of polyester with DMF, DCM and PCE on dyeability of polyester fabric was studied for disperse dyes (Jahagirdar and Tiwari, 2004; Patel and Bhat, 1986). The dye uptake depended on the solvent and the temperature and duration of pretreatment. All the pretreated samples showed a higher dye uptake than the untreated one. The temperature close to the boiling point of the solvent was found to be the best temperature for increased dyeing. The enhanced dyeability was associated with the plasticization and reduction in glass transition temperature of polyester. Similar studies on effect of swelling treatments with benzyl alcohol and formic acid was carried out for nylon-6 filaments. When the pretreated filaments were dyed with disperse dye, a considerable increase in the equilibrium dye uptake was observed. Although these filaments showed increase in lateral order (as evident from X-ray diffraction), the increase in dye uptake was explained due to structural rearrangement creating larger voids (Subramanian et al., 1982).

In the chemical grafting, the first step is to create radicals on the textile to initiate copolymerization reactions with different monomers. Deo and Gotmare have carried out grafting of acrylonitrile monomer on grey cotton to impart high water absorbency (Deo and Gotmare, 1999). They have used  $\text{KMnO}_4$  as an initiator. Tsukada et al. have used ammonium peroxydisulfate as an initiator to graft benzyl methacrylate on wool fibres (Tsukada et al., 1997). They have also reported that the tensile strength of grafted fibres increases while elongation and breaking strength decreases.

### 2.2 Mechanical abrasion

It also leads to non uniform and non repeatable surface modification. We do not have good control over the process as in wet processing. This in turn hampers mechanical properties of the materials under process.

### 2.3 Flame treatment

The reactive oxygen is generated by burning an oxygen rich gas mixture. It incorporates hydroxyl, aldehyde and carboxylic acid functional groups onto the surface and is utilized to enhance surface properties for better printability, adhesion and wettability. Flame treatment is non-specific surface functionalization technique that bombards the polymer surface with ionized air generating large amounts of surface oxidation products. One drawback of flame treatment is that it can reduce the optical transparency of polymers. It depends upon flame temperature, contact time and composition that must be accurately controlled to maintain uniform and reproducible treatment and to avoid burning.

### 2.4 Enzymatic surface modification

Enzymatic surface modification of textile material involves processing of fibres to modify physical and chemical surface properties or introduction of functional groups on the surface.

Research on the enzymatic surface modification of textiles contributes to environment friendly processes through the sustainable development of novel processes for textile. While much research focuses on chemical modification or structuring of the surfaces, the introduction of functionalities using enzymes is relatively unexplored scientific area. The advantage of enzyme technology over the other technologies is their high specificity towards a certain reaction and / or substrate. Review articles (Araujo et al., 2008; Cavaco and Gubtz, 2003; Lenting, 2004) describe importance and potential of enzyme technology in textiles. Enzyme technology has already been proven to be very profitable in industrial pre-treatment processes of natural fibres predominantly. Taking into account the current international state of art, bio processes are getting more and more important. Over the past two decades, much research has been carried out on reactions catalyzed by enzymes that are relevant for the textile industry such as desizing of cotton, depilling of cotton, enzymatic ageing of denim fabric, enzymatic scouring of grey cotton fabric, shrink-resistant treatment of wool and enzymatic degumming of silk (Nierstrasz, 2009). These studies clearly indicate that the surface modification of textiles with enzymatic treatment has the potential to replace conventional wet treatment. Conventional wet processes requires long residence time, high concentrations of harsh chemicals, large amount of water and are generally carried out at high temperatures leading to high energy consumption.

## 2.5 Sonication

Ultrasonic waves are acoustic waves with frequencies between 20 KHz to 20 MHz. When ultrasonic waves are communicated through media, several effects occur such as mechanical, thermotic and cavitation. These effects are recognized as beneficial to physical and chemical processes (Liu et al., 2007). It has been known that ultrasonic waves in liquids are used to clean surfaces. They produce bubbles in liquids and when the bubbles burst substantial amounts of energy is released. When compared with hand washing, ultrasonic agitation has many advantages. It has negligible effects on the strength and colour of fabrics and causes less fibre migration (Hurren et al., 2008). Vankar and Shankar have carried out dyeing in Ultrasonic bath of cotton fabric pretreated with enzymes (Vankar and Shankar, 2007). Their results show better and faster dye uptake after enzyme pretreatment on cotton fabric and results of dyeing are better than those obtained using metal mordanted fabric. They also observed considerable improvement in wash fastness and light fastness. The improved properties were observed without using metal mordants thereby proving ultrasound to be an effective tool in textile dyeing for cleaner production.

## 2.6 Surface modification using nano-particles

Nanotechnology has touched every nook and corner of the life and textiles cannot remain aloof. Nanotechnology deals with materials having at least one dimension less than 100 nm. It includes nano-particles, nanorod, nanowires, thin films and bulk materials made of nanoscale structures (Cao G, 2004). Application of nanotechnology on textile materials could lead to the addition of several functional properties. Deposition of silver nano-particles can be used to create shiny metallic yellow to dark pink colour while simultaneously imparting antibacterial properties to the fabric. Gold nano-particles allow the use of molecular ligands so that the presence of biological compound surroundings is rapidly detected. Metal oxide nano-particles such as  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{ZnO}$  possess photo-catalytic and antibacterial activity and UV absorption properties. More often these nano-particles can be impregnated



onto textile materials without significantly affecting their texture or comfort. It is reported that the padding of colloidal silver solution onto textile fabric made from cotton, polyester, cotton/polyester and cotton/spandex blended fabrics shows efficient antibacterial activity with good laundering stability (Lee and Yeo, 2003; Lee and Jeong, 2005). Silver nanoparticles coated fabric exhibited better antibacterial properties and protection against UV radiation owing to nano-silver absorption in the near UV region (Vigneshwaran et al., 2007). Super hydrophobic (water repellent), dirt repellent nano-structured surfaces of textiles having self cleaning property have attracted attention of scientists. It is also called the lotus effect. Bozzi et al. have reported on RF plasma, MW plasma, and UV irradiation as pretreatments for synthetic textile surfaces, allowing the loading of TiO<sub>2</sub> by wet chemical techniques, in the form of transparent coatings. These materials show a significant photocatalytic activity (Bozzi et al., 2005). Various functional properties such as comfort and easy care can be imparted with the advent of nano-technology, which otherwise were difficult. Though many people are working in this area of nanofinishing of textiles, their commercial exploitation has only just begun.

## 2.7 Radiation induced surface grafting

It is relatively a new technique that offers a variety of ways to alter the surface morphology and chemical composition of textile substrates and, thus imparts new or improved functional properties. The surface grafting can be achieved by a) light (generally UV light) induced grafting, b) plasma induced grafting and c) irradiation ( $\gamma$ -rays, electron beam) induced grafting. These three methods share the same objectives i.e. creating free radicals onto the polymeric substrates and then these radical sites are used as initiators for copolymerization reactions with vinyl monomers present in the grafting solution. Various parameters such as concentration of the monomer, time of treatment, radiation dose, type and concentration of catalyst used, if any, could greatly affect the grafting efficiency and need to be optimized.

Radiation induced grafting involves the use of high energy radiation to create free radicals onto the textile substrates. It can be carried out in two ways: in-situ grafting and post exposure grafting. Compared with chemical grafting, radiation-induced grafting has many advantages such as no chemical initiators are used and grafting yield can be controlled by controlling dose and the time of irradiation. Shao et al. used an electron beam to induce grafting of 2-hydroxyethyl methacrylate (HEMA) on silk fabric (Shao et al., 2001). They showed that the degree of grafting was related to the irradiation dose. Uyama et al. have given excellent review on the subject (Uyama et al., 1998).

Plasma induced grafting is another important techniques and the details of it are described in a book (Yasuda, 1984). Plasma-induced grafting has emerged as an alternative and attractive method for surface modification of textiles. Under this technique, first radicals are created by exposing fabric in the gaseous plasma such as O<sub>2</sub>, N<sub>2</sub>, NH<sub>3</sub>, Ar, air etc. and then fabric is immersed in the monomer bath followed by washing. Similarly *in situ* polymerization is also carried out, in which fabric is treated with gaseous plasma followed by plasma polymerization of monomer vapour onto the fabric surface in the plasma reactor. Bhat and Benjamin have successfully grafted acrylamide onto cotton and polyester fabrics using RF plasma (Bhat and Benjamin, 1999). They have observed that the crease recovery angle increases and tensile strength decreases slightly. Abidi and Hequet have studied graft copolymerization of vinyl laurate monomer on gaseous microwave plasma processed cotton fabrics (Abidi and Hequet, 2004, 2005). The grafted cotton fabric showed excellent water

repellency properties. Repeated home laundering of the treated cotton fabrics revealed no significant effect on the water contact angle or on the quantity of grafted vinyl laurate monomer as determined by universal attenuated total reflectance Fourier transform IR, demonstrating the good durability of the treatment that was applied. Graft copolymerization of various monomers onto variety of fibres was carried out by means of RF plasma (Zubaidi and Hirotzu, 1996). The monomers used were HEMA, Acrylamide (AAm), N-isopropyl AAm, acrylic acid, 2-methoxyethyl acrylate and 2-hydroxyethyl methacrylate. The textile fibres used were cotton, cellulose acetate, rayon and cupraammonium cellulose. Authors have reported that HEMA monomer was graft polymerized more readily than other monomers investigated and cotton fabrics were shown to be more reactive than other fabrics. Oktem et al. have incorporated acrylic acid onto the surface of polyester fabric to impart soil resistance and improve dyeability using two approaches (Oktem et al., 1999). In the first approach, *in-situ* polymerization of acrylic acid monomer was achieved in a glow discharge reactor. In the second approach, the fabric was first treated in Ar plasma, followed by immersion in an aqueous bath containing different amounts of acrylic monomers. The advantage of plasma treatment over the wet chemistry technique is that the effects of plasma do not penetrate more than few 100 Å from the surface and hence bulk properties of the substrate remains unaltered.

