
Surface Modification Methods for Improving the Dyeability of Textile Fabrics

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1. Introduction

Polymer and textiles have a vast number of advantages and attractiveness as a material. However, despite these advantageous, polymers have limitations. In general, special surface properties with regard to chemical composition, hydrophilicity, roughness, crystallinity, conductivity, lubricity, and cross-linking density are required for successful application of polymers in such wide fields as adhesion, membrane filtration, coatings, friction and wear, composites, microelectronic devices, thin-film technology and biomaterials, and so on. Unfortunately, polymers very often do not possess the surface properties needed for these applications. In fact, polymeric fibers that are mechanically strong, chemically stable, and easy to process usually will have inert surfaces both chemically and biologically. Vice versa, those polymers having active surfaces usually do not possess excellent mechanical properties which are critical for their successful application.

Due to this dilemma, surface modification of the polymeric fibers without changing the bulk properties has been a classical research topic for many years, and is still extensive studies as new applications of polymeric materials emerge, especially in the fields of biotechnology, bioengineering, and most recently in nanotechnology.

Modification is used to designate a deliberate change in composition or structure leading to an improvement in different type of fiber properties.

The challenge is, however, that there does not exist an ideal modification that eliminates all the negative properties and preserves all the positive properties of the fibers. This is why there are a great number of different single-purpose modifications. [1]

In spite of the great number of existing modification methods no consistent classification is available as yet. Some authors divide the methods into two groups depending on whether they involve changes in fiber composition (chemical modification) or changes in fiber structure (physical modification).

Surface modification of polymers has become an important research area in the plastic industry. Because polymers are inert materials and usually have a low surface energy, they often do not possess the surface properties needed to meet the demands of various applications. Advances in surface treatment have been made to rather chemical and physical properties of polymer surfaces without affecting bulk properties. Technologies such as surface modifications, which convert inexpensive materials into valuable finished goods, will become even more important in the future as material cost becomes a significant factor in determining the success of an industry. [2]

There are a few factors to consider when modifying a surface:

1. Thickness of the surface is crucial. Thin surface modifications are desirable, otherwise mechanical and functional properties of the material will be altered. This is more so when dealing with nanofibers as there is less bulk material present.
2. Sufficient atomic or molecular mobility must exist for surface changes to occur in reasonable periods of time. The driving force for the surface changes is the minimization of the interfacial energy.
3. Stability of the altered surface is essential, achieved by preventing any reversible reaction. This can be done by cross-linking and/or incorporating bulky groups to prevent surface structures from moving.
4. In some cases a transparent scaffold is desired, especially in optical sensors or ophthalmology; after surface treatment they should remain transparent. Any cloudiness introduced is of real concern.
5. Uniformity, reproducibility, stability, process control, speed, and reasonable cost should be considered in the overall process of surface modification. The ability to achieve uniform surface treatment of complex shapes and geometries can be essential for sensor and biomedical applications.
6. Precise control over functional groups. This is a challenging yet difficult scope. Many functional groups might bond to the surface such as hydroxyl, ether, carbonyl, carboxyl, and carbonate groups, instead of one desired functional group.

This review is focused on the application of recent methods for the modification of textiles using physical methods (corona discharge, plasma, laser, electron beam and neutron irradiations, Ion beam), chemical methods (ozone-gas treatment, surface grafting, enzymatic modification, sol-gel technique, micro-encapsulation method and treatment with different reagents). Nowadays, surface functionalization of synthetic fibers for various applications is considered as one of the best methods for modern textile finishing processes especially for improving the dyeability of fabrics. [3] Combination of physical technologies and nano-sci-

ence enhances the durability of textile materials against washing, ultraviolet radiation, friction, abrasion, tension and fading. Textile fibers typically undergo a variety of pre-treatments before dyeing and printing is feasible. Nonetheless, these treatments still create undesirable process conditions which can result in increased waste production, unpleasant working conditions and higher energy consumption. Therefore reducing pollution in textile production is becoming of utmost importance for manufacturers worldwide. In coming years, the textile industry must implement sustainable technologies and develop environmentally safer methods for textiles processing to remain competitive. [4, 5]

1.1. Physical methods for modification of textile fabrics

1.1.1. Plasma types and applications

Plasma is by far the most common form of matter. Plasma in the stars and in the tenuous space between them makes up over 99% of the visible universe and perhaps most of that which is not visible.

The coupling of electromagnetic power into a process gas volume generates the plasma medium comprising a dynamic mix of ions, electrons, neutrons, photons, free radicals, metastable excited species and molecular and polymeric fragments, the system overall being at room temperature. This allows the surface functionalisation of fibres and textiles without affecting their bulk properties. These species move under electromagnetic fields, diffusion gradients, etc. on the textile substrates placed in or passed through the plasma. This enables a variety of generic surface processes including surface activation by bond breaking to create reactive sites, grafting of chemical moieties and functional groups, material volatilisation and removal (etching), dissociation of surface contaminants/layers (cleaning/ scouring) and deposition of conformal coatings. In all these processes a highly surface specific region of the material is given new, desirable properties without negatively affecting the bulk properties of the constituent fibres.

