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Chapter

The Role of Surface Modification Methods for Sustainable Textiles

Gürsel Korkmaz, Mehmet Kılınç, Nur Kılınç and Y. Dilek Kut

Abstract

Sustainability aims to provide a livable future for the next generations. Studies on reducing high chemical, energy, and water consumption make significant contributions to sustainability in many sectors. The textile sector consists of many processes such as fiber production, yarn and fabric production, dyeing, and finishing processes. Each of these processes consumes a significant amount of water and energy. Cotton fiber production consumes approximately 1559 kg of fresh water per kg, and polyester fiber production consumes approximately 108 kWh of electricity per kg. Clean water consumption can be up to 200 L/kg in subsequent processes such as bleaching, dyeing, printing, and finishing. Surface modification techniques in textile production can play a role in sustainability, especially in areas such as reduction, reuse, and recycling. In this chapter, we aim to investigate the effects of surface modification techniques on reducing chemical, energy, and water consumption in textile production, improving textile performance properties, and altering the service life of textiles.

Keywords: sustainable textiles, energy consumption, water consumption, surface modification, finishing

1. Introduction

The textile and apparel industries consume large amounts of energy, chemicals, and water [1]. Especially high amounts of water and chemicals used in dyeing and finishing processes cause concerns. Approximately 50–200 liters of water are required to produce 1 kg of textile products. In addition to the amount of water consumed, this water can be seriously contaminated during textile production due to dyeing and chemical treatments [2]. This pollution can lead to damage to water resources and the environment. Inadequate water treatment systems and low-efficiency production methods can increase pollution. The textile industry is an important industry that has developed since the beginning of humanity and will probably continue until the end of humanity. For this reason, sustainability, reduce, reuse, and recycling are important concepts in the textile industry. Many brands and manufacturers are taking various measures to make their production processes water-friendly. Steps such as more efficient production machines, dyeing and finishing processes with low water consumption, and the use of organic and recycled materials are becoming common in the industry.

Some countries and sectors have sustainability standards and certification programs. For example, certificates such as the Global Organic Textile Standard (GOTS) and Bluesign regulate issues such as water consumption and environmental impacts in textile production. These standards promote sustainability and water saving in the sector. Many textile companies known in the global market organize projects on sustainability: Adidas Parley for the Oceans; Nike Grind; H&M Conscious Collection; Levi's, Water <Less; Patagonia Common Threads Initiative; Dry Indigo – Arvind; DYECOO – DYECOO Textile Systems; ECOSENSOR – Hohenstein Institute; Dry Dye – Yeh Group. In addition, award organizations organized on sustainability, some projects to reduce energy consumption, and some projects to reduce chemical consumption are given below:

Awards and competitions

- The Global Change Award – H&M;
- Organic Cotton Round Table (OCRT) Innovation Award – Textile exchange;
- The Global Leadership Award in Sustainable Apparel – Sustainable Apparel Coalition;
- Redress Design Award.

Projects to reduce energy consumption

- Lighting Energy Efficiency in Retail -Marks & Spencer;
- Energy Management System – Inditex;
- Renewable Energy Integration – H&M;
- Energy Efficiency in Textile Manufacturing – Textile Exchange;
- Sustainable Energy Solutions for Textile Industries – Sustainable Apparel Coalition;

Projects to reduce chemical consumption:

- Detox Campaign – Greenpeace;
- Clean by Design Program – Natural Resources Defense Council (NRDC);
- Roadmap to Zero Program – Zero Discharge of Hazardous Chemicals (ZDHC);
- Chemical Management and Sustainability; Sustainable Apparel Coalition (SAC);

Sustainability is a concept that basically aims to provide a livable environment for present and future generations. The waste management hierarchy, which has many rules, is an important part of sustainability. Some of these rules are called R rules: reuse, reduce, and recycle. In addition, some researches also give refuse, rethink, and recover [3]. The concept of reduction basically means reducing waste. For this, reducing unnecessary

consumption comes first. Reuse encourages the preference for durable, reusable products over disposable products and the use of second-hand products. After that, recycling supports the reintroduction of nonreusable products into the production line as raw material or supporting material. We can adopt these concepts individually and turn them into our lifestyles. We can also adapt production processes to these concepts. Surface modification techniques can reduce water, chemical, and energy consumption and extend the life of products. Thus, it contributes to the concepts of reduce and reuse in production processes.

Some methods such as dyeing with supercritical fluids can reduce or eliminate water consumption and the use of chemicals; As another example, the use of reducing and oxidizing agents is reduced in the electrochemical dyeing method. This reduces water pollution and the amount of waste. There are also different aspects to reducing chemical pollution: use of green chemicals, use of more efficient methods; advanced treatment and recycling systems; alternative methods such as digital printing; training to be given to employees on sustainability; and creating sustainable supply chains that encourage stakeholders to use less chemicals; Participating in sustainability standards and certification programs. In addition, surface modification techniques can increase processing speeds, thereby reducing energy consumption. In this chapter, surface modification techniques and alternative methods that benefit sustainability are classified under biological, physical, and chemical subheadings. We aimed to summarize these methods that contribute to the reduction of water, chemical, and energy consumption in the textile sector and to contribute to the widespread use of these methods.

2. Surface modification methods

Surfaces can be modified by chemical, biological agents, or physical mechanisms. Surface modification can change some properties on a substrate with some methods. For example, adding new functional substances by grafting [4]; changing the area and structure of surfaces by plasma treatment [5]. Thus, different properties such as antibacterial, water-repellent, and UV resistance can be given to the substrate; on the other hand mechanical properties of the substrate can be changed [4]. There are various classifications for surface modification ways in the literature. In this chapter, we have given some surface modification techniques with physical, biological and chemical subtitles (**Figure 1**).

2.1 Physical-based surface modification methods

2.1.1 Plasma treatment

Ionized gasses, defined as the fourth state of matter, are called plasma. Sir William Crookes was the first to describe the existence of an ionized gas, the fourth state of matter, in 1879 [6–8]. The scientist who used the term plasma in 1929 was Irving Langmuir [6]. After the discovery of the plasma state of matter, interest in this field increased in the following years, and this technique began to be used to give many different properties to materials used in various industries. The properties of materials used in the ceramics, plastics, textiles, inorganic biomaterials, paper, and electronics industries were developed using plasma technology [9].