Light induced grafting basically uses, UV light energy for creation of free radicals onto the textile surfaces. UV radiation induced surface grafting of textiles is another technique that has attracted attention because of its simplicity. Radicals thus generated onto the surface are used to initiate copolymerization reactions with various monomers. UV radiations are not as penetrating as high-energy gamma ( $\gamma$ ) radiations, free radicals thus produced mainly close to the surface rather than uniformly distributed throughout the fibres (Reinhardt and Harris, 1980). Radiation induced grafting using high energy sources such as UV radiation or electron beams has been explored as an alternative to chemical grafting. However, if the conditions are not controlled, radiation grafting may result in deterioration of physical properties of the substrate and may lead to photo-degradation of the substrate (Abidi, 2009). Shulka and Athalye have successfully grafted HEMA onto the Polypropylene staple fabrics using UV radiation (Shulka and Athalye, 1994). The choice of grafting with HEMA was based on its hydrophilic properties. They used three different photo-initiators. They observed that the moisture regain of the PP fabric was increased and build-up of static electricity was diminished. The parameters affecting the efficiency of grafting, such as time and temperature of the reaction as well as concentrations of the initiators, were optimized in this study to maximize the amount of grafted monomer on the PP fabric surface. UV induced grafting of water soluble monomers onto the surface of polyester fabrics was performed by Uchida et al. to permanently change the surface properties from hydrophobic to hydrophilic (Uchida et al., 1991). UV grafting technique was also used to impart water repellency. Ferrero et al. have reported the use of silicone containing monomer with different formulations on cotton fabrics in order to impart water repellency (Ferrero et al., 2008).

## 2.8 Plasma processing

The above mentioned methods particularly chemical wet processing have disadvantages that they require the disposal of polluted water and the treatments are non uniform. Plasma treatment of textiles is attractive in that it is clean, dry technology and much less energy is consumed than equivalent conventional treatments. Gas plasma treatments are highly surface specific; they do not affect the bulk properties of the textile fibres. Plasma processing

is environmentally friendly, since no wet chemistry is involved. It does not produce any waste/ load on the environment. Therefore, low temperature plasma treatments are set to revolutionize textile processing technology. Although gaseous plasmas have been known for several decades, it is only recently, after the introduction of equipments on an industrial scale, the commercial interests have began. Nowadays, textile fabrics of breadth  $>1$  m can be successfully treated on a commercial scale with low pressure plasma, in a roll to roll manner. The technology is widely perceived as being confined to batch processing. The book edited by Shishoo highlights the huge potential of plasma treatment for textile processing (Shishoo, 2007). An overview of the literature on potential uses of non-thermal plasmas for the modification of textile products and benefit from the plasma treatment is given by Morent et al. (Morent et al., 2008).

Plasma treatments of textiles alter surface morphology and chemical composition without affecting their bulk properties. The depth of surface modification is of the order of few hundred angstroms. Plasma treatment can alter hydrophobic surface to hydrophilic and vice-versa, depending upon the type of gas / monomer used for the generation of plasma. Thus plasma treatment can lead to improved wettability or water repellency, depending on whether greater chemical affinity or inertness has been conferred / transformed on the textile surfaces. Similarly, other properties that can be improved are bio-compatibility, adhesion, resistance to wear and tear, rate and depth of dyeing, cleaning of fibre surfaces, and desizing.

Low temperature glow discharge consists of high energetic electrons, positive and negative ions, free radicals, excited atoms and molecules, neutrals and UV radiation. The mixture of species composing plasma is therefore highly complex and in general all these species can interact with textile surfaces during the plasma treatment. There are basically two kinds of plasmas that can be produced in laboratory, hot plasma and cold plasma. Hot plasmas are thermally in equilibrium and the temperature is of the order of 1000 K. Therefore, hot plasmas are not suitable for polymers and textiles treatments. Whereas, the electrons in the cold plasma acquire energies in the range of 0.1 to 10 eV, much higher than the energies of ions and molecules, so equilibrium between all the species is far from equilibrium. Cold plasma temperature is around room temperature or slightly above, so it can be successfully applied for the surface modification of textiles. Plasma can be generated by applying electric fields of low frequency (50 KHz. to 500 KHz.), radiofrequency (13.56 MHz.) or microwave (915 MHz. or 2450 MHz.). The extent and nature of the modification of a textile surface by plasma treatments is governed by / depends upon several parameters such as, working pressure, power, distance between two electrodes, time of treatment, type of gas / monomer, the type of textile, used etc. In spite of the complexity of all these factors, several effects can be broadly identified. One is cleaning or etching of substrate surface. This process involves removal of tiny amount of contaminant, process aids, adsorbed species etc. So cleaning of surfaces is regarded as first step of plasma processing. After this step actual deposition / etching of the material starts. It is associated with the changes in surface properties and wetting behavior. In general, polymers containing oxygen groups are more sensitive to etching than polyolefins. Under the same conditions of plasma treatment, polyester fibres are more prone to etching than nylon 6 fibres, which in turn are more prone than polypropylene (Radu et al., 2000). An enormous variety of plasma treatments are now available, and so the changes that can be brought to textile surface characteristics are numerous. Plasma treatments are therefore, capable of giving rise to innovative type of textile and moreover on a commercial scale.



### 2.8.1 Atmospheric pressure plasmas

There are three types of atmospheric pressure plasmas: a) Corona Discharge, b) Dielectric Barrier Discharge (DBD), and c) Atmospheric pressure glow discharge (APGD).

- a. Corona Discharge: It is the oldest type of plasma treatment employed for modification of polymeric surfaces. It consists of two parallel electrodes, one of which is cylindrical in shape while other one is knife shaped. A very high voltage 10 to 15 kV is applied between the two electrodes separated by ~1 mm distance. Corona discharges are weak and too inhomogeneous for plasma treatments for textiles. The density of the plasma falls dramatically with the distance from the point of generation, a factor that accounts for smaller gap between the two electrodes. Thicker fabric therefore cannot be treated by corona discharge.
- b. Dielectric Barrier Discharge (DBD): It consists of two parallel plate electrodes separated by narrow gap and around 20kV potential difference applied between them. In order to prevent arcs and short circuit between the electrodes, one or both the electrode plates are covered with suitable dielectric material such as ceramic or glass. Therefore it is called as dielectric barrier discharge. The DBD is powered by AC with a frequency of 1-20KHz. DBD is homogeneous as compared with corona discharge.

Olievera et al. have shown the effectiveness of Dielectric Barrier Discharge for the surface modification of Polyamide (PA) fibres (Olievera et al., 2010). PA fibres contain amines and carboxylic acid terminal groups, therefore, both anionic and cationic dyes can be used for dyeing. However, dyeing conditions needs to be controlled properly for better and uniform dyeing. The physical and the chemical changes imparted by DBD plasmas on the PA fabric show excellent dyeing properties. The process of surface modification using DBD plasma can also be used to improve hydrophilic properties of naturally coloured cotton fabric. Atmospheric plasma treatments could influence not only the chemical properties but also the physical properties of naturally colored cotton fibers (Demir et al., 2011). The degree of modification of plasma treatments are influenced significantly by the duration, power, and plasma type. In general, the argon-plasma treatment showed more effective results than the air-plasma treatment.

- c. Atmospheric Pressure Glow Discharge (APGD): APGD is generated at much lower voltages and at high frequencies (MHz, RF) as compared with DBD. RF source is connected between two parallel plate electrodes, which are separated from each other by just few millimeters. Therefore, APGD is relatively uniform and stable as compared with DBD. APGD has many advantages over DBD. It does not require electrode(s) to be covered / coated with dielectric layer. However, the discharge is generated in helium (other gases are used with helium), which on commercial scale becomes expensive, unless helium is substantially recovered.

The atmospheric-pressure He and He + O<sub>2</sub> plasma treated nylon 6 films showed increased surface roughnesses, increased surface oxygen contents, and hydrophilic polar groups; this led to lower water contact angles and improved bonding strength (Gao et al., 2011). They have further observed that, when the amount of oxygen increased from 1 to 2% in the plasma-gas mixture, all of these favorable effects were further enhanced.

### 2.8.2 Low temperature plasma processing

The relative advantages of low pressure and atmospheric pressure plasma treatments on textile substrates are still the subject of considerable debate. Both the treatments have their

merits and demerits therefore, final selection of the process will be decided by the requirement of the process speed and the extent of modification. Low pressure equipments are equipped with vacuum pumping system, which consumes more electricity/energy than atmospheric pressure equipment but low pressure equipments require less power to generate and sustain plasma as compared to atmospheric pressure equipment. On the other hand, low pressure equipment requires much smaller quantities of gases / monomer(s), a particularly important consideration where expensive gases / monomers are used. The modifications achieved by low pressure plasma are more uniform than atmospheric plasma. One has a better control over the surface modifications achieved by low temperature plasma. Atmospheric pressure equipment can be utilized as part of an overall continuous process (which industry prefers), whereas low pressure equipment is restricted to batch-to-batch processing.

Gawish et al. have studied the effect of low temperature plasma for improving wool fabric properties (Gawish et al., 2011). They have used plasma treatment to modify the surface properties of wool fabrics by partial removal of the scales and the lipid layer. They have discussed dyeing behavior of untreated and pretreated wool fabrics. Three dyes were used, namely acid dye, 1:2 metal complex dye and reactive dye. Different exposure times (1-5 min) of oxygenated plasma treatment were effected to improve the hydrophilicity, wettability, dyeability and the washing and light fastness properties of the dyed wool fabrics (which were increased by increasing the plasma exposure time). Wool has some technical problems that affect the quality and performance of the finished fabric such as felting, shrinkage, handle, luster, pilling and dyeability. These problems are mainly due to scales on the fibres and lipid layer. They act as barriers for diffusion processes, which adversely affects sorption behavior of fibres. Oxygenated plasma treatment of wool fabrics results in removal of the lipid layer and scales from the fibres leading to the improved wetting, dyeing and shrink resistance (Hartwig Höcker, 2002; Hesse 1995; Meade et al., 2008; Rakowski, 1997). The effect of plasma of non-polymerizable gases on wool fabric is discussed quantitatively (Kan et al., 1999). Three different nonpolymerizing gases—oxygen, nitrogen, and a 25% hydrogen/75% nitrogen gas mixture, were used to study the influence of the nature of each gas on the properties of wool substrates. The properties which include fiber-to-fiber friction, feltability, fabric shrinkage, surface structure, dyeability, alkali solubility, and surface chemical composition depend on the nature of the plasma gas used. Shahidi et al. have studied the effect of low temperature on dyeing properties of PP fibres (Shahidi et al., 2007). PP fibres were subjected to O<sub>2</sub> and N<sub>2</sub> plasma. It was found that after the plasma treatment, PP fabrics achieve necessary hydrophilicity because of incorporation of polar functional groups such as hydroxyl, carbonyl, ester and carboxyl. Similarly, improvement of dye adsorption on polyester fibres by low temperature plasma pre-treatment is demonstrated (Lehockey and Mracek, 2006). Low temperature plasma of two gases mixture particularly ammonia and acetylene was used by Hossain et al. to modify polyester fabric (Hossain et al., 2009). They have observed some deposition which contains amine groups as evident from XPS studies. The plasma treatment significantly improved the dyeability and colorfastness properties of dyed polyester fabric with an acid dyestuff. The acid dye molecules were found to diffuse into the amine-functionalized nano-porous film and formed ionic bonds with amine end groups. The dye uptake was strongly correlated with the plasma process time, that is, with the deposited film thickness, and this indicated that only the plasma coating on the polyester fibers was dyed, not the fibers themselves. The K/S values could be controlled