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

- Their unparalleled physical, chemical and thermal range, allowing the tailoring of surface properties to extraordinary precision.
- Their low temperature, thus avoiding sample destruction.
- Their non-equilibrium nature, offering new material and new research areas.
- Their dry, environmentally friendly nature. [5, 6]

Plasma reactors

Different types of power supply to generate the plasma are:

Low-frequency (LF, 50–450 kHz)

Radio-frequency (RF, 13.56 or 27.12 MHz)

Microwave (MW, 915 MHz or 2.45 GHz)

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

Low-pressure plasmas

Low-pressure plasmas are a highly mature technology developed for the microelectronics industry. However, the requirements of microelectronics fabrication are not, in detail, compatible with textile processing, and many companies have developed technology of low pressure reactors to achieve an effective and economically viable batch functionalisation of fibrous products and flexible web materials.

A vacuum vessel is pumped down to a pressure in the range of 10^{-2} to 10^{-3} mbar with the use of high vacuum pumps. The gas which is then introduced in the vessel is ionised with the help of a high frequency generator.

The advantage of the low-pressure plasma method is that it is a well controlled and reproducible technique.

Atmospheric pressure plasmas

The most common forms of atmospheric pressure plasmas are described below.

Corona treatment

Corona discharge is characterised by bright filaments extending from a sharp, high-voltage electrode towards the substrate. Corona treatment is the longest established and most widely used plasma process; it has the advantage of operating at atmospheric pressure, the reagent gas usually being the ambient air. Corona systems do have, in principle, the manufacturing requirements of the textile industry (width, speed), but the type of plasma produced cannot achieve the desired spectrum of surface functionalisations in textiles and nonwovens. In particular, corona systems have an effect only in loose fibres and cannot penetrate deeply into yarn or woven fabric so that their effects on textiles are limited and short-lived. Essentially, the corona plasma type is too weak. Corona systems also rely upon very small interelectrode spacing (1 mm) and accurate web positioning, which are incompatible with 'thick' materials and rapid, uniform treatment.

Dielectric barrier discharge (silent discharge)

The dielectric barrier discharge is a broad class of plasma source that has an insulating (dielectric) cover over one or both of the electrodes and operates with high voltage power ranging from low frequency AC to 100 kHz. This results in non-thermal plasma and a multitude of random, numerous arcs form between the electrodes. However, these microdischarges are nonuniform and have potential to cause uneven treatment.

Glow discharge

Glow discharge is characterised as a uniform, homogeneous and stable discharge usually generated in helium or argon (and some in nitrogen). This is done, for example, by applying radio frequency voltage across two parallel-plate electrodes. Atmospheric Pressure Glow Discharge (APGD) offers an alternative homogeneous cold-plasma source, which has many

of the benefits of the vacuum, cold-plasma method, while operating at atmospheric pressure. [5]

Cold plasmas can be used for various treatments such as: plasma polymerisation (gaseous monomers); grafting; deposition of polymers, chemicals and metal particles by suitable selection of gas and process parameters; plasma liquid deposition in vaporised form.

In general, reactions of gas plasmas with polymers can be classified as follows:

1. Surface reactions: Reactions between gas-phase species and surface species and reactions between surface species produce functional groups and cross-links, respectively, at the surface. Examples of these reactions include plasma treatment by argon, ammonia, carbon monoxide, carbon dioxide, fluorine, hydrogen, nitrogen dioxide, oxygen, and water.
2. Plasma polymerization: The formation of a thin film on the surface of polymer via polymerization of an organic monomer such as CH_4 , C_2H_6 , C_2F_4 , or C_3F_6 in plasma. It involves reactions between gas-species, reactions between gas-phase species and surface species, and reactions between surface species.
3. Etching: Materials are removed from a polymer surface by physical etching and chemical reactions at the surface to form volatile products. Oxygen plasma and oxygen and fluorine-containing plasmas are frequently used for the etching of polymers. [6, 7]

Plasma treatment play very important role for improving the dyeing properties of textile fabrics. Some of these improvements are discussed as follow.

1.1.1.1. Surface modification of polypropylene non-woven fabrics by atmospheric-pressure plasma activation followed by acrylic acid grafting

Polypropylene (PP) non-woven fabrics have been activated by an atmospheric-pressure plasma treatment using surface dielectric barrier discharge in N_2 and ambient air. Subsequently, the plasma activated samples were grafted using catalyst-free water solution of acrylic acid. Surface properties of the activated and polyacrylic acid post-plasma grafted non-woven were characterized by scanning electron microscopy, Fourier transform infrared spectroscopy, electron spin resonance spectroscopy, surface energy and dyeability measurements.

The grafted non-woven exhibit improved water transport and dyeing properties.

The plasma activation in nitrogen plasma gas was more efficient than in air. Post-plasma surface grafting lead to a stable and homogeneous grafting of pAA onto PP non-woven fabrics, which made PP fabrics easily coloured by conventional water-soluble acid dye. Supposedly, peroxy radicals formed at a short ambient air exposure of the plasma activated fabrics were responsible for initiating the grafting process. Regarding the surface peroxy radicals generation, the nitrogen plasma gas was superior to ambient air and provided better grafting. [7-9]

1.1.1.2. *One-bath one-dye class dyeing of pes/cotton blends after corona and chitosan treatment*

The feasibility of one-bath one-dye class dyeing of PES/cotton blend with direct (Direct Red 80) or reactive (Reactive Red 3) dye after pre-treatment with corona discharge (CD) and chitosan has been investigated by Ristic and his coworkers. It has been confirmed that corona discharge treatment enhances hydrophilicity of cotton and PES fibers due to surface modification of the material and formation of C-O, C=O, and COOH groups. Increased hydrophilicity of PES and cotton induced only slightly increased color intensity (K/S) with both dyes investigated. Nevertheless, subsequent treatment with biopolymer chitosan noticeably enhanced the color intensity obtained, especially with PES fiber. The dyeability improved proportionally with the concentration of chitosan treatment solutions. However, the highest values of color intensity were obtained for the PES/cotton fabric subjected to the combined CD and chitosan treatment, suggesting that CD pre-treatment enhances efficiency of chitosan application.