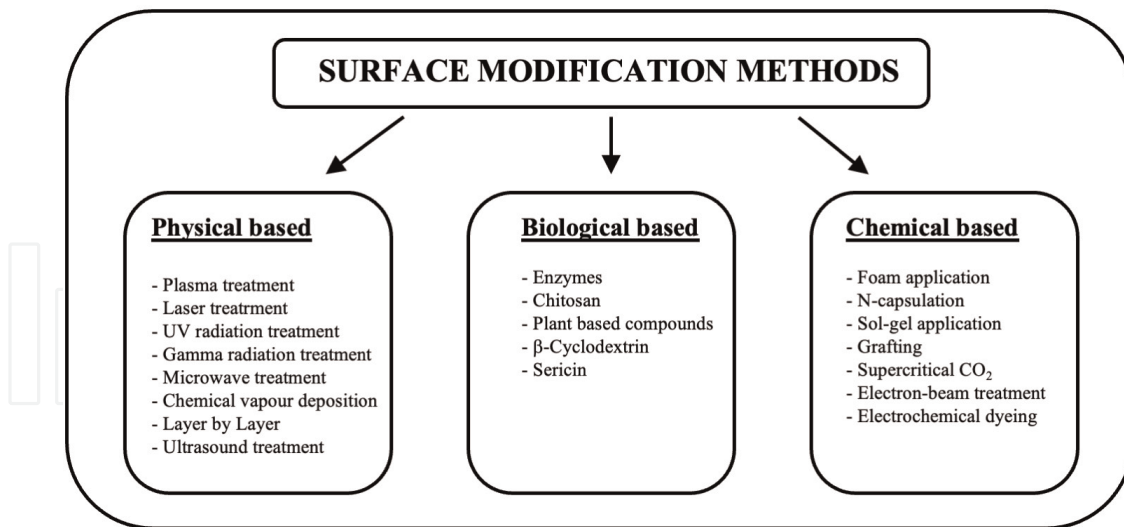


Figure 1.
Surface modification methods.

A basic distinction is made between cold and hot plasma applications, but not all plasma forms can be applied to textile materials. In particular, hot plasma applications change the structure of the textile material and cause deformation, which leads to a deterioration of the physical and chemical properties of the material [10]. Cold plasma applications are preferred for textiles because hot plasmas damage the material, application costs are high, and energy requirements are high under ambient conditions [7, 10]. Cold plasma applications are divided into atmospheric and vacuum plasma [11]. Atmospheric plasma is classified as dielectric barrier discharge, thermal discharge, and corona discharge. Vacuum plasma, on the other hand, is classified into two groups: Low frequency and high frequency [10]. Plasma application can impart water-repellent, oil-repellent, wettable, antifelting, flame-retardant, dyeable, and antimicrobial properties to the textile product [12].

The type of gas used, the flow rate, the system pressure, the discharge power, the duration of treatment, the aging of the plasma-treated surface, and the temperature change during plasma treatment are the parameters that affect the application [10, 12, 13].

The importance of plasma technology for sustainability is mentioned below [13–16].

- Since the process is carried out in the gas phase, drying after the process is not required, which reduces energy consumption.
- In general, the energy consumption of the process is low compared to conventional systems.
- The consumption of water and chemicals is negligible.
- Requires a shorter application time compared to conventional systems.
- The same desired effect can be achieved with less water and chemical consumption.

- No effect on the bulk properties of the product.
- Plasma technology produces no waste after application.

2.2 Laser treatment

Laser is the abbreviation for “light amplification by stimulated emission of radiation” [17]. The basis of laser is based on electron transitions between atomic or molecular energy levels. The first laser forming the basis of this laser technology was manufactured in 1960 [18]. Lasers are classified as gas lasers (He-Ne, argon, carbon dioxide, and excimer), solid-state lasers (ruby, Nd:YAG, erbium-doped glass, and F-center), metal vapor lasers (helium-cadmium and copper vapor), and other lasers (dye and free electrons) [18]. Laser technology is used in engineering and technology, health sciences, security, and defense [19].

The technologies used in the textile industry are increasing daily to meet the requirements. One of these technologies is laser technology. This technology is used in the textile industry for fading (marking), engraving (laser printing), cutting, and welding [20]. From the studies conducted so far, laser technology is used in textile defect detection, cutting, body size scanning, denim fading, printing, thermoplastic welding, evaluation of seam pucker, barcode scanning, marking, surface metal substance detection, and surface decoration [21]. The advantages of laser application in terms of sustainability are listed below [17, 21–24].

- Processing without the use of water and chemicals
- Zero waste
- Lower probability of errors, consumables, and production costs, since it is a computer-controlled automatic system
- Being a dry process
- Low labor requirements
- Low energy consumption compared to conventional methods
- Fast, precise, and accurate production

2.3 UV radiation treatment

In the electromagnetic spectrum, the rays with a wavelength between 100 nm and 400 nm are called UV rays [25]. The existence of UV rays was noted by Johann Ritter in 1801 [26]. UV rays are divided into three different groups: UV-A (320–400 nm), UV-B (280–320 nm), and UV-C (200–280 nm) rays [27].

UV technology is used in various industrial fields (enzyme immobilization, tissue engineering, etc.) [28]. One of these application areas is the textile industry. Studies can be found in the literature where UV rays have been applied to polypropylene, polyethylene, cotton, and wool fibers [27, 29, 30]. In these studies, it was found that the application of UV rays for surface modification improved hydrophilicity, adhesion, dye uptake, and decrease in pilling on product surfaces

[27, 31, 32]. UV rays cause weak bonds to break and functional groups to form on the applied surfaces. It has been reported that UV rays form carboxyl, aldehyde, hydroxyl, carbonyl, and other reactive groups on the surface, resulting in an increase in hydrophilicity and dye uptake [25]. Another advantage is that the modification does not cause a significant change in fabric strength during this application [33]. In addition to these advantages, the benefits in terms of sustainability are as follows:

- It is an accessible technology
- It is a dry process
- Reduction of the consumption of chemicals needed for the processes to be carried out
- No waste after the application

2.4 Gamma radiation treatment

Gamma rays were observed in 1900 by chemist Paul Villard [34]. Gamma rays ($\lambda < 10$ pm) are electromagnetic radiations with high energy (energy >100 keV) [35]. Gamma rays are rays emitted by radioactive isotopes (Cs-137 or Co-60) [25]. Gamma rays are used in medicine, genetics, the textile industry, the nuclear industry, and various industries where disinfection and sterilization are required [36]. Gamma irradiation is defined as penetrative ionizing radiation. Due to this ionizing property, ions, free radicals, excited states, and reactive intermediates are formed as a result of ionization and excitation on the treated surfaces.

In the textile industry, there have been studies on cationization of textile surfaces by gamma irradiation, adding functional groups on the surface, mercerization, increase in dye uptake, and finishing [36]. In related studies, it was found that dye uptake, hydrophilicity, color fastness and strength, and interfacial strength (composites) increased on the surface, and the degree of wrinkling decreased [35, 37, 38]. Gamma rays are known to cause both physical and chemical changes in textile products [25]. In this direction, it is assumed that the above-mentioned changes have occurred. Gamma radiation also has advantages in terms of sustainability. Each of these is listed below [37–39].