by the adjustment of the film thickness during plasma polymerization. Because K/S values are enhanced with the number of incorporated accessible amine groups, the surface hydrophilicity does not strongly influence the dyeability. It is obvious that the entire dyeing process is independent of the substrate material because merely the functional film is dyed. Hence, the same dyeing principle can also be applied to all hydrophobic synthetic textiles. Low temperature DC glow discharge plasma was used to modify / improve hydrophilicity of grey cotton fabric (Navneetha and Selvaraj, 2008). The fabrics were treated for different exposure times, discharge potentials and pressure levels. Effect of plasma treatment on the wettability of the fabric was studied by measuring contact angle. The changes in surface energy were estimated using contact angle measurements. Dyeability of the fabrics was determined by computer colour matching procedure. It was observed that DC glow discharge plasma is useful technique for the improvement in wettability and hence Dyeability.

It is observed that the improvement in wettability / hydrophilicity achieved by gaseous plasma treatment changes with time. This phenomenon is commonly called ageing, which takes place possibly due to surface contamination, orientation of polar groups, blooming of additives, or adsorption of ubiquitous contaminants. In many applications a hydrophobic polymer is converted into a hydrophilic one by suitable treatment and when a sample is stored in air, a driving force exists to restore the original structure or at least lower the surface energy (SE) of treated surface. As a result the high energy polar groups can be lost. It is shown that the hydrophobic recovery depends on the polymer and on treatment (Morra et al., 1989). This ageing itself can be considered as one of the steps of the treatment in the sense that influences the outcome as determined by the properties imparted to the polymer surface. Our previous studies shows that though there is a decrease in surface energy (SE) because of ageing, it is clear that the SE value of aged samples is still sufficiently high in comparison with the untreated one. Hence such polymer films can be suitable for further applications (Deshmukh and Shetty, 2007; Bhat et al., 2003). In order to avoid the effect of ageing, it is necessary to use freshly prepared (gaseous plasma processed) polymer / textiles for the best results of dyeing. However, plasma polymerized and plasma surface grafted polymers do not show much decrease in surface energy and the modifications thus achieved are comparatively permanent. Plasma polymerization and plasma grafting is already covered in 2.7 of this article. Efforts have been made to control / manipulate the chemistry of plasma polymerized films by varying plasma process parameters such as monomer flow rate, distance between two electrodes, working pressure and plasma power. However the success in controlling film chemistry is limited. Timmons and Griggs have showed that by using RF pulsed plasma polymerization technique, a wide range of plasma film chemistry can be achieved in comparison with conventional continuous wave (CW) RF plasma (Timmons and Griggs, 2004). Recently, such pulsed plasma polymerization technique was successfully used to control film chemistry and found useful in bio-logical applications (Bhattacharyya et al., 2010, Xu et al, 2011). So far this technique has not been used for the modification of textile surfaces. There is tremendous scope in this area.

### 3. Experimental

A tubular type of plasma reactor was used in the present experiment and is shown in the Fig.1 given below.

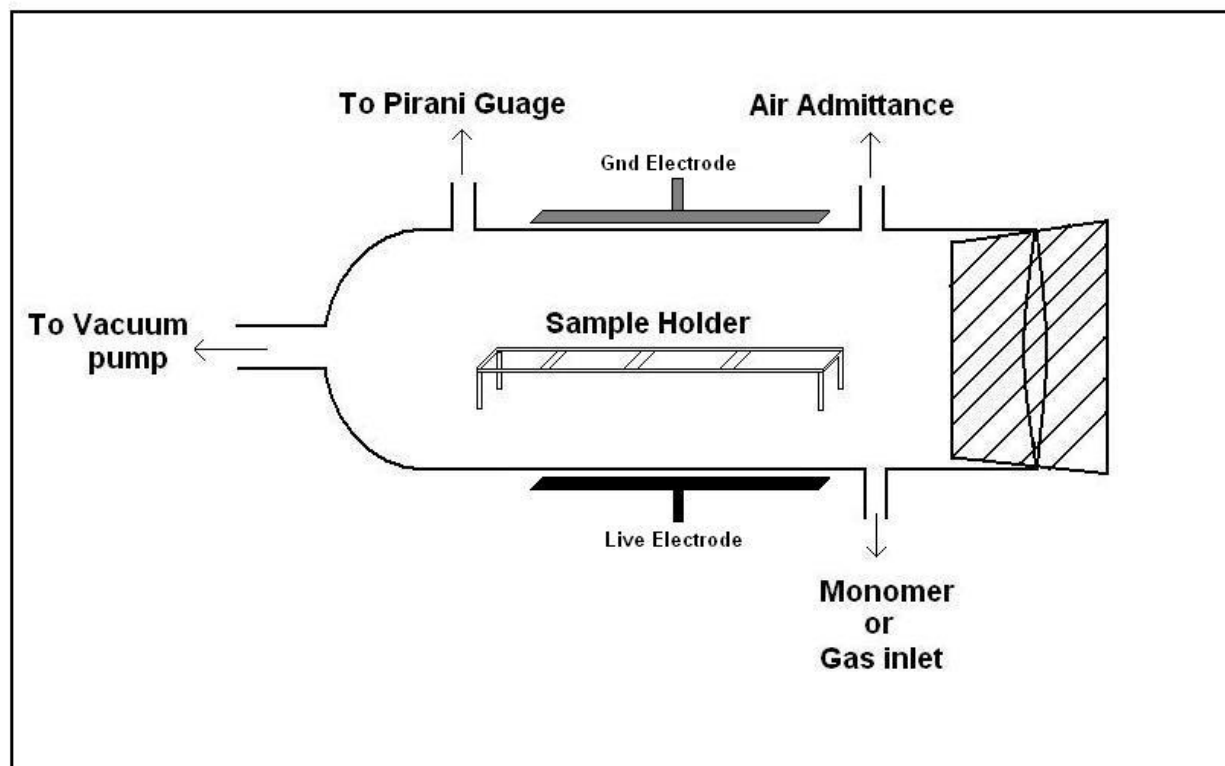


Fig. 1. Schematic of Plasma Unit.

It consists of a glass tube having diameter 8 cm. and length 30 cm. The length and the breadth of the electrode was 25 cm and 3 cm respectively. The sample was kept at the centre of the reactor on a glass stand as shown in Fig 1. The reactor has an inlet for monomer and / or gas. A Pirani gauge was fitted to the reactor to monitor pressure in the reactor. The aluminum electrodes were kept outside the glass tube and were connected to RF (13.56 MHz.) power supply capable of delivering 100W power. The system was evacuated to 0.05 mtorr with rotary pump before inserting the gas / monomer vapours. The system was purged three times with the relevant gas / monomer vapours and the desired working pressure 0.2 mtorr was obtained with the help of fine control needle valve. The sample was mounted on a glass sample holder inside the chamber as shown in Figure 1 above. The gases and the monomer used were of AR grade.

**Dyeing Procedure:** Acid Dye (Blue coloured) supplied by Clariant India Ltd was used. 1% shade was prepared and its pH. was adjusted to 4.8 by adding formic acid. The liquor to fabric ratio was maintained at 50:1. The temperature of the dyeing bath was adjusted to 85 °C. The nylon fabric (untreated and plasma processed) were immersed in dye-bath for 15 min. Then the fabric was washed in the soda soap solution with 5gpl soap and 2 gpl soda for 30 min. followed by distilled cold water wash (three times) and then the samples were dried in air. Such samples were used for colour measurement. Colour measurements were performed on Spectra-flash SF 3000 (Datacolour International). Dye Exhaustion was measured using UV visible spectrometer.

The amount of dye absorbed by the sample was determined by measuring the optical densities of the initial solution and also the exhausted one by using an ultraviolet/visible (UV/Vis) spectrophotometer. The percentage dye absorption was calculated as,



$$\% \text{ Dye exhaustion} = \frac{(\text{O.D. of original solution}) - (\text{O.D. of exhausted solution})}{\text{O.D. of original dye bath}} \times 100 \quad (1)$$

Where, O.D. is the optical density at the maximum absorption wavelength.

Nylon fabric was treated in O<sub>2</sub> and N<sub>2</sub> plasma for different durations of time. Similarly plasma polymerization of acrylic acid was carried out onto the nylon fabric for different durations of time. These samples were tested for their hydrophilicity, FTIR, dyeability and surface morphology. In order to study the characteristics of plasma polymerized acrylic acid film, KBr disc was kept in the plasma chamber while carrying out deposition onto the fabrics. Such deposited film was used for FTIR study. The wettability of the untreated fabric was measured by contact angle measurement with respect to water and for treated samples; the time required for water drop to disappear was measured and recorded as wetting time. Average of 5 readings is reported here. The shorter is the average wetting time, better is the fabric wettability. The surface energy of untreated sample was calculated from the contact angle data using the equation given by Deshmukh and Shetty (Deshmukh and Shetty, 2008). Surface morphology was studied using SEM.