Satisfactory values of dye fastness and fixation degree of reactive dye were obtained. [10]

1.1.1.3. *Surface and bulk cotton fibre modifications: plasma and cationization. influence on dyeing with reactive dye*

In similar research work, the single or combined effects of corona air plasma and cationising with an epihalohydrin have been evaluated on the surface and dyeing properties of open-work twill cotton fabrics. Dyeing was performed with a hetero-bis functional reactive dye. Wetting properties of cotton fabrics were improved with a very short corona plasma treatment and a double side-effect was observed on the dyed fabric by contact angle analysis, because of the low penetration of the plasma on the fabric. Exhaustion of the dye and colour intensity of the cotton fabrics were increased due to the plasma treatment. This is well explained by the functionalisation of the surface with oxygenated moieties, without any significant alteration in surface topography of the fibres. Cationising of the cotton fabrics using an epihalohydrin as cationising agent increases the exhaustion of the dyestuff as high as 90%, and produces a dramatic improvement (80% increase) in the colour intensity (K/Scorr) on both sides of the fabrics. The improvement in colour intensity of the cationised cotton fabrics can be explained taking into account that the hydrolysed reactive dye has high anionic character which can be bound to the cationic amine of the cationic agent on the cotton fabrics. It has been observed that plasma treatment previous to cationising increases the impregnation of the fabrics. [11] All these possible effects are schematically represented in Figure 1.

1.1.1.4. *The impact of corona modified fibres' chemical changes on wool dyeing*

Corona/plasma treatment is an environmentally friendly process applied to wool fabrics. The main contribution of the present work was to study the impact of Corona on dyeability of wool fibers. First, the different chemical aspects of a woven wool fabric's surface were determined using two different analytical skills (XPS and polyelectrolyte titration). The results show that, low-temperature plasma treatment has ability to change wool fibre morphology which could have an impact on sorption properties. fabrics were dyed with blue acid and

blue metal-complex dyes, and dyeing behaviour were studied by means of on-line VIS spectrophotometry. Finally, dyed samples were colourimetrically evaluated and colour differences were calculated. The results provided evidence that the overall carbon content was decreased while oxygen and nitrogen atoms were increased when using ionized air for fabric modification. It has also been noted that the amount of positive-charged functional groups in various pH ranges are higher for Corona-treated wool fabric in comparison with the untreated sample.

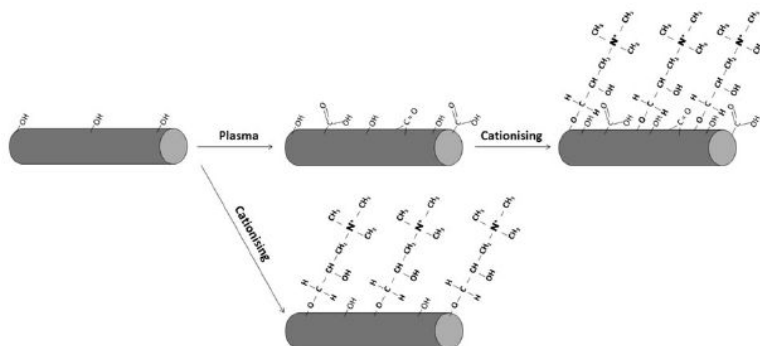


Figure 1. Effects of plasma and cationising processes in the surface functionalization of the cellulose constituting the cotton fibre

The surface performances of untreated and Corona-treated wool fabrics were studied both morphologically and chemically. Corona treatment is confirmed as inducing chemical and physical changes on the surface such as oxidizing/removing external fatty-acid monolayer, enlarging positively charged functional groups, creating new dyesites, and therefore, improving the exhaustion rate during dyeing.

Corona treatment applied in the pre-treatment stages of wool production can lead to an optimization of different dyeing procedures, implying lower dyeing temperatures and shorter dyeing time, achieving the same or even better colour exhaustion in comparison to conventional pre-treated wool fabric. For these reasons, the energy consumption can be reduced, thus also enhancing environmental protection. [12]

1.1.2. Surfaces modification with ionization radiation

Ionization radiation such as high-energy electrons, X-rays, and gamma-rays can displace electrons from atoms and molecules, producing ions. It differs from other types of radiation such as infrared, visible, and UV in that it is highly energetic and delivers to the irradiated material a large amount of energy, much greater than that associated with chemical bonds. Common industrial ionization radiation sources are high-energy electrons (0.1-10 MeV) and cobalt-60 sources, and gamma radiation.

Electron beams from 0.1 to several mega electron volts are used for high doses and high speeds in various industrial processes, with penetration up to several millimeters for polymeric materials.

Surface modification by UV and IR lasers is useful in some specific applications. One key advantage of laser treatment is that the area to be treated can be very small and localized. Depending on the level of power chosen, ablation or chemical and physical changes can occur. Various chemical changes occur on photon-irradiated polymer surfaces. When PTFE was irradiated with ArF laser at high fluencies, defluorination and surface oxidation occurred. For polypropylene, formation of oxygen functional groups such as C-O and C=O groups was detected after UV laser irradiation in air and water, and in ozone. The treated surfaces were shown to have improved bond ability with an epoxy adhesive. The surface of poly(vinyl chloride) becomes electrically conductive after successive UV irradiation in chlorine and nitrogen and argon laser irradiation in air. These types of surface modification are very useful for increasing the dyeability of polymeric textile fabrics. [2] Some of irradiation dyeability modification is discussed below.