- Uninterrupted operation
- Short application time
- Less pollution for the atmosphere
- Applicability at ambient temperature
- Easy and dry application
- Design flexibility
- No waste after application

2.5 Microwave treatment

Microwave has a frequency of 300 to 300,000 megahertz (MHz) and a wavelength of 1 cm to 1 m [40]. The development of microwave technology began during World War II [41]. In addition, microwave technology was commercialized in 1947 [40]. Microwave technology is used in various fields of industry for drying, accelerating chemical reactions, and organic synthesis [42].

In the textile industry, microwave technology is used in drying and application processes in textile finishing. The relevant literature states that microwave energy has some positive impact on uptake of dye, dyeing time, effective and homogeneous drying, and dye fastness [25, 43–46]. In addition, the effects of microwave application on sustainability are explained point by point below [25, 41, 47–49].

- Short processing time compared to conventional applications
- Energy saving
- Efficient and homogeneous application
- No direct impact on air pollution

2.6 Chemical vapor deposition

Chemical Vapor Deposition (CVD) is one of the thin film and vapor phase deposition methods [50]. In the CVD method, the gaseous material to be coated is deposited on the surface in the form of a film, powder, or fiber with the help of a carrier gas (e. g., He, Ar, and N₂) and chemical reactions such as pyrolysis, hydrolysis, oxidation and reduction [50, 51]. It is known that the produced coatings are thinner than 10 micrometers [52]. It is claimed that the development of the CVD system took place between 1880 and 1890 with the help of studies conducted with the aim of strengthening carbon filaments [53]. There are also different types of CVDs. Among them, some methods are used in textile applications: plasma-enhanced chemical vapor deposition (PECVD) and initiated chemical vapor deposition (ICVD) methods [50, 54, 55].

CVD is used in various fields (microelectronics, electronics, ceramics, ferroelectrics, superconductors, etc.) due to its advantages [53]. The textile industry is one of these areas. The CVD process has the advantages of fast and pure film generation, deposition of difficult-to-evaporate materials, and reproducibility. However, in general, the CVD process has the disadvantage of requiring high temperatures, involving complex processes, and releasing harmful gasses (toxic and corrosive) as by-products [50–54]. These disadvantages are also problematic in terms of sustainability.

2.7 Layer-by-layer

In the layer-by-layer method, oppositely charged macromolecules are arranged one after the other on the surface to be coated [56]. This method was first started in 1966 with the work of Iler [57]. Later, LBL was further developed by the work of Decher in 1990 [58]. The coating thickness of the layer on the material can vary from 1 nm to 500 nm [57, 59]. This application is used in various fields (electronics,

medicine, textiles, machinery, and other technical fields). The literature reports that the mechanical, magnetic, optical, thermal, electrical, and macroscopic properties of the materials used are improved [58, 60].

In the studies conducted on textiles using the LBL method, it was found that the textile surfaces are provided with UV protection, antibacterial, hydrophobic, flame retardant, self-repairing, and antifelting properties and that the color and tear resistance is increased [56, 57, 60]. In addition to these benefits, the LBL method also offers sustainability advantages. These advantages are listed below [47, 56–60].

- The process is simple, cost-effective, repeatable, and energy-efficient
- No expensive and hazardous solvents are required for the application
- Aqueous solutions are used in the application
- The application is made fast, at room temperature, and under atmospheric pressure

2.8 Ultrasound treatment

Ultrasonic waves are vibrations with a frequency of more than 20 kHz in a range that is imperceptible to humans [61, 62]. The chemical and biological effects of ultrasonic energy have long been known. In industry, it is used primarily for sterilization due to its cavitation properties [63]. Ultrasonic technology is used in pharmacology, chemistry, food, medical, polymer, textile, and metal industries for cleaning, cutting, drying, mixing, and combining [61]. It is well known that ultrasonic technology is used in the textile industry for desizing, scouring, bleaching, dyeing, washing, compounding, printing, enzyme applications, wastewater treatment, and extraction of natural dyes [64]. In these applications, ultrasonic technology offers the following advantages thanks to its cavitation function [61–66].

1. Achievement of a homogeneous printing paste in the printing process
2. Increased whiteness, wettability, and reduced fiber degradation in the desizing process
3. More ecological and better fiber strength in washing processes compared to traditional methods
4. Achievement of similar values to traditional methods in a shorter time in the bleaching process
5. Acceleration of mass transfer to the fabric surface in enzyme applications
6. Achieving close and high color values at low temperatures in the dyeing process compared to traditional methods
7. Achieving a more efficient product in terms of content in less time in the dye extraction process

8. Maintaining the structural properties of textile fibers by processing at lower temperatures than in autoclaves in the sterilization process
9. Decolorization, chemical, and dyestuff removal during the purification of textile effluents

In addition to these advantages of ultrasonic technology, its sustainable effects are listed below [47, 61–64].

- Ultrasonic technology has lower consumption of processing time, energy, water, and chemicals compared to conventional methods.
- Ultrasonic technology enables processing at low temperatures and atmospheric conditions.

3. Biological-based surface modification methods

The pressure on global consumption and the environment is increasing due to the growing world population and the developing economies of countries. The use of alternative technologies that can be produced with less consumption of natural resources to meet the needs of people is one of the most important steps that can be taken in terms of sustainability [67].

The use of bio-based materials and nature in production processes, known as industrial biotechnology, is one of the technologies that offer an alternative to conventional technologies for cleaner production [68]. The apparel and textile industry is considered one of the main polluters of surface and groundwater resources due to its excessive water and energy consumption, as well as the use and discharge of nonbiodegradable synthetic chemicals [69, 70].

Along with the environmentally and sustainability-conscious societies, textile and readymade garment manufacturers have also recognized the importance and need for eco-friendly products and processes that prevent the use of harmful chemicals [71]. The biological surface modification methods used in the textile industry are classified in this chapter as follows:

- Enzymes
- Chitosan
- Plants based compounds
- β -Cyclodextrin
- Sericin

3.1 Enzymes

Enzyme processes are considered a promising and sustainable biotechnological alternative to conventional processes. The use of enzymes for human needs dates back to 2000 years ago. The use of microorganisms in processes such as bread baking and the

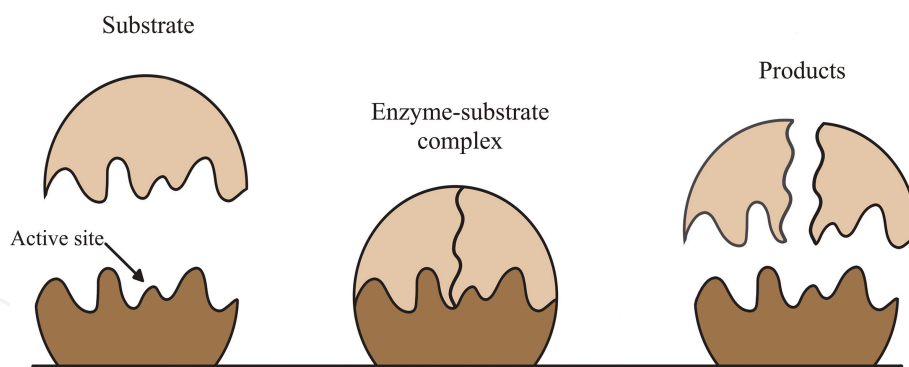


Figure 2.
Lock & key Model of enzymes [75].

conversion of rice to sugar in koji production can be cited as examples of the use of enzymes [72]. Enzymes are biocatalysts consisting of metabolites derived from bacterial derivatives of living organisms. The substances that participate in chemical or biochemical reactions and remain unchanged at the end of the reaction are called catalysts [73].