## 4. Results and discussions

### 4.1 Morphological studies

Nylon fabric was treated with nitrogen and oxygen plasma. It can be seen from Figure 2 that the surface morphology changed after the plasma treatment. The untreated nylon fibres are smooth as shown in Fig. 2 (a) and (b). The etching, roughening effect of oxygen plasma on the surface (Fig. e and f) is more as compared with the nitrogen plasma as shown in Fig. 2 (c) and (d). It is probably due to oxygen is more reactive than nitrogen. The treated surfaces look damaged or abraded. This is due to the removal of some material by etching. Similar abraded surface topography for plasma processed wool and cotton fibers, respectively, was observed by Karahan and Ozdogan (Karahan et al., 2009; Ozdogan et al., 2009). In the case of wool fibers this helped to impart anti-felting properties to the fabrics due to loss of the scales. Significant fiber surface roughness was also observed by McCord et al. for nylon and polypropylene fibers with He and He+O<sub>2</sub> atmospheric plasmas (McCord et al., 2002). It may be of interest to try to understand the morphology and mechanism of the etching process. It has been confirmed through various studies that only the amorphous portion gets degraded and etched away in the initial stage (Bhat and Deshmukh, 2002; Thomas et al., 1998; Yoon et al., 1996). The plasma process is such that the electrons and ions attack the amorphous portion, as it is loosely bound. On the other hand, the crystalline regions are more compact and hard as compared to amorphous regions and therefore the amorphous region gets removed easily in the plasma etching. As a result, the percentage crystallinity increases to some extent. This has been concluded by previous studies using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) for silk (Bhat and Nadiger, 1978). Navaneetha and Selvaraj have also observed that the effect of plasma on the amorphous zone is more predominant than the crystalline zone of the cotton fabrics (Navaneetha and Selvaraj, 2008.).

Similarly when nylon fabric was subjected to the plasma polymerization of acrylic acid (PPAA), we observed deposition as shown in Fig. 2 (g) and (h). This deposition leads to decreased capillaries present in the texture. The choice of acrylic acid monomer was based on its hydrophilic properties.



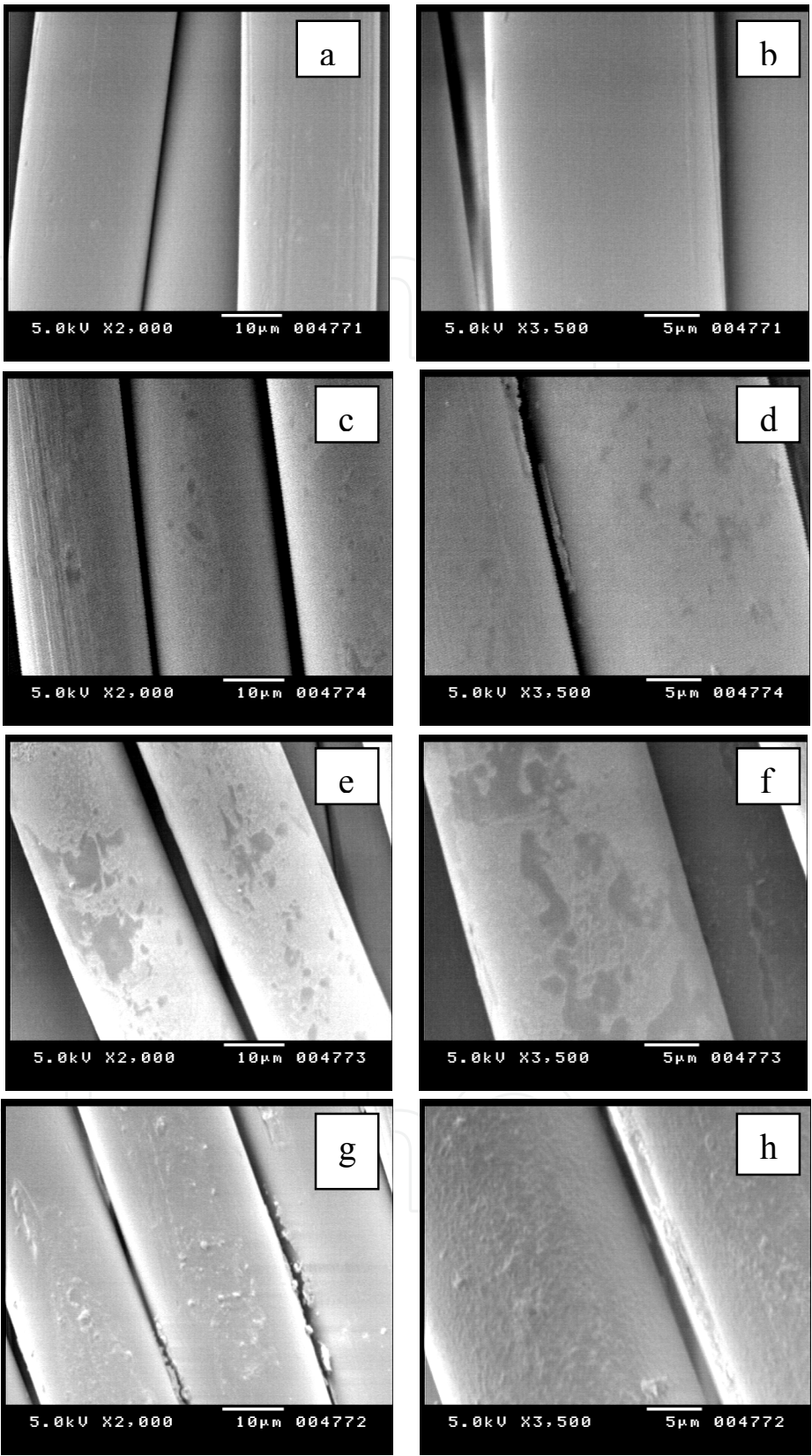


Fig. 2. SEM micrograph of (a) and (b) Untreated Nylon fabric, (c) and (d) 4 min. N<sub>2</sub> plasma treated Nylon fabric, (e) and (f) 4 min. O<sub>2</sub> plasma treated Nylon fabric, (g) and (h) 4 min. PPAA deposited on Nylon fabric.

#### 4.2 FTIR study

Polar functional groups are incorporated onto the polymer film during the plasma treatment. These polar groups are readily detected by ESCA (XPS), but are often missed by ATR-FTIR spectroscopy (Wu S, 1982). XPS is the best technique to study such modified surfaces. Several studies showed that air, N<sub>2</sub>, O<sub>2</sub>, NH<sub>3</sub>, etc. plasma incorporates hydrophilic functional groups onto the polymer surfaces thereby increasing wettability and surface energy (Bhat et al., 2011; Navaneetha et al., 2010; Píchal and Klenko, 2009). It has been reported that the treatment carried out in inert gases like Ar introduces oxygen moieties onto the polymer surface because of post plasma exposure of samples to atmosphere (Deshmukh and Bhat, 2003(b); Gupta et al., 2000). Therefore, IR spectra of N<sub>2</sub> and O<sub>2</sub> plasma treated nylon samples is not given here. The IR spectra of plasma polymerized acrylic acid (PPAA) is given in Fig. 3 below.

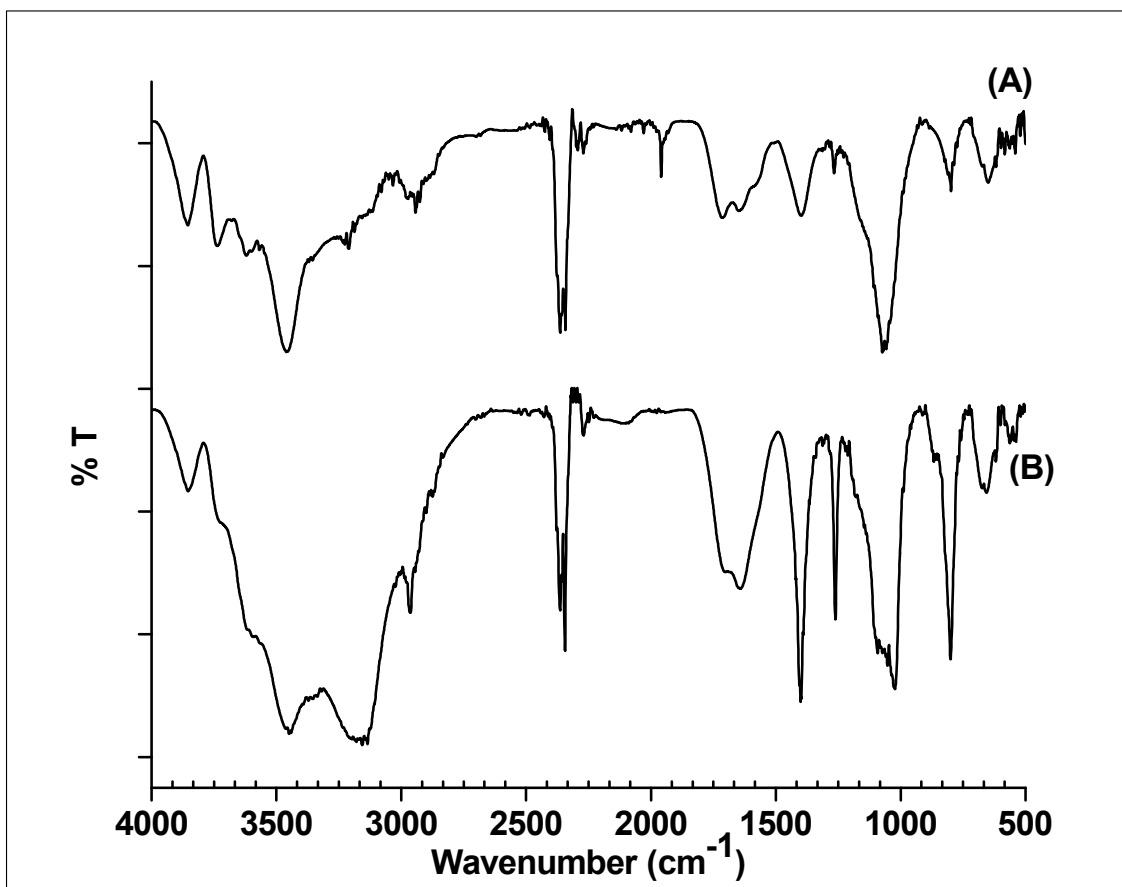


Fig. 3. FTIR spectra of PPAA (A) 2min. deposition, (B) 4min. deposition.