1.1.2.1. Effect of UV and gamma radiation on the fabric dyed with natural dyes

The irradiation of fabric is also another factor which affects the colour strength of the fabric. Previous studies show that UV irradiation adds value to colouration and also increases the dye uptake ability of the cotton fabrics through oxidation of surface fibers of cellulose. Gamma rays are ionizing radiations that interact with the material by colliding with the electrons in the shells of atoms. They lose their energy slowly in material being able to travel through significant distances before stopping. The free radicals formed are extremely reactive, and they will combine with the material in their vicinity. Upon irradiation the cross linking changes the crystal structure of the cellulose, which can add value in colouration process and causes photo modification of surface fibers. The irradiated modified fabrics can allow: more dye or pigment to become fixed, producing deeper shades, more rapid fixation of dyes at low temperature and increases wet ability of hydrophobic fibers to improve depth of shade in printing and dyeing. [13]

1.1.2.2. Surface modification of meta-aramid films by UV/ozone irradiation

Meta-aramid films surface was modified by UV/O₃ irradiation, and surface properties have been investigated by reflectance, ATR, ESCA, and surface energy. Upon UV/O₃ treatment, the surface roughness and the O1s/C1s atomic ratio obviously improved, resulting from the implantation of carbonyl and hydroxyl groups. The surface energy of the meta-aramid films increased substantially due to the significantly enhanced Lewis acid parameter, which promoted the acid-base interaction of the surfaces with increase in UV energy. Also meta-aramid films became hydrophilic as indicated by substantially decreased water contact angle.

The dyeability of aramid films to cationic dyes was significantly increased due to higher hydrophilic surface and strong electrostatic attraction between the cationic dyes and anionic dyeing sites of the meta aramid. [14]

1.1.2.3. Modification of polypropylene fibers by electron beam irradiation. i. evaluation of dyeing properties using cationic dyes

The dyeing properties of hydrophobic polypropylene fibers using cationic dyes were investigated to improve dyeability by electron beam irradiation and sulfonic acid incorporation. The best dyeing result was obtained when polypropylene fibers incorporated by sulfonic acid group after electron beam irradiation were dyed with cationic dyes at alkaline conditions and 30~75 kGy irradiation ranges. In order to improve the dyeing properties of electronic beam irradiated polypropylene, sulfonic acid group which has good reactivity was introduced on the fiber. To incorporate sulfonic acid with the electronic beam irradiated (70.5 kGy) polypropylene fiber, the fibers were added and reacted to the solution of 1,4-dioxane and ClSO_3H at 70 °C (Figure 2).

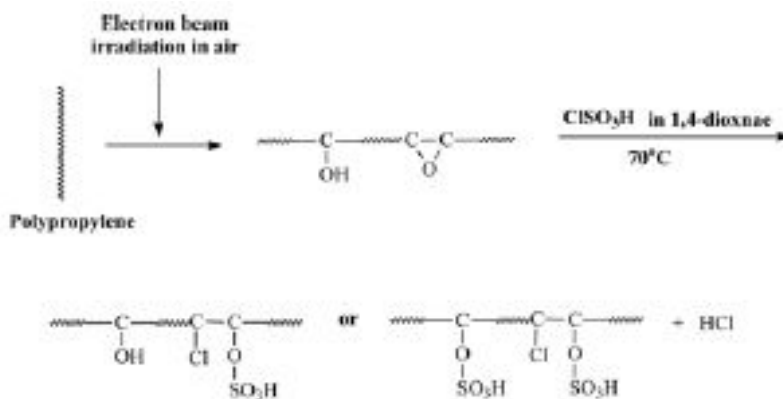


Figure 2. Introduction of sulfone groups on electron beam irradiated PP.

In order to make hydrophobic polypropylene fibers dyeable, it was shown that functional group such as carboxylate was formed on fiber substrates by electronic beam irradiation.

Concerning the pH and amount of absorbed electronic beam irradiation, the color strength increased as pH increased in alkaline conditions, and also increased as the absorbed dose increased to 30~75 kGy. As a result, it was confirmed that the pH of the dyebath and the amount and the range of the absorbed irradiation could be important variables for color strength but it seemed difficult to get deeper colors.

In the case of polypropylene fibers incorporated by sulfonic acid group to improve dyeability, the introduction of sulfonic acid group was confirmed by ESCA analysis and it was judged that such introduction has some advantages in color strength over only electronic beam irradiated fibers. Finally, the wash fastness of dyed fabrics using cationic dyes showed satisfactory ratings of 4~5 on both electronic beam irradiated fibers and sulfonic acid incorporated fibers. [15]

1.1.2.4. UV Excimer laser modification on polyamide materials: effect on the dyeing properties

Polyamide materials irradiated with 193 nm ArF Excimer laser developed ripple-like structures of micron size on the surface. (Figure 3)