Enzymes act like molecular machine that allows molecules to react with each other. Like a key fitting into a lock, chemical molecules fit into pocket-like structures on the enzyme. These pockets hold the molecules in a position where they can react with each other so they are close enough together and properly aligned. In this way, the enzymes speed up the reactions. When the reaction is complete, the enzymes release the products and are ready to assemble more molecules and catalyze more reactions [74]. Enzymes have active sites, which are sites to which the substrate molecule can bind. Just as a particular key fits the lock, a particular substrate molecule fits the active site of the lock enzyme. The substrate forms a complex with the enzyme [75]. The substrate molecule is then converted to the product and the enzyme is regenerated (**Figure 2**).

Enzymes are in demand in the textile industry, pulp, and paper industry, cosmetics industry, food and beverage industry, biodiesel industry, detergent industry, and leather industry in many industrial applications [67].

Enzymatic surface modification of textiles is a process that involves treating fibers or attaching functional groups to the surface to change their physical and chemical surface properties [76]. **Figure 3** shows the enzymes used in textile manufacturing processes [77]. Many enzymes can be used in textile processes and they provide some advantages as follows [78].

- Removal of cotton impurities (desizing, washing, and bleaching)
- Biotreatment to improve appearance and remove surface hairiness;
- Bio-sanding to create a trendy weathered look
- Bleaching to remove H_2O_2 residue before dyeing

Enzymes, which are available from many sources, are of great importance for the sustainable development of the textile industry. The use of enzymes in wet processes of the textile industry is increasing day by day due to the following benefits [77, 79–81]. These are:

- Accelerates responses
- Works in bright environments

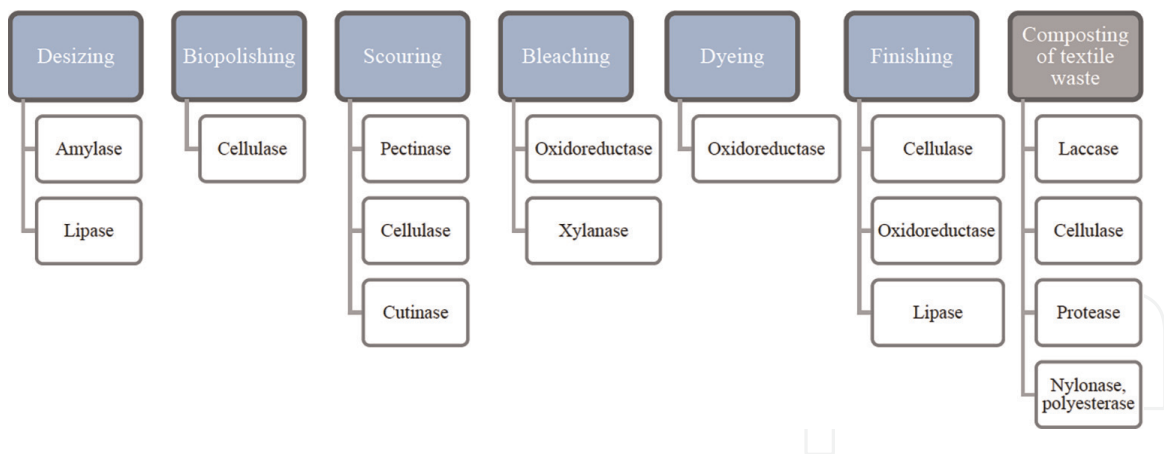


Figure 3.
 The names of enzymes used in textile processes.

- It is easy to operate
- It saves energy
- Less chemical and water consumption
- Reduces CO₂ emissions and waste
- Biodegradable
- Low production costs
- Environmentally friendly

There are some limitations to the application of enzymes in textile processes [25, 77, 78]. Some of them are listed below:

- Due to the extreme pH and temperature conditions that prevail in textile processing, enzymes are accepted in the industry in a limited manner, which leads to a deterioration of their properties and efficacy.
- Enzymes are sensitive and should be stored carefully under prescribed conditions.
- Reuse of enzymes after application is a difficult process.
- The use of some enzymes is not economically viable.

Therefore, enzyme-based biotechnology is one of the environmentally friendly processes that contribute to sustainability in the textile industry, but it is an area that still needs to be developed.

3.2 Chitosan

Chitin is the second most abundant natural polymer in the world. It is usually extracted from the exoskeleton of fungi and crustaceans. Chitin was boiled in potassium hydroxide and found to become soluble in organic acids.

This observation led to the discovery of chitosan in 1859, and Hoppe-Seyler named this material chitosan in 1894 [82–84]. Reactive amino and hydroxyl functional groups in the chain structure of chitosan can make chemical bonding to the inorganic reinforcement network and processability even more efficient through various modifications [85, 86].

Chitosan is biodegradable, odorless, and nontoxic, which makes it a versatile green material that can contribute to environmental sustainability [87–90]. Due to its interesting properties, chitosan is considered one of the most promising bio-based polymers with a wide range of applications to solve numerous problems in fields such as biotechnology, pharmaceuticals, food, medicine, textile, environment, paper, and agriculture [88, 90, 91].

Today, purification of water by adsorption with low-cost adsorbents is considered an effective, economical, and environmentally friendly method. The natural and low-cost products to be developed are considered as popular alternatives to synthetic polymers [92].

In recent years, chitosan and its blends/composites have been intensively researched as they are excellent bioadsorbents with high adsorption properties [93, 94]. The solubility property of chitosan increases its usability and the effectiveness of the reactive sites. There are some limitations to the use of chitosan. Particle size, porosity, and crystallinity, that is, physical factors, can affect the adsorption properties of chitosan materials. Due to its low adsorption capacity, surface area, hydrophilicity, high crystallinity, nonporosity, and mass transfer resistance, the use of chitosan in applications is limited [95]. Due to its polycationic nature, chitosan can form strong ionic bonds with tissue materials. In addition, chitosan is widely used in textile dyeing and finishing [96]. Due to the nanofiber structure of chitosan, it is widely used in medical textiles, especially as wound dressing [97]. In addition, polysaccharide fibers coated with a chitosan film or modified chitosan can impart improved properties to textile products. Some of these properties include the following [85, 98]:

- Antistatic property
- Stain repellent property
- Antibacterial property

The biocompatibility, biodegradability, and bioactivity of chitosan are extremely important properties for human well-being. From textile finishing to wastewater treatment of textiles, the demand for eco-friendly biopolymers such as chitosan is increasing day by day in addition to sustainability in many sectors of the textile industry [94].