The FTIR spectrum of a PPAA film prepared using the technique of plasma polymerization was very similar to the spectrum of Poly (acrylic acid) prepared by conventional polymerization techniques and it shows all the characteristic bands. In particular, the FTIR spectrum shows that the film contains a high density of C(O)OH groups. The absorption peaks assignment is given in table below (Alaa et al., 2011; Cho et al., 1990; Chilcoti and Ratner, 1993; Eun-Young Choi and Seung-Hyeon Moon, 2007; Jafari et al., 2006; Mirzadeh et al., 2002).

Frequency, cm-1	Peak Assignment
814	O-H out of plane bending vibration of carboxylic acid
1265	C-O stretching of carboxylic acid
1425	O-H bending of carboxylic acid
1710	carbonyl group of acrylic acid, C=O stretching absorption band between 1828 to 1559 cm <sup>-1</sup> with maximum at ~1710 cm <sup>-1</sup>
2800 to 3800	a broad OH stretching absorption band due to monomeric and dimeric C(O)OH

Table 1. IR peak assignment of PPAA

It has been observed that our result of plasma polymerization of acrylic acid is in relevance with the literature. PPAA incorporates considerable amount of polar functional groups such as hydroxyl, carbonyl, carboxylic acid, etc. The peak intensity increases with the deposition time.

4.3 Wettability study

The contact angle of untreated nylon fabric was observed to be 83<sup>0</sup> (±2). Its surface energy comes to be 33.6 mJ/m<sup>2</sup>. Fig. 4 shows the photograph of water droplet taken on untreated and 4 minute oxygen plasma treated nylon fabric.

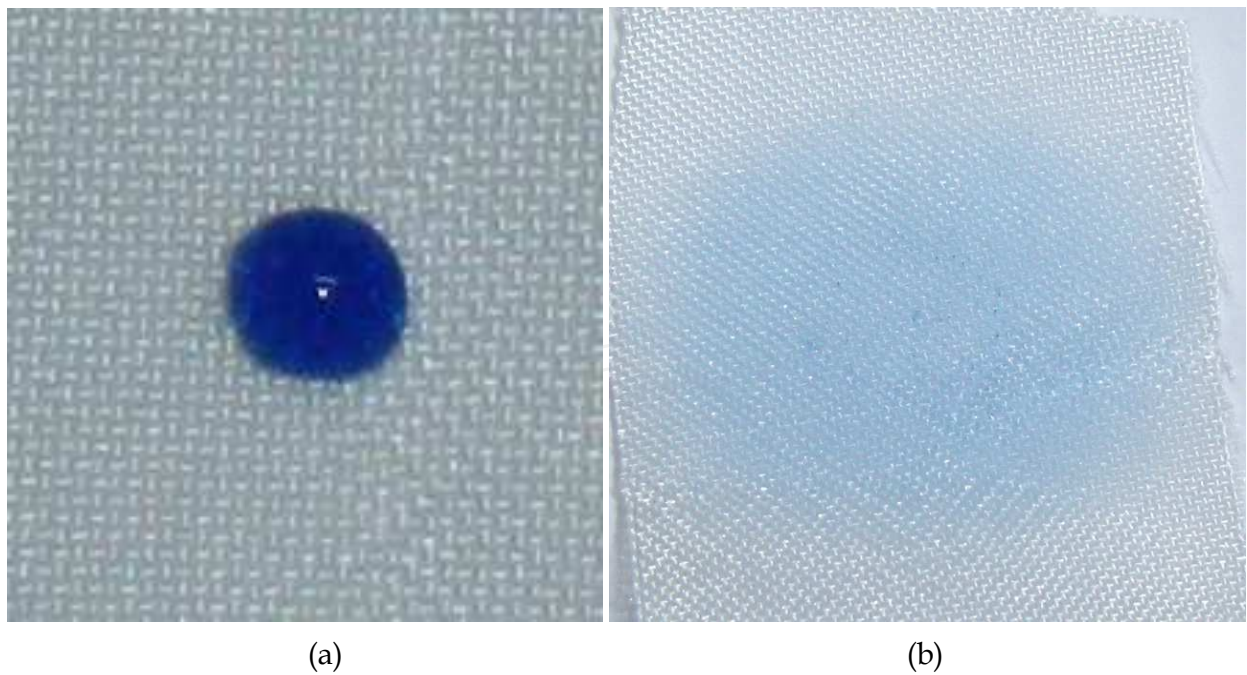


Fig. 4. Water droplet on the nylon fabric. (a) untreated, (b) Oxygen plasma treated.

However, we could not measure contact angle for any plasma processed samples. It shows that the surface energy of all the samples increases rapidly after the plasma processing. Therefore we have measured wetting time of the samples as given in Table 2.

Treatment Time (min.)	Time to absorb water droplet on the Plasma Processed Nylon Fabrics (in Sec.)		
	N <sub>2</sub> Plasma	O <sub>2</sub> Plasma	PPAA
0	112	112	112
0.5	18	12	20
1	15	9	16
2	8	6	14
4	4	3	19

Table 2. Wetting time of untreated and plasma processed nylon samples.

It may be noted from Table 2 that the wetting time of the untreated nylon fabrics was 112 seconds, which dramatically decreases after N<sub>2</sub>, O<sub>2</sub> and acrylic acid plasma treatment. The decrease is more significant in case of O<sub>2</sub> plasma treated samples as etching action and oxidation reaction is predominant. On the other hand, the decrease in the wetting time of PPAA treated sample is rather slow. It may be also be noted from the SEM micrographs that the formation of etch-pits and voids is very predominant for O<sub>2</sub> plasma treated nylon fabrics, whereas PPAA treated samples reveal coating on the surface due to formation of PPAA. Due to such thin film formation on the surface the water drop may not easily reach the fabric and as a result the capillary action is reduced.

4.4 Dyeing studies

Plasma processed samples were dyed using acid dye-blue. The dye absorption was determined spectroscopically by measuring the absorption band maximum of the dye-bath solution before starting and after exhaustion. In addition, the amount of dye uptake was also determined from the color matching instrument. The color values are expressed in terms of K/S as the ratio of reflectivity to absorptivity. For each kind of plasma processing, the dye uptake of plasma-treated sample was compared with the untreated sample of the same variety.

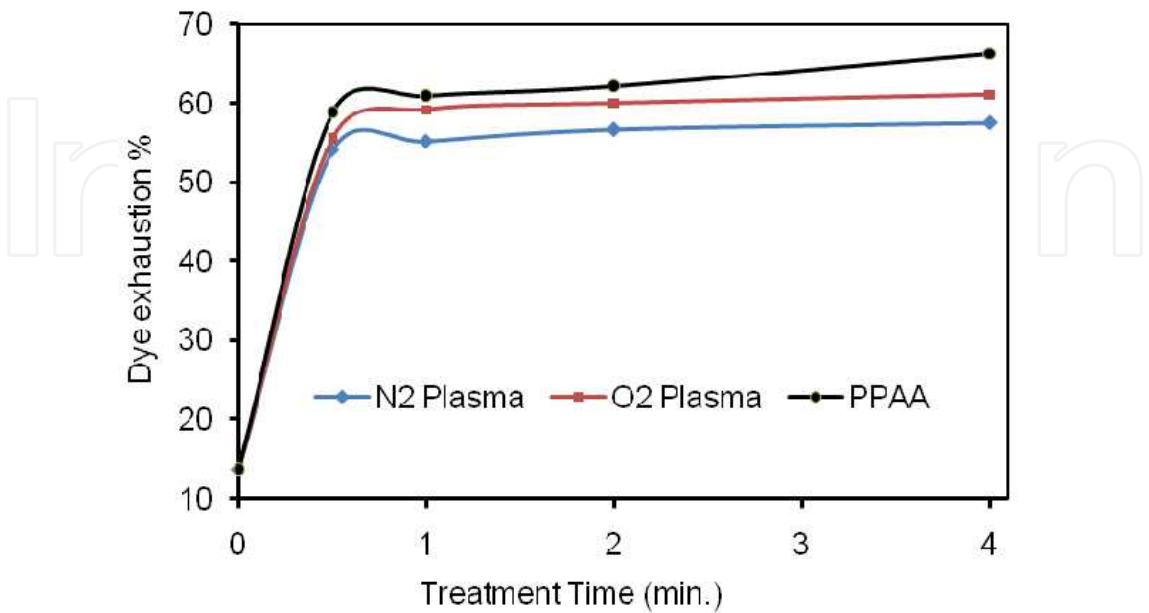


Fig. 5. Relation between the dye bath exhaustion and plasma processing time.



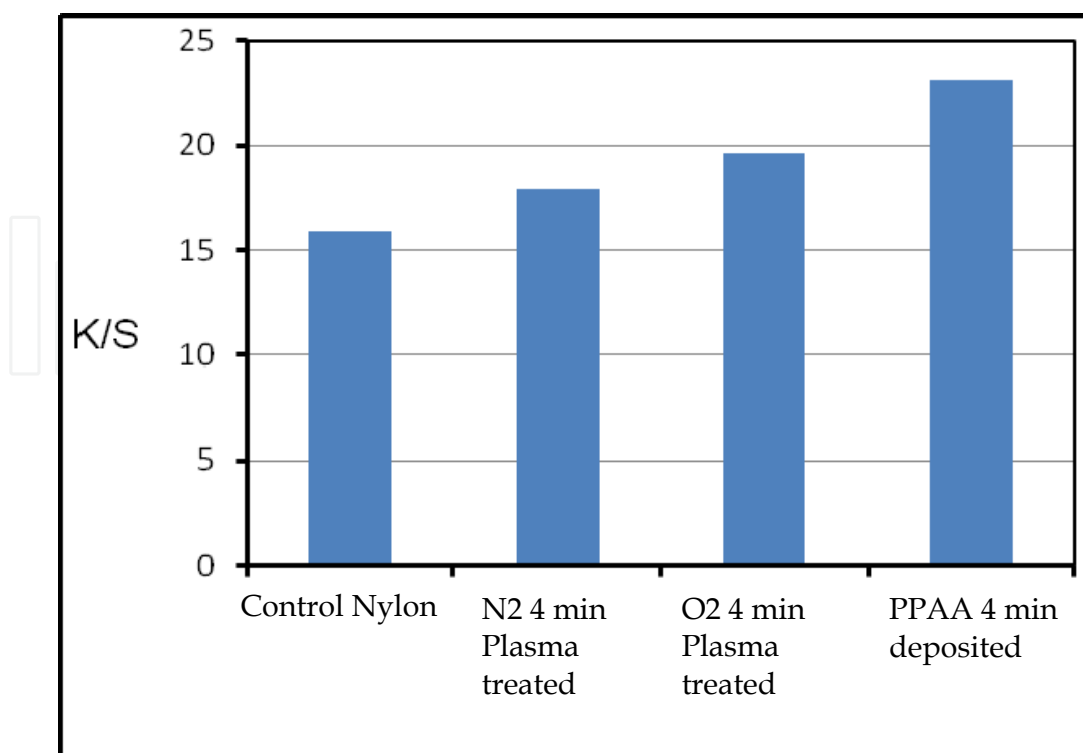


Fig. 6. K/S values of nylon fabric subjected to RF plasma treatment.