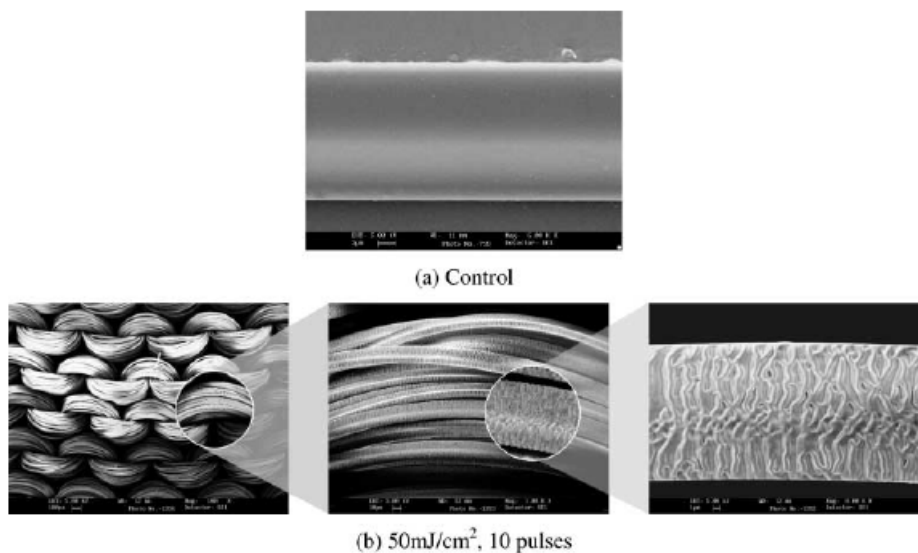
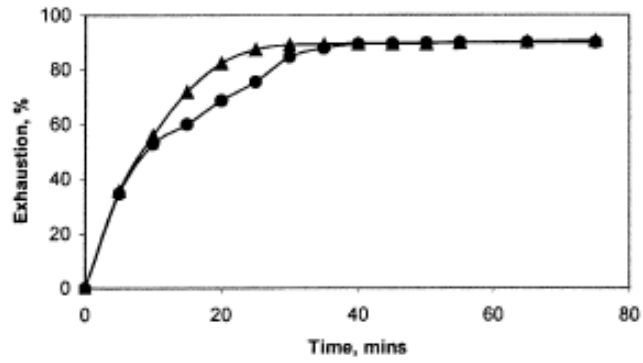


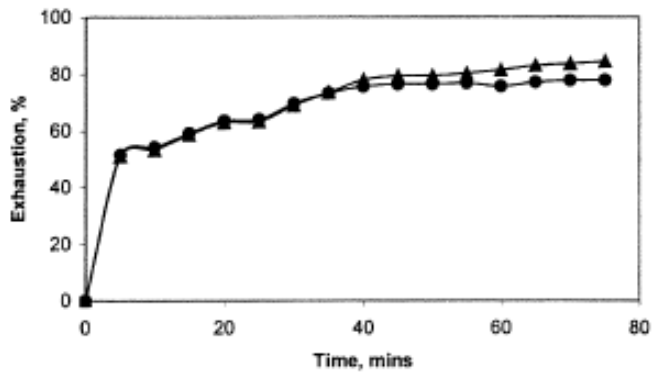
Figure 3. Morphological features of untreated and laser treated nylon 6 fabric

These structures are strictly perpendicular to the stress direction of the fiber. Dyeing results revealed that the dyeing properties of all dyes on polyamide fabrics changed remarkably after the treatment.

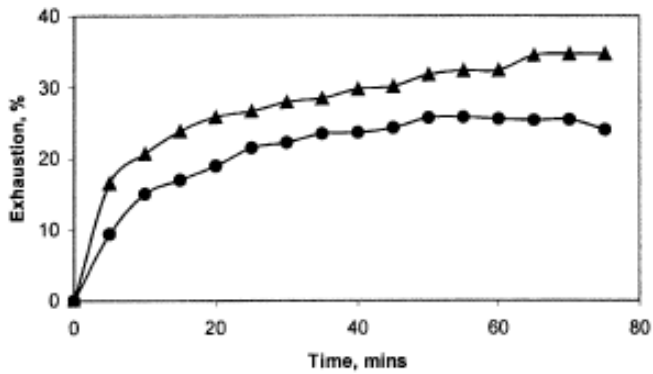
Results suggest that the change in coloration closely correspond with the ripple-like structures and the changes in chemical properties induced by laser treatment. It should be noted that the increased rate of exhaustion of acid dyes by laser treatment is not beneficial for dyeing polyamides since this will enhance the non-uniformity of the dye. While deeper dyeing is a greater advantage for disperse and reactive dyes since darker shades are obtainable using only the usual amounts of dyestuffs. To conclude, the excimer laser modification process has a high industrial potential, as it is an environmentally friendly dry process not involving any of the solvents required for a wet chemical process. After laser treatment, the dyeing properties of disperse and reactive dyes are improved and this provides an alternative choice for dyeing polyamide materials. (Figure 4) [16]



(a) Acid Dye



(b) Dispersive Dye



(c) Reactive Dye

Figure 4. Dye bath exhaustion study of laser treated nylon 6 fabrics; (●) Control (▲) Laser treated

1.2. Chemical modification of fabrics

Chemical treatment has been used in industry to treat large objects that would be difficult to treat by other commonly used industrial technique such as flame and corona-discharge treatments. Chemical etchants are used to convert smooth hydrophobic polymer surfaces to rough hydrophilic surfaces by dissolution of amorphous regions and surface oxidation. Chromic acid is the most widely used etchant for polyolefins and other polymers. [2]

Alkaline, acidic and solvents hydrolysis is another method to improve various physical and chemical properties of synthetic fibers. The alkaline hydrolysis of PET fibers is usually carried out with an aqueous alkaline solution, such as sodium hydroxide. In the alkaline hydrolysis process, PET undergoes a nucleophilic substitution. Chain scission of PET occurs, resulting in a considerable weight loss and the formation of hydroxyl and carboxylate end groups, which improves the handling, moisture absorption and dyeability of the fabric with enhanced softness.