3.3 Plant-based compounds

Plants have some active compounds such as diketones, flavonoid and chalcones. These compounds may provide some functional properties: for example, antibacterial, antifungal, and antioxidant [99]. The literature presents some studies that textile materials are tried to be functionalized with some of these compounds [100].

In recent years, the textile industry in particular has come under a lot of environmental criticism. As a result, environmental and economic restrictions have been placed on the chemicals used, up to and including bans [101].

Specific concepts where plant-based compounds can be used in textile finishing that are environmentally friendly, biocompatible, low toxic, and sustainable have become very fashionable in recent years [102].

The exploration of natural products and plant substances for various finishing techniques is important due to their sustainability, cost-effectiveness, and environmental friendliness [103]. Plant-based products used in the production of eco-friendly textiles are considered as one of the most important textile applications. The growing health awareness among people is mainly due to the frequent occurrence of infectious diseases worldwide. Therefore, antibacterial textiles are becoming more and more popular day by day [68]. Due to the sustainability and environmental friendliness of plant-based compounds, they are widely used to impart deodorizing/aromatizing, insect repellent, antioxidant, flame retardant, UV protective, antifungal, and antimicrobial properties to textile products [102].

The use of plant-based compounds in textile products has some advantages [104–107]. These are:

- Minimum damage to the environment
- No need for complex chemical reactions
- Can add functional properties to surfaces
- Biodegradable and Renewable
- Environmentally friendly
- Abundant in nature

On the other hand, the use of plant-based compounds in textile products has some disadvantages [103, 104, 108]. These are:

- Low resistance (low resistance The resistance can be increased by various techniques such as microencapsulation)
- High prices due to limited quantity
- The difficulty of standardizing
- Poor solubility in water

The use of plant-based compounds in the textile industry is eco-friendly and sustainable. No harmful chemicals are used, and therefore no wastewater treatment is required, which reduces production costs.

3.4 β -Cyclodextrin

Nowadays, the production of functional textiles with environmentally friendly materials and processes is very popular in the textile industry. β -Cyclodextrin (β -CD) is bioconsistent, biodegradable, environmentally friendly, and clean. Many auxiliaries are used together with basic chemicals in textile finishing processes. Cyclodextrins

(CD) are one of these auxiliaries. However, excipients used in the textile industry today are expected to have properties such as lower fabric consumption, biodegradability, less waste, and multifunctionality, especially in textile auxiliaries. Biopolymers, biocompatible, sustainable, and clean cyclodextrin molecules have been the subject of numerous scientific studies [86, 109, 110].

The most commonly used and well-known cyclodextrins are α -CD, β -CD, and γ -CD. They are named after the number of glucose units and are the predominant examples of cyclodextrins with 6, 7, and 8 glucose units, respectively, and a hydrophilic surface and a hydrophobic cavity formed by enzymes [109]. They are water-soluble and insoluble organic solvents. β -CD is the least water-soluble CD. β -Cyclodextrin and its derivatives are the most popular cyclodextrins because they are easy to process, have a low price, do not cause skin sensitization and irritation, and are nonmutagenic [111]. The hydroxyl (-OH) groups of β -CD can scavenge water contaminants through adsorption. It can also capture β -CD metal oxides [106, 107]. In addition to the textile industry, β -cyclodextrin is used in medicine, other paint industry, chemistry, agriculture, food industry, etc. [110, 112, 113]

Cyclodextrin is generally preferred in printing, dyeing, and finishing applications in the textile industry. Cyclodextrins are used in textile applications for imparting functional properties such as UV protection, antifungal, odor properties, antibacterial activity, insecticidal properties, and dyeing [114, 115].

β -CDs can be used in the dyeing process to improve the dye uptake of textile fibers and minimize dye loss in wastewater, increase color uniformity, and prevent dye bleeding during cleaning [109]. The biocompatible cyclodextrin biopolymer used in the finishing process is one of the promising materials for the production of high-value-added textile products.

3.5 Sericin

Silk is a natural polymer synthesized by silkworms and spiders. It is most commonly obtained from the silkworm *Bombyx mori* and some spider species such as *Araneus diadematus* and *Nephila calavipes* [116]. The ease of processing, biocompatibility, biodegradability, and high mechanical properties of silk fibers, which are available in natural and regenerated forms, make them a popular material for the production of functional materials [117]. Silk is composed of two main proteins, fibroin (fibrous protein) and sericin (globular, rubbery protein). The fibroin protein in silk is 70–80% crystalline and insoluble in water. Sericin, on the other hand, is 20–30% amorphous and water-soluble. Sericin acts as an adhesive that holds fibroin filaments together [118].

Today, silk fibroin is recognized as a valuable textile material; on the other hand, it is also a remarkable biomaterial in various fields such as tissue engineering, drug delivery, electronic devices, and environmental restoration [116, 119, 120]. Sericin has received less attention than fibroin; however, this protein has been recognized as a potential biomaterial due to its biocompatibility, immunocompatibility, biodegradability, anti-inflammatory, antibacterial, antioxidant, and photoprotective properties [116, 121]. Sericin is generally used in the textile industry for absorbing moisture in fabrics, improving antibacterial activity, producing nanofibers, creating self-cleaning, and improving UV protection [122]. On the other hand, sericin has the potential to improve some properties in textile material: tear resistance, antiwrinkle, dyeability, fiber strength, tensile strength, and fabric handle [123].

Silk fibroin and sericin must be separated before processing because they differ greatly in appearance, solubility, amino acid composition, and number of reactive groups. In the textile industry, a process called degumming (also called washing) is required to obtain silk fibroin filaments with excellent handle, high luster, and high capillary height [120, 124]. Conventional degumming processes using soap, alkali, or both can cause environmental damage, high water and energy consumption, and damage to silk fiber. Today, the following environmentally friendly degumming methods are used [120, 125, 126].

- Enzyme degumming,
- CO₂ supercritical fluid (CSCF) degumming,
- Acid removal,
- Steaming,
- Ultrasonic degumming.

In the textile industry, there are studies on the reuse of sericin as a bioactive excipient in the fields of medicine and cosmetics. Textile companies can generate revenue by selling waste sericin as part of environmentally friendly production and sustainability, thereby reducing wastewater treatment costs [127].