The increase in the dyeing in the initial stage could be due to the fact that gaseous plasma etches out the surface of the nylon fibers, creating a rougher surface with irregularities as discussed earlier. The effective surface area increases after the plasma treatment. Thus the interaction and diffusion of the dye molecules is facilitated. The etching of the surface has been confirmed by other researchers (Karahan et al., 2009; Ozdogan et al., 2009). The chemical changes in the nylon fiber surface can lead to the possibility of the formation of free radicals on the nylon chains and the subsequent formation of hydroxyl, carbonyl and carboxyl groups. It is also important to mention that the dyeing process mainly occurs through the amorphous regions. The etching away of the amorphous regions during the plasma treatment (particularly for longer treatment time) can lead to lowering of the dye uptake. Therefore the optimum treatment time needs to be found. Yoon et al. and Thomas et al., have found that longer plasma treatment decreases dye uptake (Thomas et al., 1998; Yoon et al., 1996). It may be noted that the oxygen is more reactive than nitrogen and hence the dye uptake is slightly more for oxygen treated samples. The etching caused due to oxygen plasma is also more as shown in Fig. 2 (e and f).

Plasma polymerization of acrylic acid (PPAA) onto the nylon fabric incorporates good amount of hydroxyl, carbonyl and carboxylic acid groups onto the surface as evident from FTIR studies. These functional groups are responsible for wettability and hence dye uptake. The dyebath exhaustion is slightly more in case of PPAA deposited nylon fabric as compared to that of gaseous plasma treated samples, because of the functional groups which are incorporated during the deposition of PPAA. Deposition causes reduction in the capillary action therefore; we have observed slightly more wetting time for PPAA samples as shown in Table 2. However, when dyeing is carried out for 15 minutes, which is sufficient time for the penetration of dye into the fabric, a major role of functional groups is observed



on the dyeing behavior rather than wetting time. The deposition is evident from SEM micrographs as shown in Fig. 2 (g and h).

The increase in the dye uptake due to plasma treatment is also evident from the measurement of K/S values shown in the Fig. 6. The bar-graph shows K/S values for control and plasma treated samples for four minutes in different gases. The highest gain is seen to be for PPAA deposited nylon fabrics followed by oxygen treated sample. This trend is similar to that observed for the data of dye bath exhaustion.

#### 4.5 Few results of case studies

##### 4.5.1 Dyeing behavior of nylon fabric treated in APGD

Similarly, nylon fabric was treated in atmospheric pressure glow discharge, for various durations of time, it was found that there is increase in the dye uptake with time as shown in Fig. 7. The dye used in these studies was acid dye-red. It may be seen that when the dyeing time was 15 minutes, the differences in the K/S values of the control and the atmospheric pressure plasma (He +air) treated is quite noticeable. The increase in dye is significant. However, as the dyeing time is increased to 60 minutes the equilibrium dye uptake is reached for control as well as plasma treated samples and the difference reduces. This proves that the plasma pretreatment can reduce the time of dyeing and as a result power can be saved.

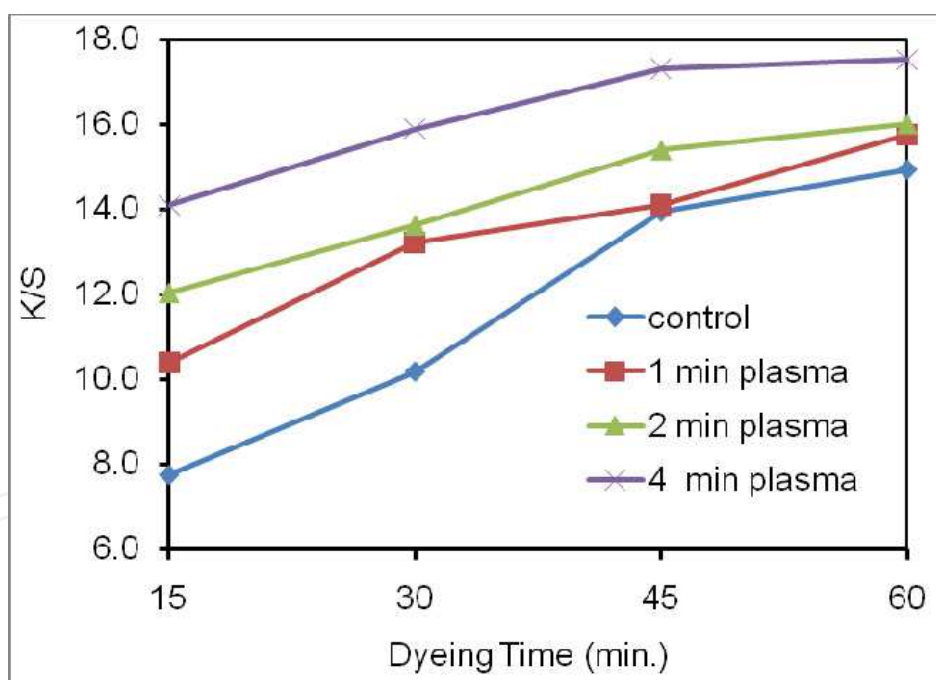


Fig. 7. K/S values of Nylon fabrics dyed with reactive dye after subjecting the fabrics to atmospheric pressure plasma for different duration of time.

##### 4.5.2 Dyeing behavior of cotton fabric treated in air plasma

In another recent study (just results are summarized), cotton fabrics (desized, scoured and bleached) were treated with air plasma (RF), for 4 minutes. In order to understand the effect of such treatment on dyeing behavior, it was decided to use three different dyes namely, direct dye, reactive dye and natural dye. The direct dye used was Congo red, the reactive

dye used was Red-M and natural dye was Thar. When dyeing was carried out and measurements were done for the dyed samples, it was noticed that, in the case of direct dye, the colour strength after plasma treatment were found to have decreased by 2.1 %. However, in the case of reactive dye, there was an increase in colour strength by 3.2%. The natural dye Thar showed a marginal decrease by 1%. It was surprising that, when the plasma treatment, enhances the wettability of cotton fabrics to a great extent, the increase in the dye uptake was not similar. This makes us believe that, the interaction of dye with the polymer (fibre) is important for improved dye uptake. The tremendous work carried out for wool fibres has revealed that while the plasma treatment, invariably leads to increase in the dye uptake, it is not so for other types of fibres (polyester, cotton, nylon etc.). There are several conflicting results of increase at times and decrease for other cases. Our analysis shows that, in addition to the type of gaseous plasma, the structure and morphology of the fibre is important. If a proper group of dye is used, the interaction of the dye with the fibre becomes compatible leading to increase in the dye uptake. Our conflicting results in case of cotton fabric just described above may be explained as follows:

In case of direct dye, the dyeing phenomena is supposed to be due to diffusion of the dye molecule into the fibre, whereas reactive dye reacts with the OH group of the cellulose chain. The natural dye Thar has a very long chain with many CH groups and possibly cannot diffuse into the fibre. The very short (few seconds) plasma treatment of cotton fabrics leads to removal of wax and other impurities from the surface of the fibre. Further treatment with plasma (up to 5 min) leads to removal of the amorphous portions of the material, thereby decreasing the possibility of interaction with the OH groups of the cellulose chain. There also occurs cross linking on the surface, which would hinder the diffusion of the dye molecules. The plasma interaction etches the surface and the effective area is enhanced and also oxygen moieties are incorporated and will contribute to synergistic effect leading to enhanced dye uptake. However, there is a competitive process of cross-linking and as a result the net dyeing may not always show increase.

#### **4.5.3 DC plasma effect on polyester fabric**

Similarly in another experiment, we thought interesting to see the effect of DC plasma on polyester fabric. Oxygen was used as precursor gas. Plasma treatment of polyester fabrics was carried for different durations of time. The morphological changes in the fiber structure were assessed by SEM which revealed the formation of rough surface together with voids and cracks. The loss of weight increased with the treatment time while the tenacity was affected to a small extent. Moisture regain and wettability was found to be improved with increasing treatment time. The fabrics developed yellowness after the plasma treatment that increased with time. Such plasma treated fabrics were dyed with disperse dye in HTHP machine. The dye uptake was found to have increased initially up to 10 minutes and slightly decreases at higher time of treatment. The increase in the dye uptake was due to combined effect of the production of polar group on the surface, etching of the surface creating higher effective area and the creation of voids and cracks, which can facilitate entry of dye molecules into the interior of the fibre. The maximum increase was found to be 2% . Such minor rise in the dye uptake is probably due to other competitive process of cross linking reaction on the surface which do not allow penetration of the dye into the interior. Therefore when the time of treatment was increased beyond 10 min there appears to be slight reduction in the dye uptake. This behavior is shown in Fig. 8 below.