There are different kinds of auxiliaries that are used to modify the surface properties of textile fabrics. Some of new chemical and their applications in textile industry are described below:

1.2.1. Aminolysis

Several studies have assessed the effects of amine interaction with polyester. Early studies assessed the aminolysis of polyester as a means of examining fiber structure without regard to maintaining the integrity of the polymer.

The degradation effects on polyester of a monofunctional amine versus alkaline hydrolysis have been studied. These studies, which again involved high levels of fiber degradation, demonstrated that alkaline hydrolysis has a more substantial effect on fiber weight without extensive strength loss. In contrast, aminolysis had less effect on fiber weight but decreased fiber strength, indicative of a reaction within the polymer structure rather than simply at the surface. It was later demonstrated that bifunctional amine compounds could be reacted with the polymer with minimal loss in strength while generating amine groups at the fiber surface. The early stages of the reaction were largely confined to the fiber surface and the resulting fiber had modified wetting properties and improved adhesion with the matrix when used in composites. A recent paper has re-examined the interaction of untreated and alkali hydrolyzed polyester with a range of aliphatic diamines. 1,6-Hexanediamine, 2-methylpentamethylene diamine, 1,2- diaminocyclohexane, tetraethylenepentamine, and ethylene diamine were applied to untreated polyester. Ethylene diamine was also applied for a range of solution concentrations in toluene. The treatment generated amine groups on the fiber surface and was revealed by staining with anionic dyes under conditions in which the amine group was protonated. Unexpectedly, the reaction resulted in the simultaneous formation of carboxylic acid groups in a manner similar to alkaline hydrolysis, revealed by staining with Methylene Blue

(Figure 5). The reaction thus resulted in a bifunctional polyester surface. The ratio of amine and carboxylic acid groups differed with unhydrolyzed and hydrolyzed starting materials (Figure 5). Strength loss was somewhat greater than with alkaline hydrolysis. [17]

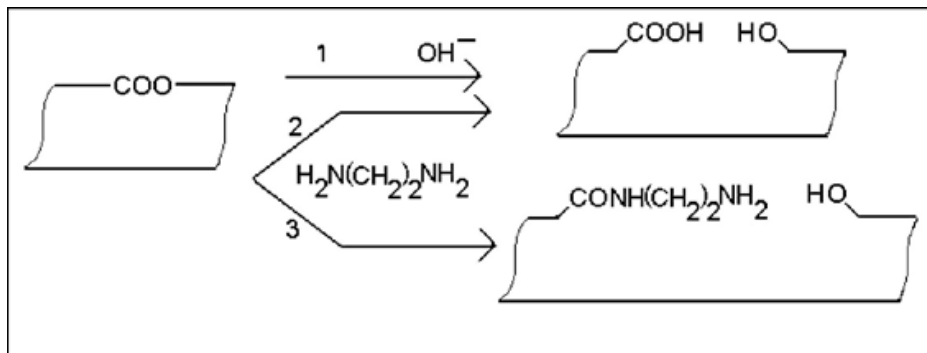


Figure 5. Hydrolysis and aminolysis of polyester

1.2.2. Sol gel pre modification of fabrics

The sol-gel process is an excellent tool to obtain ordered hybrid organic-inorganic nanocomposites. The method involves the mixing of precursors in an aqueous or alcoholic medium. Precursors are molecules, which contain a central metal or semimetal atom, to which reactive alkoxy groups and/or organic groups are bonded. These reactive groups are subjected to an acidic or alkaline catalyzed hydrolysis and condensation reaction, thus forming a sol and subsequently a gel. Aging or drying step enables the production of powders, xerogels, aerogels, fibers, or coatings [18]. The latter procedure renders possible surface modification of textiles, thus imparting novel properties to the material.

The sol-gel technology was also applied to influence the dyeing properties. Luo et al. [19] succeeded in improving the wash fastness of cotton materials that had been dyed with direct dyes using GPTMS and TEOS. Mahltig incorporated dyes into a silica matrix [20-22]. Du investigated the fixation properties and mechanism of direct dyes on silk, nylon 6 and cotton applying various organotrialkoxysilanes. They found that the most suitable precursors for silk and nylon 6 are amide- and vinyl-containing sols [14]. Yin also managed to enhance the fastness properties of cotton material that had been dyed with direct dyes [22].

1.2.2.1. Dyeing Treatment of Sol-gel Pre-treated Cotton Fabrics

Schramm and his coworker investigated the impact of alkoxy silanes (TEOS, GPTMS, APTES, and TESP-SA) on the dyeing process of cotton substrates, which were dyed with 4 % owf C.I. Reactive Red 141 and 4 % owf C.I. Reactive Black 5. (Figure 6) For this purpose cotton samples were pre-treated with the alkoxy silanes and subsequently dyed. The results show that TESP-SA are lowering the L^* values significantly, whereas TEOS, GPTMS, and

APTES give rise to a moderate change of L^* . The after-treatment of dyed cotton fabrics with alkoxy-silane causes almost no effect with respect to the colorimetric data. The direct incorporation of the alkoxy-silanes into the dyeing bath resulted in a reduction of the color properties, when APTES or TESP-SA was employed. The crease-proof finishing treatment caused an increase in the a^* value of red-dyed samples. [23]