4. Chemical-based surface modification methods

4.1 Foam application

Foam application was developed in the early 1970s [128]. Foam is formed by inflating any liquid with a suitable gas, thus increasing the surface area of chemicals. This makes the application possible by using less water and chemical [129]. In addition, using less water also reduces the energy consumption required for drying [130]. By stirring at high speed, a large volume fraction of air is introduced into the solution. Thus, a small amount of finishing solution can be converted into a large amount of foam [131].

There are two types of foams: round-cell foams and angular-cell foams. Round foams are not used in textile finishing because they contain too much water. Another reason for using angular foams is that their durability is better than round foams. There are some important parameters for the foam application to be successful: The foam should remain stable until it reaches the fabric; it should decompose quickly when it reaches the textile; it should be resistant to other chemicals; and it should not contain too much water. In the textile industry, air is used as gas and application solution is used as liquid [132].

The foam application is as follows: liquor preparation, foam formation, foam application, foam destruction, drying, and fixation. Foam production is performed by two methods or a combination of them: air-blowing, stirring, or combining these two methods [133]. After surfactants are dissolved in water, surfactants cover the air bubbles that are formed in the bath by the rotation of the rotor around the stator in the foam generator. When air bubbles with low density rise toward the surface, they are

covered with a second layer of surfactants on the surface. Thus, the application liquid is trapped between the two surfactant layers, and the foam cell is ready to use [132]. After the production of the foam, the textile surface is treated with a foam applicator. The textile industry uses several methods to apply foam to the textile material. Some of them are doctor blade, roller coater, slot applicator, pad mangles, kiss coating, knife systems, and printing [134].

Compared to conventional methods, it has the advantages of chemical cost, working time, and working flexibility. Foam application makes it possible to process with much lower water consumption by increasing volume of the foam. However, there is no need for defoaming chemicals. With rapid wetting and high penetration on the product surface, it increases the working speed and reduces the energy used [135]. Compared to classical methods, it provides lower water, chemical, energy consumption, and working time. In addition, both sides of the fabric can be coated with this method. In addition to its advantages in sustainability, it also contributes to the textile and production process as follows:

- Allows application on different surfaces.
- Application efficiency is not dependent on fabric surface speed.
- The application is not dependent on the surface composition and structure.
- Homogeneous coatings are provided.
- Efficiency is increased by the controlled application of chemicals.
- Low use of thickener,
- Uniform and repeatable foam production.
- Low wet pick-up rate.
- First quality production increases.
- Allows application on both sides of the fabric [132]

4.2 N-capsulation

'N-capsulation method provides the production of capsules that includes several functional properties such as antimicrobial, insect repellent, and anti-inflammatory [136]. The inner material that has functional features is called core, while the material covering the core is called shell [137]. Wall material choice depends on some parameters such as reactive groups of the core material and textile surface. The capsules are classified according to their size as nanocapsular ($<1\ \mu\text{m}$), microcapsules ($1\text{--}1000\ \mu\text{m}$), and macrocapsules ($>1000\ \mu\text{m}$). However, dimensions of the capsules below 40 mm are recommended to avoid coating breakage in the finishing process [138].

Microcapsules can be produced in different shapes; different numbers of core; single or multi-shell layers; or in matrix structures [137]. In capsules with a matrix structure, the core material is evenly distributed within the wall [139]. This method allows for extending the service life of core material [140], bonding the surface of the

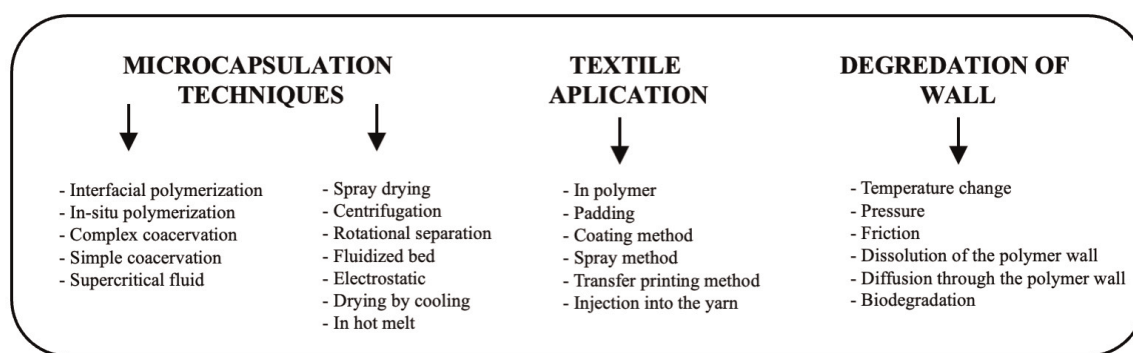


Figure 4. Some methods for microcapsulation, textile application, and wall degradation.

material and core, and controlling releasing mechanisms [136]. Various methods are available for microencapsulation, textile application, and wall degradation. **Figure 4** shows some of these methods.

In the microencapsulation technique, it is used in many areas depending on the characteristics of the multi-core material. In the textile sector, this method allows many functional properties such as spreading odor, trapping bad odor, adding anti-microbial properties, adding antioxidant properties, releasing vitamins in wound healing can be added.

4.3 Sol–gel application

Textile materials and many different types of materials can be coated with sol–gel application. This method provides many properties such as water repellency, ultraviolet protection, and electrical conductivity can be added to the material separately or together. In this production, solvents could be recycled to reuse. In addition, the energy requirement in the drying step is low due to the organic solvents used in this method. Attention should be paid to the coating thickness since flexibility is inversely proportional to the thickness of the coating. In the textile sector, this value is below the micrometer. In some cases, materials such as polysiloxane and softener are used to provide softness [141].

Some terms used for the sol–gel method are explained below.

- **Sol:** It is a colloidal suspension in which solid particles are homogeneously dispersed in a liquid.
- **Gel:** It is a reticulated structure interconnected in three dimensions. It is a form between solid and liquid.
- **Sol–Gel:** It is the process that turns the molecules or particles in the ‘sol’, a colloidal solution, into a two-phase ‘gel’.
- **Nanosol:** It is a nano-structured sol–gel process obtained by applying molecules or particles in ‘sol’ at ‘nano’ scale.

A sol–gel process consists of three basic components: Initiators (Metaloxides or Metal salts); Solvents [Water or Nonaqueous solvents (methanol, ethanol, propanol, butanol)]; Catalysts (acidic or basic). Stable solutions are prepared with metal oxides

in aqueous or nonaqueous medium. The size of the colloidal particles does not exceed 500 nm. First of all, homogeneous solutions of the initiators are prepared. Then, alkoxides dissolved in alcohol are hydrolyzed by the addition of water at any pH range. Third, in the condensation step, it is seen that the hydrolyzed materials are connected by an oxygen bridge. In this step, the increase in condensation forms the polymers; polymer networks cover the entire solution; and gelation occurs [142]. Different techniques used in the drying step result in the formation of different gels (**Figure 5**).

Sol-Gel method is used in many fields: Composites; Porous gels and membranes; Fiber production; Electronic materials; Powder, grain, and spheres; Glass and glass ceramics; Thin film and coatings, etc. Films and coatings were the first commercial applications of the sol-gel method.

In sol-gel coatings made by immersion and spin method, undamaged thin films (<1 mm) are obtained by using a low amount of material. Sol-gel method allows to production of thin films (<1 mm) in safely with low material, chemical, and energy consumption. In addition to these, the following benefits are seen.

- Providing easier coating of some materials such as pipes, tubes, and fibers than conventional methods
- Increasing the mechanical resistance of glasses

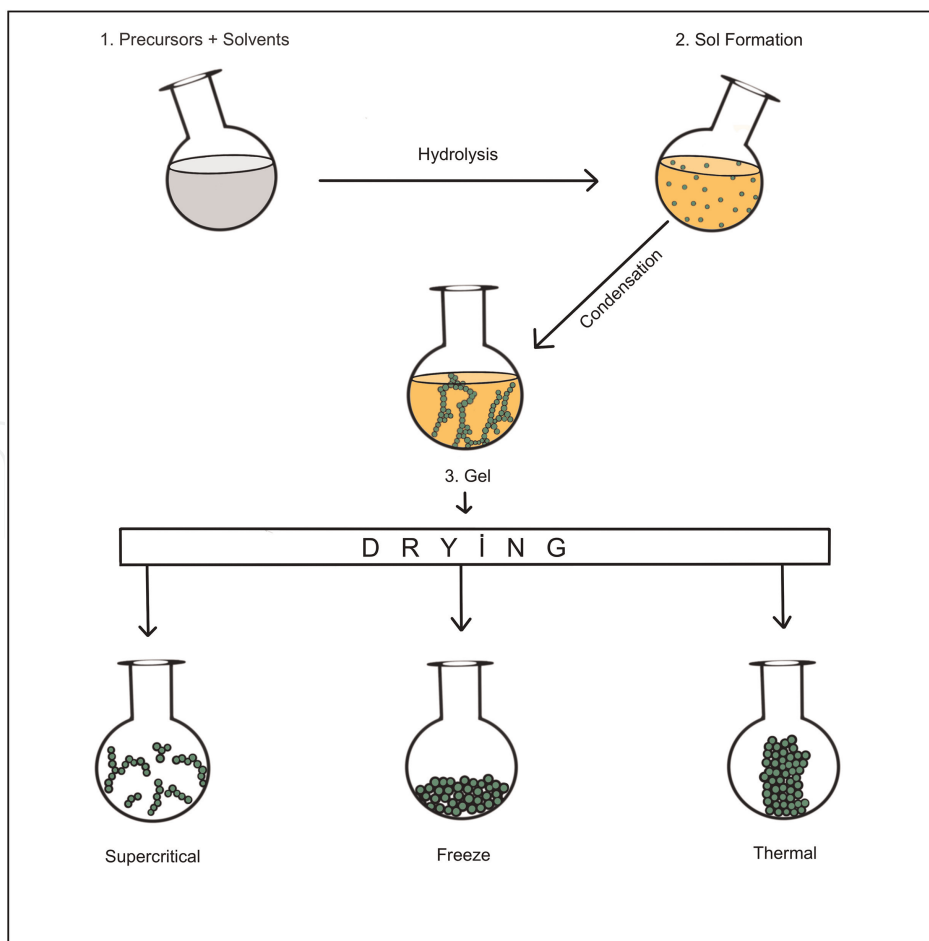


Figure 5. Production of sol-gel [143].

- Protection of steel surfaces against high temperature and corrosion
- Increasing abrasion resistance and flexibility of polyester
- Possibility of very thin surface coatings in medical
- Functional coating materials for textiles

4.4 Grafting

The grafting method can bring in different desired properties to a polymer. By grafting onto textile surfaces, we can obtain functional textiles such as antibacterial, water-repellent, or flame-retardant textiles. However, when we use grafting as a pretreatment, we can increase the efficiency of the subsequent processes and reduce the use of water, energy, and chemicals. The important point here is to ensure the formation of physical, chemical, or ionic bonds between the functional groups that are planned to be added and the macromolecule chain of the textile polymer. In order to achieve this, free radical areas are first formed on the macromolecule chain. Four methods are used for grafting textile surfaces: chemical grafting; vaccination with radiation; inoculation with plasma; and grafting with UV light. Free radical fields formed by these methods play a role as initiators in copolymerization [142].

Many different properties can be added depending on the type of monomer, as follows.

- Water repellency: outerwear, outdoor furniture, tents, awnings
- Water, oil, and stain resistant: interior textiles, automotive textiles
- Antibacterial textiles: hospital textiles, public transport textiles, hotels
- Antistatic: Gas station uniform
- Flame retardant feature: firefighter suit

4.5 Supercritical CO₂

The substances transform into supercritical fluids from on or higher critical temperature and critical pressure values. Supercritical fluids have properties of liquid and gaseous states [144]. Easier and more efficient dyeings are made because of the lower viscosity of supercritical materials compared to liquids, higher diffusion rates, and the swelling effect on the fibers. Carbon dioxide is the most widely used gas for this method because of its advantages such as low critical temperature and pressure, nonexplosive and nonflammable, nontoxic, and inexpensive [145]. Long years the critical point, known as the Cagniard de la Tour point, was discovered in 1822 by Baron Cagniard de la. Hannay and Hogarth discovered in 1879 that solids could be dissolved by supercritical fluids. Many years of work made it possible to use supercritical fluids commercially in 1970. The use of supercritical fluids in textiles began in Germany in the 1980s [2].

Carbon dioxide gas turns into a supercritical fluid at a temperature of 31.1°C and a pressure of 73 atm [146]. Supercritical carbon dioxide can dissolve hydrophobic dyes

such as pigment dyes and disperse dyes, and swell polyester fibers. In this method, dyestuffs show higher dissolution than in water. In this way, the diffusion of the dyestuff into the fibers becomes easier [145].

In this method, first of all, textile material and dyestuff are put into the dye boiler. Then the gas is fed to the boiler at the appropriate pressure. After the three components take their place in the boiler, the temperature is increased to the dyeing temperature by exceeding the critical temperature. In the third step, the critical temperature is exceeded, the dye begins to dissolve, and the fibers swell. Ending the dyeing period, the gas is discharged by reducing the pressure below the critical temperature, and the fabric is taken as dry (**Figure 6**). This method does not require postwashing processes.

Supercritical fluids are also used in distillation and extraction processes besides dyeing. Its usage areas are pharmacy, food industry, polymer science, materials science, environment, chemical processes, hydrocarbon processes, and textile. These methods have some advantages on sustainability such as zero water, zero auxiliary chemicals, low energy, low dyeing time, reuse of carbon dioxide, nontoxic, not harmful to the environment, no need for postwashing, reduced use of dyestuffs due to its high dyeing efficiency. In addition, the advantages encountered in the production process are as follows.

- No auxiliary chemicals are used to dissolve dyestuffs
- No dyebath is prepared for the process
- If dyestuff remains in the boiler after dyeing, it can be reused
- Easy to control painting depth and color
- Diffusion is faster

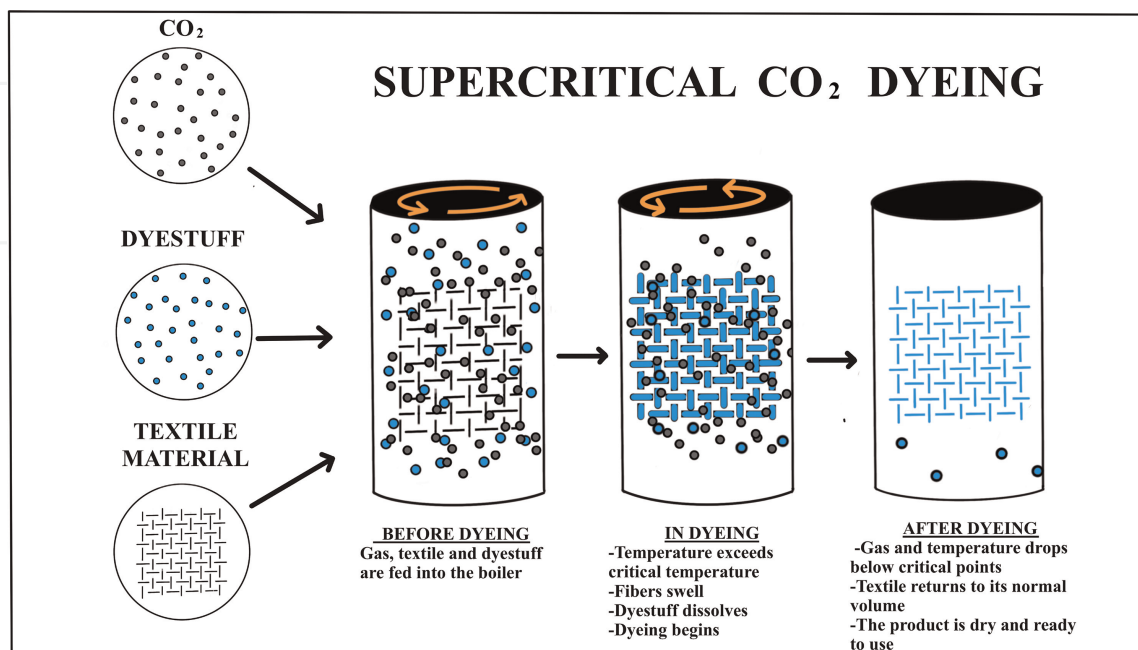


Figure 6.
Processes of supercritical CO₂ dyeing.

- Circulation in the tank is easier with low viscosity
- High dyeing efficiency
- Good color fastness results, bright, and homogeneous colors
- Drying is not required

4.6 Electron beam treatment

The functionalization of textiles can be achieved by processes such as chemical initiators, plasma treatment, and high radiation treatment. Gamma radiation and electron beam are the most common types of radiation. The electron beam offers short processing time, low penetration, and efficient energy use. Since the electron beam process does not require the use of solvents, it reduces the emission of organic compounds during drying. Compared to gamma radiation, electron beam radiation provides some advantages: high efficiency, low maintenance cost, high safety, short processing time, low cost, and high dosing rate [147–149]. Another advantage over gamma radiation is that the electron beam is applied in a single box [149].

In order to provide surface modification with the E-beam method, active sites are created on the surfaces by electron-electron interactions. The electron beam is produced with a high voltage, usually in the range of about 300 keV – 12 MeV. Curing of surface coatings requires low penetration, and electron beam accelerators with an energy range of 150–300 KeV are used [47]. These accelerated electrons interact with polymers physically, physicochemically, and chemically, respectively. In the physical process, short-lived reactive species are formed; In the physicochemical process, these species turn into polymer radicals; and finally, in the chemical process, polymer radicals initiate various reactions in the polymer [147].

4.7 Electrochemical dyeing

In the electrochemical dyeing method, it is made without the use of nonrecyclable chemicals for the reduction and oxidation processes needed in the methods that are widely used in cellulosic fibers such as cube and sulfur dyeing. In this way, there are no regenerated oxidized by-products in the dyebath, no sulfites and sulfates caused by the use of dithionite, and a decrease in chemical oxygen demand values that increase due to organic reductants [47].

In this method, the reduction and oxidation of dyes are done electrochemically by direct or indirect methods [135]. In direct electrolysis, after the dyestuff is partially reduced with a conventional reductant, it is completely reduced by electrochemical reaction, thereby increasing the stability of the dye. Renewable reductants such as Fe₂ Fe₃ are generally used in indirect electrolysis. These reductants are oxidized after reducing the dyestuff and become reusable after being reduced at the cathode [47].

5. Conclusion

Surface modification techniques can transform textiles into functional materials. They can also make basic operations applicable or more efficient when used as preprocessing. These techniques can extend the service life of textile materials.

In this way, it contributes to reduction, reuse, and recycling, which are valuable in terms of sustainability. Some alternative methods allow more “reduction” than conventional methods: oxidative and reductive reduction by electrochemical methods, water and chemical reduction by supercritical fluid method, energy reduction by electron beam method. In addition, some methods may indirectly contribute to sustainability. For example, fabrics treated with environmentally friendly, nontoxic, biodegradable antimicrobial agents prevent microbial contamination as well as prevent the formation of bad odors, thus reducing the use of energy, water, and detergent.

Our resources are running out day by day. We should integrate the concepts of reduce, reuse, and recycle into our daily lives. We suggest some points for a sustainable future: adopting environmentally friendly green production processes, supporting studies on the development of surface modification techniques, and accepting these techniques that support sustainable production as new conventional production methods after they are developed at a sufficient level.

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Author details

Gürsel Korkmaz^{1*}, Mehmet Kılınc², Nur Kılınc³ and Y. Dilek Kut⁴

1 Department of Textile Technology, Sivas Vocational School of Technical Sciences, Sivas Cumhuriyet University, Sivas, Turkey


2 Department of Fashion Design, Şebinkarahisar School of Applied Science, Giresun University, Giresun, Turkey

3 Department of Fashion Design, Şebinkarahisar Vocational Schools of Technical Sciences, Giresun University, Giresun, Turkey

4 Faculty of Engineering, Department of Textile Engineering, Uludag University, Bursa, Turkey

*Address all correspondence to: gurselkorkmaz7@gmail.com

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