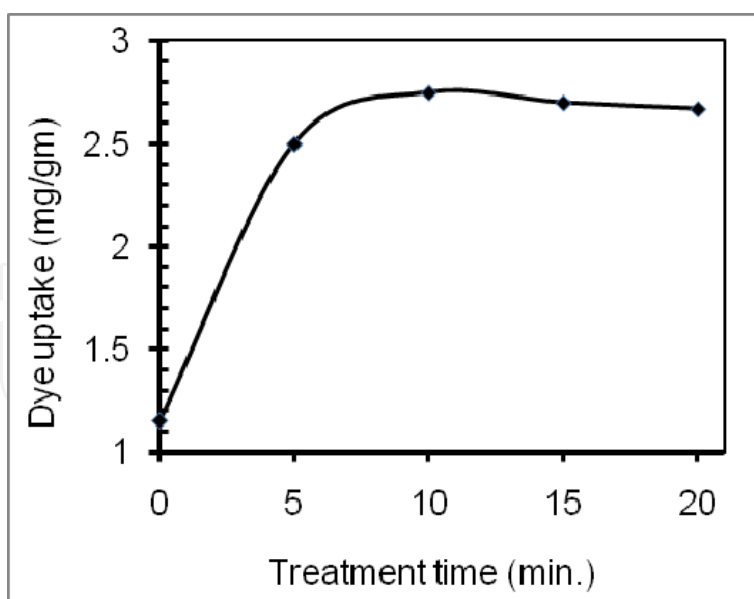


Fig. 8. Dye uptake of DC plasma treated polyester fabric

## 5. Conclusions

The present paper has described the results of dyeing behaviour for plasma treated nylon, polyester and cotton fabrics. Mainly air, nitrogen and oxygen gases were used together with vapours of acrylic acid in a low pressure atmosphere. There is substantial enhancement in the dye uptake of nylon fabrics. This result is similar to the observation when plasma processing is done in APGD. In case of polyester and cotton, however, the enhancement in the dye is not substantial. Rather the type of dye (acid, disperse or natural) played an important role.

The survey of literature as well our own work regarding the effect of plasma on dyeing behaviour shows that whereas there is always enhancement in the dye uptake of wool fibers, it is not necessarily so for polyester, cotton and other fibers. Although etching of surface, creation of voids and formation of C=O, COOH, OH groups occurs to facilitate higher dye uptake, there exist competing processes of increased crystallinity and cross-linking on the surface which may not allow the diffusion of the dye molecules. Therefore the selection of the fibre, nature of gas, process time and the type of dye all play a major role. Thus clear understanding of plasma process is of utmost importance to utilize the technology on the industrial scale. Further the type of plasma i.e plasma produced by different power sources like A.C., D.C., low pressure, atmospheric pressure gives more or less similar results as far as dyeing property is concerned, although morphology and structural differences are observed.

## 6. Scope for future work

It is necessary to standardize experiments with reference to several process parameters such as pressure, flow rates, power etc for each type of fabrics. Further the type and structure of dye molecule should also be considered. Surface analysis in terms of morphology, radical formation, bond formation and its lifetime need to be understood. This understanding may help in deciding about the importance of plasma process if enhanced dye uptake is the aim.

Even if the increase is small, if the process can lead to sufficient dye uptake at a reduced temperature or time, it would serve a good purpose. Advantages of the process in terms of eco-friendliness, water saving and energy saving be explored and emphasized so that the technology is acceptable to all.

Further work needs to be carried out by using pulsed plasma as it may avoid the degradation of fabrics when subjected to longer durations of treatments. In-situ cooling of the samples is also desirable to maintain the temperature of substrate constant. It is also necessary to find the electron and ion densities or rather the number of ions hitting the sample to calculate the energy deposited during processing.

## 7. Acknowledgement

We thank Miss. G. A. Arolkar and Mr. Kiran Kale for helping us to treat samples in low pressure and in atmospheric pressure plasma respectively.

## 8. References

- Abidi N. and Hequet E., Cotton Graft Copolymerization Using Microwave Plasma. I. Universal ATR-FTIR Study, *J. Appl Polym Sci.*, 93, 145-154, (2004).
- Abidi N. and Hequet E., Cotton Graft Copolymerization Using Microwave Plasma. II. Physical Properties, *J. Appl Polym Sci.*, 98, 896-902, (2005).
- Abidi N, in *Surface modification of textiles*, Q. Wei (Ed), Woodhead publishing in Textiles, UK (2009).
- Alaa Fahmy, Renate Mix, Andreas Schoenhals, Joerg F. Friedrich., Structure of Plasma-Deposited Poly(acrylic acid) Films, *Plasma Process. Polym.*, 8, 147-159, (2011).
- Araujo R., Casal M., and Cavaco-Paulo A., Applications of Enzymes for textile fibre processing. *Biocat.Biotrans.* 26(5), 332-349, (2008).
- Bhat N.V. and Nadiger G.S., Effect of nitrogen plasma on the morphology and allied textile properties of tassar silk fibres and fabrics. *Textile Res J*; 48: 685-691, (1978)
- Bhat N.V. and Benjamin Y.N., Surface Resistivity Behaviour of Plasma Treated and Plasma Grafted Cotton and Polyester Fabrics, *Textile Res J.*, 69(1), 38-42, (1999).
- Bhat N.V. and Deshmukh R.R., X-ray crystallographic studies of polymeric materials *Indian Journal of Pure & Applied Physics*, 40 (5) 361-366, (2002).
- Bhat N. V., Upadhyay D. J., Deshmukh R. R., and Gupta S. K., Investigation of Plasma-Induced Photochemical Reaction on a Polypropylene Surface, *J. Phys. Chem. B*, 107, 4550-4559, (2003).
- Bhat N.V., Netravali A.N., Gore A.V., Sathianarayanan M.P., Arolkar G.A. and Deshmukh R.R., Surface modification of cotton fabrics using plasma technology, *Textile Res J.*, 81, 1014-1026, (2011).
- Bhattacharyya D., Xu H., Deshmukh R.R., Timmons R.B. and Kytai T.N., Surface chemistry and polymer film thickness effects on endothelial cell adhesion and proliferation, *Journal of Biomedical Materials Research Part A*, Volume 94A, Issue 2, pages 640-648, (2010).
- Bozzi A., Yuranova T. and Kiwi J., Self Cleaning of Wool, Polyamide and Polyester Textile by TiO<sub>2</sub> Rutile Modification Under Daylight Irradiation at Ambient Temperature, *J. Photochem Photobiol A: Chem* 172, 27-34, (2005).
- Cao G., *Nanostructures and Nanomaterials-Synthesis, Properties and Applications*, Imperial College Press, London. (2004).

- Cavaco-Paulo A, Gubtz G.M. Catalysis Processing in Cavaco-Paulo A, Gubtz G.M. (Eds), Textile processing with Enzymes Cambridge, Woodhead publishing (2003).
- Chilcoti A., Ratner B. D., Surface Characterization of Advanced Polymers, L. Sabbatini, P.G. Zambonin, Eds., VCH, Chapter 6, p. 221, (1993).
- Cho D.L., Claesson P.M., Golander C-G. and Johansson K., Structure and Surface Properties of Plasma Polymerized Acrylic Acid Layers., J. Appl Polym. Sci., 41, 1373-1390, (1990).
- Deo H.T. and Gotmare V.D., Acrylonitrile Monomer Grafting on Gray Cotton to Impart High Absorbency, J. Appl. Polym Sci., 72, 887-894, (1999).
- Demir A, Esen O' zdog'an, Nilgu'n O' zdil and Aynur Gu' rel, Ecological Materials and Methods in the Textile Industry: Atmospheric-Plasma Treatments of Naturally Colored Cotton, J. Appl Polym Sci, Vol. 119, 1410-1416, (2011).
- Deshmukh R.R. and Bhat, N.V., AFM studies of Plasma processed Polyester films. J. Electron Microscope Society of India Bulletin, Vol. 4(1), 6-14, (2003)(a).
- Deshmukh R. R. and Bhat N. V., The mechanism of adhesion and printability of plasma processed PET films, Mat Res Innovat 7, 283-290, (2003)(b).
- Deshmukh R. R. and Shetty A. R., Surface Characterization of Polyethylene Films Modified by Gaseous Plasma, J. Appl Polym Sci., Vol. 104, 449-457, (2007).
- Deshmukh R. R., and Shetty A. R., Comparison of Surface Energies Using Various Approaches and Their Suitability, J. Appl Polym Sci., Vol. 107, 3707-3717, (2008).
- Eun-Young Choi, Seung-Hyeon Moon, Characterization of Acrylic-Grafted PP Membranes Prepared by Plasma-Induced Graft Polymerization, J. Appl Polym Sci., Vol. 105, 2314-2320, (2007).
- Ferrero F., Periolatto M., Sangermano M. and Bianchetto S.M., Water Repellent Finishing of Cotton Fabrics by Ultraviolet Curing, J. Appl Polym Sci., 107, 810-818, (2008).
- Gao Z., Jie S., Peng S, Yao L. and Qiu Y., Surface Modification of Nylon 6 Films Treated with an He/O<sub>2</sub> Atmospheric Pressure Plasma Jet, J. Appl Polym Sci, Vol. 120, 2201-2206, (2011).
- Gawish S. M., Saady M. A., Abo El-Ola S.M. and Abou-El-Kheir A., The effect of low-temperature plasma for improving wool and chitosan-treated wool fabric properties Journal of the Textile Institute., Volume 102, Issue 2, 180 - 188, (2011).
- Gupta B, Hilborn J, Hollenstein CH, Plummer CJG, Houriet R and Xanthopoulos N., Surface modification of polyester films by RF plasma, J. Appl Polym Sci 78:1083-1091, (2000).
- Hartwig Höcker, Plasma treatment of textile fibers Pure Appl. Chem., Vol. 74, No. 3., 423-427, (2002).
- Hesse A., Thomas H. and Hocker H., Zero-AOX Shrink Proofing Treatment for Wool Top and Fabric Part I: Glow Discharge Treatment, Text Res J 65, 355-361, (1995).
- Hossain M.M., Mussig J., Hermann A.S. and Hegemann D., Ammonia/acetylene plasma deposition: An alternative approach to the dyeing of poly(ethylene terephthalate) fabrics at low temperatures, J. Appl. Polym. Sci., 111(5), 2545-2552, (2009).
- Hurren C., Cookson P. and Wang X., The Effects of Ultrasonic Agitation in Laundering on the Properties of Wool Fabrics, Ultrasonics Sonochemistry, 15, 1069-1074, (2008).
- Jafari R., Tatoulian M., Morscheidt W. and Arefi-Khonsari F., Stable plasma polymerized acrylic acid coating deposited on PE films in low frequency discharge, Reactive and functional polymers., 66(12), 1757-1765, (2006).
- Jahagirdar C. J. and Tiwari L. B., Study of Plasma Polymerization of Dichloromethane on Cotton and Polyester Fabrics, J. Appl Polym Sci., Vol. 94, 2014-2021, (2004).
- Kan C.W., Chan K., Yuen C.W.M. and Miao M.H., Low Temperature Plasma on Wool Substrates: The Effect of the Nature of the Gas, Text Rest J, 69, 407-416, (1999).