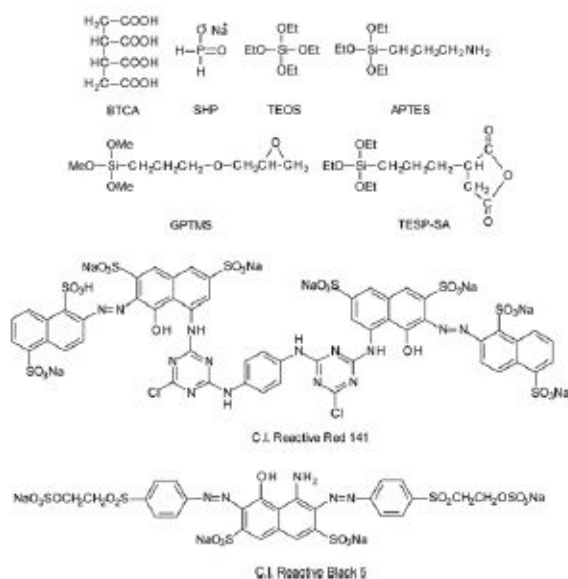


Figure 6. Chemical formula of the substances of interest.

1.2.2.2. An evaluation of the dyeing behavior of sol-gel silica doped with direct dyes

Direct dyes are important dyes used on cellulose fiber directly. They can be applied in the same dyeing bath with other dyes. Moreover, the price is much lower than that of other dyes. However, several problems often occur in dyed fabric with direct dyes, such as lower washing and rubbing fastnesses. Some direct dyes perform rather poorly with respect to washing and rubbing fastnesses. They are mainly caused by the water-soluble groups, sulfonic and/ or carboxyl groups. Without an appropriate treatment, direct dyes bleed a little with each washing, lose their color on fabric and endanger other clothes washed in the same bath. At present, copper salt fixing reagent and cationic fixing reagent are widely used in textile industry to improve the fastness by cross-linking reactions between metal ion or formaldehyde and other molecules. But metal ions in fixing reagent such as cupric cation (Cu^{2+}) will aggravate the difficulty of waste processing. Also some reagents and intermediates used in diazotization or crosslinking reactions such as formaldehyde, nitroaniline seriously affect the human health and the environment.

Moreover, the vividness after copper salt or diazotization finishing usually fades away, so that the application scope of direct dyes have been seriously limited in textile industry. A novel dyeing solution containing silica and direct dyes has been prepared by the sol-gel process. During this process, EtOH, tetraethoxysilane (TEOS), H₂O and 3-glycidoxypropyltrimethoxysilane (GPTMS) were added in turn. The molar ratio of TEOS:H₂O:EtOH was 1:5:8 and the concentration of GPTMS was 0.05 mol/L. Fabric was dyed at 90°C for 40 min. The concentration of NaCl added into the dyeing solution was 10 g/L. The dyed fabrics were baked at 150°C for 5 min. With this process, the results indicate that the K/S value is enhanced by more than 10%, the rubbing fastness and the washing change fastness are improved by one grade and the washing staining fastness is improved by half a grade. Not only is the K/S value enhanced from 9.3 to 11.5, but also the wet rubbing fastness and the washing change fastness are increased half a grade. Using a video microscope, a smoother fiber surface is observed. The calculated sol-gel weight gain is 4.6%. As a nonpolluting process, the sol-gel technology shortens the dyeing process and brings a better fixation property, meeting the needs of energy-saving and pollution-free processes.

1.2.3. Application of nanoparticles for surface modification of fibers

The dyeability of synthetic fibers depends on their physical and chemical structure. Dyeing process consist of three steps including the diffusion of dye through the aqueous dye bath on to the fiber, the adsorption of dye into the outer layer of the fiber and the diffusion of dye from the adsorbed surface into the fiber interior. It was shown by researchers that functional groups of PET and water molecules play a great role in this process. The terminal carboxylic and hydroxyl groups in PET chains interact with water molecules. This makes a swelled fiber resulting to increase the attraction of disperse dye by these functional groups of fiber.

The proportion of crystalline and amorphous regions of polymer is another factor influencing the dyeability. Researchers are concerned with the development and implementation of new techniques in order to fulfill improvement in dyeability of various polymers. Blending of polymeric fibers with nanoclays as inexpensive materials is still claimed as cost effective method to enhance dyeability. Up to now, only two research articles are focused on dyeing properties of polypropylene- and polyamide 6- layered clay incorporated nanocomposites prepared by melt compounding. Toshniwal et al. suggested that polypropylene fibers could be made dyeable with disperse dyes by addition of nanoclay particles in polymer matrix [25].

The previous study on dyeability of PET/clay nanocomposites stated the following type of interactions between the disperse dye and clay surfaces:

- Hydrogen bonding between OH groups of modified clays and the NH₂ and CO groups of disperse dye molecules.
- Electrostatic bonding between the negatively charged oxygen atom of carbonyl groups in disperse dye molecule and positively charged nitrogen atom of quaternary ammonium salt in modified clays.
- Direct π interactions and van der Waals forces between methyl and ethyl groups of modified clays on one hand and methoxy group and benzene rings of disperse dye molecule on the other hand.

1.2.4. Application of cyclodextrins in textile dyeing

Cyclodextrins can be considered as a new class of auxiliary substances for the textile industry. Cyclodextrins can be used for textile application because of their natural origin and their biodegradability. Cyclodextrins play an important role in textile scientific research area and should play a significant role in the textile industry as well to remove or substitute various auxiliaries or to prepare textile materials containing molecular capsules which can immobilize perfumes, trap unpleasant smells, antimicrobial reagents and flame retardants. As cyclodextrins can incorporate different dyes into their cavity, they should be able to act as retarders in a dyeing process. Various auxiliary products are used in wet finishing processes, especially in dyeing and washing. One of the dyeing auxiliary products are leveling agents. Leveling agents help to achieve uniform dyeing by slowing down the dye exhaustion or by dispersing the dye taken by the fibre in a uniform way. They can be classified into two groups: agents having affinity to the dye and agents having affinity to the fibre. Agents having affinity to the dyes slow down the dyeing process by forming complexes with the dyes. The complex compound moves slower compared to the dye itself; at higher temperature the dye is released and it can be fixed to the fibre. Application of cyclodextrins as leveling agents having affinity to dyestuffs has been investigated in research work about dyeing of cellulose fibres with direct dyes by exhaust method where β -cyclodextrin was tested as a dye complexing agent. cyclodextrins as a dye retardant in the dyeing of PAN fibres with cationic dyes was studied; further it was reported that some azo disperse dyes formed inclusion complexes with cyclodextrins. [26]

1.2.5. Chitosan applications in textile dyeing

Nowadays, the surface modification of textile fibres is considered as the best route to obtain modern textile treatments.

Among various available biopolymers, the polysaccharide chitosan (CHT) is highly recommendable, since it shows unique chemical and biological properties and its solubility in acidic solutions makes it easily available for industrial purposes. The polysaccharide-based cationic biopolymer chitosan is poly(1,4)-2-amino-2-deoxy- β -D-glucan, usually obtained by deacetylation of chitin that is widely present in nature as a component of some fungi, exoskeleton of insects and marine invertebrates (crabs and shrimp). The chemistry of chitosan is similar to that of cellulose, but it reflects also the fact that the 2-hydroxyl group of the cellulose has been replaced with a primary aliphatic amino group. Among many other uses, it has been recently shown that chitosan improves the dye coverage of immature fibres in cotton dyeing and that it could be successfully used as a thickener and binder in pigment printing of cotton.

Also Gupta et al showed that, chitosan treated cotton has better dyeability with direct and reactive dyes and treatment with modified chitosan makes it possible to dye cotton in bright shades with cationic dyes having high wash fastness. Treated samples showed good antimicrobial activity against *Escherichia coli* and *Staphylococcus aureus* at 0.1% concentration as well as improved wrinkle recovery. [28]

In similar research work, Jovic and his coworkers assessed the interactions that could occur during dyeing of the chitosan treated wool fibres, by measuring the absorbance values of the solutions containing dye and chitosan. It has been shown that there is a 1:1 stoichiometry between protonated amino groups and sulfonate acid groups on the dye ions in low concentrated chitosan solutions. This interaction forms an insoluble chitosan/dye product. With the excess of chitosan in the solution, the dye can be distributed between the different chitosan molecules and the soluble chitosan/dye products remain in the solution. It is suggested that the mechanism of the interaction involves the possibility of adsorbed dye molecules to be desorbed and redistributed between other components present in the system, depending on system parameters (pH, temperature and electrolyte presence). This fact is important in explanation of dyeing behaviour of chitosan treated wool and enables the assessment of the mechanism of dyeing of accordingly modified textile fibres [29].

Also Kitkulnumchai et al, showed that, the KIO₄ oxidation of cellulose fabrics created more aldehydic groups on the fabric surface and the following reductive amination with chitosan afforded stable C–N bonds between cellulose and chitosan chains. The attachment of chitosan to the fabric considerably improved dye uptake of mono chlorotriazine and vinyl sulfone reactive dyes resulting in greater dye exhaustion and the color yield (K/S).

The enhanced dyeability of the modified fabric is likely resulted from the reduction of the coulombic repulsion between the fabric surface and the anionic dye molecules in the presence of the positively charged chitosan on the surface. The oxidation step can cause some drop in the fabric strength. This oxidation reductive amination with chitosan is thus a convenient method for modifying the surface activity of cellulose fabrics whereas the fabric strength is not of the great priority.[30]

In another research, Cotton fabrics have been successfully dyed by green tea extract upon chitosan mordanting, and UV protection property of the chitosan mordanted green tea dyed cotton was increased.

The following conclusions have been made from this study;

1. Chitosan mordanting can effectively increase the ΔE and the K/S, that is, the dyeing efficiency of green tea dyeing onto cotton fabrics. As chitosan concentration increased, the ΔE and the K/S of cotton fabrics by green tea extract increased gradually.
2. Chitosan mordanting can effectively increase the UV protection property of both UV-A and UV-B of green tea dyed cotton fabrics. Chitosan mordanted undyed cotton and chitosan unmordanted dyed cotton did not show an increase in UV protection property. Therefore, it can be assumed that chitosan increased the uptake of active moiety, catechin, in green tea, which would be responsible for the UV protection and subsequently increased UV protection property of the chitosan mordanted green tea dyed fabric.
3. As chitosan mordanting concentration increased, UV protection property increased in both UV-A and UV-B.

Around 7% UV protection increase from control was observed upon chitosan mordanting, which is similar value of the green tea dyed cellulose fabric using a specific metal mordant.

Therefore, it can be concluded that green tea dyeing can be used in developing UV protective cotton textiles, and the chitosan mordanting process would be necessary in green tea dyeing of cotton to increase not only the dyeing efficiency but also the UV protection property of cotton fabrics. [31]

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