- Karahan H. A., Ozdogan E, Demir A., Ayhan H and Seventekin N., Effects of atmospheric pressure plasma treatments on certain properties of cotton fabrics. *Fibers Text East Eur*; 17: 19–22, (2009).
- Lee H. J., and Jeong S.H., Bacteriostasis and Skin Innoxiousness of Nanosize Silver Colloids on Textile Fabrics, *Textile Res J.*, 75(7), 551–556, (2005).
- Lee H.J., Yeo S.Y., and Jeong S.H., Antibacterial Effect of Nanosized Silver Colloidal Solution on Textile Fabrics, *J. Mater Sci.*, 38, 2199–2204, (2003).
- Lehocky L., and Mracek A., Improvement of Dye Adsorption on Synthetic Polyester Fibres by Low Temperature Plasma Pre-treatments, *Czechoslovak Journal of Physics*, Vol 56, B1277–B1282, (2006).
- Lenting H.B.M., *Enzymes in Textile Production* In Aehle, W (Ed.), *Enzymes in Industry*, 2<sup>nd</sup> Edn. Wiley-VCH Verlag GmbH & Co. (2004)
- Liu L., Ding Z., Chang L., Ma R. and Yang Z., Ultrasonic Enhancement of Membrane-based Deoxygenation and Simultaneous influence on Polymeric Hollow Fibre Membrane, Separation and purification technology, 56, 133–142, (2007).
- McCord MG, Hwang YJ, Hauser PJ, Qiu Y, Cuomo JJ, Hankins OE, Bourham MA and Canup LK., Modifying nylon and polypropylene fabrics with atmospheric pressure plasmas. *Text Res J*, 72 (6) 491–498, (2002).
- Meade S.J., Dyer J.M., Caldwell J.P., and Bryson W.G., Covalent Modification of the Wool Fibre Surface; removal of the outer level layer, *Textile Res J.*, 78(11), 943–957, (2008).
- Mirzadeh H., Dadsetan M. and Sharifi-Sanjani N., Platelet Adhesion on Laser-Induced Acrylic Acid-Grafted Polyethylene Terephthalate, *J. Appl Polym Sci.*, Vol. 86, 3191–3196, (2002).
- Morent R., Geyter N.D., Verschuren J., Clercke K.D., Kiekens P. and Leys C., Non-thermal plasma treatment of textiles, *Surf. Coat. Technol.* 202 (14), 3427–3449, (2008).
- Morra, M.; Occhiello, E. and Garbassi, F., Contact angle Hysteresis on Oxygen Plasma treated Polypropylene surfaces., *J Colloid Interface Science*, 132(2), 504–508, (1989).
- Navaneetha Pandiyaraj and Selvarajan V. Non-thermal plasma treatment for hydrophilicity improvement of grey cotton fabrics, *Journal of Materials Processing Technology*, 199, 130–139, (2008).
- Navaneetha P., Selvarajan V., Deshmukh R.R. and Gao C., Modification of surface properties of polypropylene (PP) film using DC glow discharge air plasma, *Applied Surface Science* 255, 3965–3971, (2009).
- Navaneetha P., Selvarajan V and Deshmukh R. R., Effects of operating parameters on DC glow discharge plasma induced PET film surface., *Journal of Physics: Conference Series* Volume 208 Number 1 doi:10.1088/1742-6596/208/1/012100 (2010).
- Nierstrasz in Surface modification of textiles Ed. Q.Wei, Woodhead Publishing in Textiles, UK (2009).
- Oktem T, Ayhan H, Seventekin N and Piskin E, Modification of Polyester Fabrics by *in-situ* Plasma or Post Plasma Polymerization of Acrylic Acid, *J. Society Dyers and Colourist*, 115, 274–279, (1999).
- Oliveira F.R., Souto A.P., Carneiro N. and Nascimento J.H.O., Surface Modification on Polyamide 6.6 with Double Barrier Discharge (DBD) Plasma to optimize Dyeing Process by Direct Dyes, *Materials Science Forum*, Vol 636–637, PP 846–852, (2010).
- Ozdogan E, Demir A, Karahan AA, Ayhan H and Seventekin N. Effects of atmospheric plasma on the printability of wool fabrics. *Tekstil ve Konfeksiyon*; 19: 123–127, (2009).
- Patel V.H. and Bhat N.V., Effect of solvent pretreatment on dyeability and morphology of Poly (ethylene terephthalate), *Indian J of Textile Research*, 11, 181–187, (1986).
- Píchal J. and Klenko Y., ADBD plasma surface treatment of PES fabric sheets, *Eur. Phys. Journal D* 54, 271–279, (2009).

- Radu C.D., Kiekens P and Verschuren J, "Surface modification of textiles by plasma treatments" in *Surface Characteristics of Fibres and Textiles*, Pastore C.M. and Kiekens P (Eds), Surfactant Series Series, Vol 94, Marcel Dekker, NY, PP 203-218, (2000).
- Rakowski W., Plasma Treatment of Wool Treatments Today, Part I: Fibre Properties, Spinning and Shrink Proofing, *Journal of the Society of Dyers and Colourist*, 113, 250-255, (1997).
- Reinhardt R.M. and Harris J.A., Ultraviolet Radiation in Treatment for Imparting Functional Properties to Cotton Textiles, *Textile Res J.* 50, 139-147, (1980).
- Shahidi S., Ghoranneviss M., Mazzenchi B., Rashidi A. and Dorrani, Effect of Using Cold Plasma on Dyeing Properties of Polypropylene Fabrics, *Fibres and Polymers*, 8(1), 123-129, (2007).
- Shao J., Liu J and Chen Z., Grafting Silk With Electron Beam Irradiation, *Colouration Technology*, 117, 229-233, (2001).
- Shishoo R. (Ed.) *Plasma Technologies for Textiles*, Woodhead Publishing Ltd, UK (2007)
- Shukla S.R. and Athalye A.R., Ultraviolet Radiation Induced Graft Copolymerization of 2-Hydroxyethyl Methacrylate onto Polypropylene, *J. Appl Polym Sci.*, 51, 1567-1574, (1994).
- Subramanian D.R., Venkataraman A. and Bhat N.V., Studies on Dyeing and mechanical properties of Nylon 6 filaments subjected to swelling treatments., *J. Appl Polym Sci.*, Vol. 27, 4149-4159, (1982).
- Thomas H, Denda B, Hedler M, Kasermann M, Klein C, Merten Th, et al. Textile finishing with low temperature plasma. *Melliand Textilber*; 79, 350-352, (1998).
- Timmons, R.B. and Griggs, A. J., "Pulsed Plasma Polymerizations" in *Polymer Plasma Films*, Biederman, H., Ed., Imperial College Press, p. 217, (2004).
- Tsukada M., Shiozaki H., Freddi G and Crighton J.S., Graft Copolymerization of Benzyl Methacrylate onto wool fibres, *J. Appl. Polym Sci.*, 64, 343-350, (1997).
- Uchida E., Uyama Y. and Ikada Y., Antistatic Properties of Surface Modified Polyester Fabrics, *Textile Res J.* 61(8), 483-488, (1991).
- Uyama Y., Kato K. and Ikada Y., Surface Modification of Polymers by Grafting, *Adv Polym Sci.*, 137, 1-39, (1998).
- Vankar P.S. and Shanker R., Eco-friendly Untrasound Natural Dyeing of Cotton Fabric with Enzyme Pretreatments, *Desalination*, 230, 62-69, (2008).
- Vigneshwaran N., Kathe A.A., Varadraj P.V., Nachne R.P. and Balasubramanya R.H., Functional Finishing of Cotton Fabrics Using Silver Nano-particles, *J. Nanosci Nanotechnol*, 7, 1893-1897, (2007).
- Wu S. *Polymer interface and adhesion*. Marcel Dekker, New York. (1982).
- Xu H., Deshmukh R.R., Timmons R.B. and Kytai T.N., Enhanced Endothelialization on Surface Modified Poly(l-Lactic Acid) Substrates, *Tissue Engineering Part A.*, 17(5-6): 865-876, (2011).
- Yasuda H., *Plasma polymerization*, Academic Press, Orlando, Fl. (1985).
- Yen M.S., Chen J.S., Hong P. and Chen C.C., Pore Structures and Anti-bacterial Properties of Cotton Fabrics Treated with DMDHEU-AA by Plasma Processes, *Textile Research Journal*, vol. 76 ( 3) 208-215, (2006).
- Yoon NS, Lim YJ, Tahara M and Takagishi T. Mechanical and dyeing properties of wool and cotton fabrics treated with low temperature plasma and enzymes. *Textile Res J*; 66, 329-336, (1996)
- Zubaidi and Hirotzu T., Graft Polymerization of Hydrophilic Monomers onto Textile Fibres Treated by Glow Discharge Plasma, *J. Appl Polym Sci.*, 61, 1579-1584, (1996).



## **Textile Dyeing**

Edited by Prof. Peter Hauser

ISBN 978-953-307-565-5

Hard cover, 392 pages

**Publisher** InTech

**Published online** 14, December, 2011

**Published in print edition** December, 2011

The coloration of fibers and fabrics through dyeing is an integral part of textile manufacturing. This book discusses in detail several emerging topics on textile dyeing. "Textile Dyeing" will serve as an excellent addition to the libraries of both the novice and expert.

### **How to reference**

In order to correctly reference this scholarly work, feel free to copy and paste the following:

R. R. Deshmukh and N. V. Bhat (2011). Pretreatments of Textiles Prior to Dyeing: Plasma Processing, Textile Dyeing, Prof. Peter Hauser (Ed.), ISBN: 978-953-307-565-5, InTech, Available from:

<http://www.intechopen.com/books/textile-dyeing/pretreatments-of-textiles-prior-to-dyeing-plasma-processing>

**INTECH**  
open science | open minds

### **InTech Europe**

University Campus STeP Ri  
Slavka Krautzeka 83/A  
51000 Rijeka, Croatia  
Phone: +385 (51) 770 447  
Fax: +385 (51) 686 166  
[www.intechopen.com](http://www.intechopen.com)

### **InTech China**

Unit 405, Office Block, Hotel Equatorial Shanghai  
No.65, Yan An Road (West), Shanghai, 200040, China  
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元  
Phone: +86-21-62489820  
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](https://creativecommons.org/licenses/by/3.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen