Chapter 5
Chemical Properties of Cotton Fiber and Chemical Modification

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5.1 Chemical Properties

Cotton fibers are composed of about 95% of cellulose after ginning and mechanical cleaning. Cellulose is a polysaccharide composed of β-D glucopyranose units covalently linked through 1,4-glycosidic bonds. The number of repeating glucose units, called degree of polymerization, varies with the origin (cultivar) of the raw cotton fibers as well as with the treatment (Klemm et al. 2005; Park et al. 2010).

Cellobiose is the union of two glucose molecules through glycosidic bond (Cocinero et al. 2009). Each successive glucose unit in cellulose macromolecule is rotated 180° around the molecular axis. Each glucopyranose unit of cellulose contains three hydroxyl groups. The hydroxyl groups present on C-6 position are called primary hydroxyl groups, and those on C-2 and C-3 are called secondary hydroxyl groups (Fig. 5.1). The primary group is more easily neutralized and readily available and prominent in chemical reactions of cellulose. Hydroxyl groups are readily involved in intra- and intermolecular hydrogen bonds and lead to ordered crystalline arrangements. Cellulose molecules in cotton are organized into parallel arrangements called crystallites and, subsequently, into larger aggregates called fibrils (Maxwell et al. 2003). Thirty-six cellulosic chains are assembled to compose an elementary fibril (diameter ~3.5 nm). These elementary fibrils, which are taken as the basic crystalline unit of cotton cellulose, are assembled into microfibrils with a diameter varying from 10 to 30 nm (Lee et al. 2000; Peterlin and Ingram 1970). Between the ordered crystalline regions, cellulosic chains are randomly distributed, and these regions are called amorphous regions. While crystalline regions are responsible for the required strength of the fiber, amorphous regions are essential

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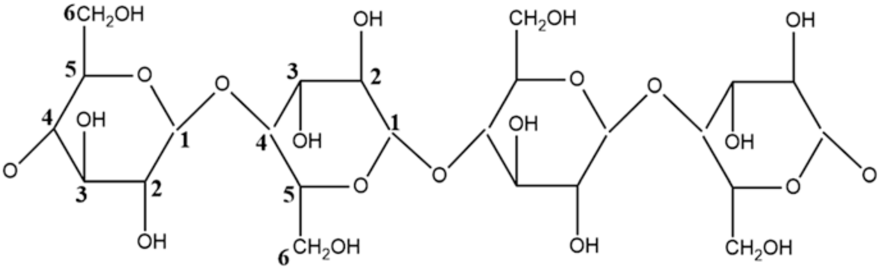

Fig. 5.1 Chemical structure of cellulose

for elasticity, flexibility, and the ability of the fibers to absorb water, dyes, and chemical finishes (Rivlin 1992). Approximately 70–80% of the cellulose in cotton is in crystalline form I_β.

5.2 Cotton Fabric Preparation

In general, cotton fibers are processed (opening, carding, drawing, spinning, and weaving/knitting) in their raw state. The presence of the primary cell wall containing wax and pectins provides the necessary lubrication and prevents static electricity buildup during processing. If waving is desired, yarn is coated with starch or polyvinyl alcohol (this process is termed sizing) to give it stiffness and allow easy waving. The sizing material (starch or polyvinyl alcohol) must be removed when the woven fabric is produced. The process of desizing is then performed, which consists of boiling cotton fabric in water bath containing nonionic wetting agent, hydrogen peroxide, and acetic acid. The desizing process is normally performed at 194 °F for 30 min followed by neutralization with acetic acid. If the size is not removed or partly removed, the remaining starch or polyvinyl alcohol could interfere with the application of the dye and chemical finishing, which may affect the properties of the end product.

Desizing starch can be also achieved using amylase enzymes (Spicka and Tavcer 2013; Eren et al. 2009). Four groups of starch-degrading enzymes exist (Eren et al. 2009): endoamylases, exoamylases, debranching enzymes, and transferases. Typical enzymatic desizing bath contains 10 ml/L of α-amylases, 10 mL/L of amyloglucosidases, and 10 mL/L of pullulanases (Spicka and Tavcer 2013).

To remove noncellulosic compounds present in/on the cotton fibers and expose hydroxyl groups of cellulose to further chemical reaction, a scouring process is performed. The scouring process is normally performed in a solution containing wetting agent (example of wetting agent is Triton X-100), caustic soda, and acetic acid. This treatment solubilizes impurities present on/in cotton fibers. The scouring process, also referred to as alkali boil-off, is typically performed with a strong alkali solution (5–10 g/L sodium hydroxide) close to or above the boiling temperature of water for 1–2 h (Rivlin 1992). The fabric is subjected to hot rinse to remove emulsified impurities followed by neutralization with acetic acid (Rivlin 1992).

To further remove and decompose colored impurities, a bleaching process is performed. This process is performed using hydrogen peroxide and/or sodium chloride. A typical bleaching process is normally performed near the boil or at temperature above the boil using a bath composed of wetting agent, caustic soda (0.5–1% on the weight of the fabric), sodium silicate (2–4% on the weight of the fabric), hydrogen peroxide 35% (4–8% on the weight of the fabric), and acetic acid. A final step of fabric neutralization is done with acetic acid (Rivlin 1992).

An optional treatment is sometimes performed which consists of treating cotton yarn or fabric with concentrated solution of sodium hydroxide (NaOH). This process is referred to as mercerization. The typical mercerization process requires immersing cotton yarn or fabric in caustic soda (20–25%) for brief period of time (less than 5 min) usually under tension followed by rinsing, boiling, and neutralization. The mercerization process has many beneficial effects such as increased tensile strength, increased softness, improved affinity to dyes, improved dyeability of immature fibers, increased luster, and higher water sorption. Changes in the microstructure of fibers occur leading to conversion of the crystal structure from cellulose I to cellulose II and reduction in crystallite size (Rivlin 1992).

5.3 Water/Oil Repellency and Self-Cleaning

The presence of hydroxyl groups on cellulose macromolecules imparts hydrophilicity to cotton fabrics. This property can be changed by altering the surface tension of the fabric to impart water repellency. Changes in the surface tension prevent water from diffusing inside the fibers. The ability of the textile substrate to repel a liquid is assessed by performing water contact angle measurements. In general, a textile fabric is classified as hydrophilic, hydrophobic, or super hydrophobic depending on the values of the contact angles. When the static water contact angle is $<90°$, the textile surface is hydrophilic. When the contact angle is $>90°$ but $<150°$, the surface is classified as being hydrophobic. When the contact angle is $>150°$, the textile surface is said to be super hydrophobic. Reducing the interaction between a drop of a liquid and a textile surface means that the water contact angle is considerably increased. This allows the liquid droplet to easily roll off the surface, which can easily carry with it the dirt on surface. This will impart "self-cleaning properties" to the surface. Functionalization of textile substrates to impart water repellency is achieved by using hydrophobic compounds such as silicones (Liu et al. 2009b; Hsieh et al. 2010) and fluorocarbons (Di Mundo et al. 2009; Favia et al. 2003; Kulinich and Farzaneh 2005; Liu et al. 2009a). However, the drawbacks of these approaches are disposal of solvents, inhomogeneous distribution of the reactants on the surface, control of the reaction, and generation of toxic effluents. To overcome these drawbacks, the focus has been on using a "dry process" such as plasma technology and molecular vapor deposition.

5.3.1 Plasma Modification

The plasma is composed of radicals, metastable molecules, photons, and charged particles such as ions and electrons (Abidi and Hequet 2004). Plasma is generally generated by exposing a gas (such as Ar, N_2, O_2, etc.) to radiofrequency or microwave electrical discharges. Because plasma density is proportional to the square root of the frequency, the degree of ionization increases with increasing frequency. Microwave plasma produces higher density of reactive particles compared to radiofrequency. Plasma technology is attractive for surface modification of textile substrates. Its advantage is that no toxic radicals are used as initiators or cross-linkers, and the amount of toxic effluents is minimized. In addition, the temperature of the plasma-treated substrate does not increase, which makes the plasma process a cold process. No thermal degradation of the textile substrate occurs. Furthermore, the effect of the plasma does not penetrate more than 100 nm from the surface. Therefore, the cotton fabric retains most of the desirable physical properties (Abidi and Hequet 2004; Bhat and Benjamin 1999).

Abidi and Hequet reported on the impact of the microwave plasma on the physical properties of cotton fabric (Abidi and Hequet 2005). In their experiments, the authors exposed cotton fabric to Ar-plasma for a period of time varying between 60 and 400 s and at varying microwave power between 100 and 500 W. the results showed that exposing cotton fabric to Ar-plasma for 240 s at 500 W resulted in only 0.4% weight loss, and no adverse effects on the cotton fabric breaking strength were observed (Abidi and Hequet 2005).

Abidi and Hequet used microwave plasma to impart water repellency to cotton fabric (Abidi and Hequet 2004). Cotton fabric was exposed to Ar-plasma for a specified period of time (240 s). This initial treatment cleans the surface from oils and contaminants and creates radicals on the surface of cellulose. Plasma-treated fabric was then immersed in a vinyl laurate monomer ($CH_3(CH_2)_{10}COOCH{=}CH_2$) solution in xylene. Treated fabrics were then dried and exposed again to Ar-plasma. Fourier transform infrared spectroscopy was used to investigate the grafting efficiency of vinyl laurate monomer on the surface of the cotton fabric. The presence of the vibrations located at 2923, 2855, and 1735 cm^{-1} in the spectra of the treated fabric illustrated the successful grafting of vinyl laurate induced by microwave plasma (Abidi and Hequet 2004). It was reported that the concentration of vinyl laurate should be below 0.664 mol/L for maximum grafting efficiency. This indicated that the use of plasma for monomer grafting on textile substrate should be optimized. The result of the water repellency test showed a water contact angle of 125°, which indicated a hydrophobic cotton fabric surface. The durability to home laundering and tumble drying indicated no effect up to ten laundering cycles (Abidi and Hequet 2004).

Cabrales and Abidi used microwave plasma to graft oleic acid ($CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$) on the cotton fabric surface (Cabrales and Abidi 2012). Cotton fabric was first exposed to Ar microwave plasma and then immersed in oleic acid solution in xylene. Fourier transform infrared spectroscopy was used to determine the efficiency of grafting, and the water repellency of grafted fabric was assessed by measuring the water contact angle.

5.3.2 Molecular Vapor Modification

Chemical vapor deposition (CVD) represents a chemical reaction process which is conducted in a vapor phase. This process allows the deposition on a surface of atoms, molecules, or both. This technique was used back in 1880 to coat filaments in incandescent lamps with carbon and metal (Pierson 1999). CVD was used in the past to make hydrophobic surfaces (Nakajima et al. 2001). Atomic layer deposition (ALD) is a subcategory of CVD. ALD leads to low and precise thickness of the deposited material (angstrom scale) as well as a high uniformity of the coating. Furthermore, because the reaction occurs in a gas phase, coating can also be deposited in the pores of the substrate surface (Pierson 1999). Aluminum oxide can be deposited onto a surface by means of ALD process. In this process, trimethylaluminum/water binary chemicals are used in the CVD and ALD processes to add additional layers through a sequential reaction (Dillon et al. 1995).

CVD technique is sometimes referred to as nanoparticle vapor deposition (NVD). NVD is similar to ALD with only one exception. In NVD, two binary chemicals are injected at the same time or when the other chemical is present. However, in ALD, each chemical is added to the reaction chamber separately.

NVD and MVD were used to prepare super hydro-/oleophobic cotton fabrics (Abidi et al. 2012; Aminayi and Abidi 2013). Cotton fabric surface was first roughened using trimethylaluminum/water nanoparticles followed by functionalization with (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane. Measurements of water contact angles indicated that this process could impart unique hydro-/oleophobic properties (contact angle >160°). The chemicals used to create this surface as well as the thickness of the coatings produced could be controlled. This leads to the generation of minimum waste of reactants as well as preserving the beneficial properties of the fabric.

Self-cleaned textiles have gained interest recently. Self-cleaning property can be imparted either by functionalizing cotton fabric to impart super hydrophobicity (contact angles >150°) (Aminayi and Abidi 2015) or by imparting photocatalytic properties (Abidi et al. 2009). Aminayi and Abidi used nanoparticle vapor deposition of aluminum oxide to create a rough surface followed by molecular vapor deposition of (tridecafluoro-1,1,2,2-tetrahydrooctyl) trichlorosilane (Fig. 5.2) (Aminayi and Abidi 2013).

The advancing contact angle, after the liquid drop advances on the surface, is in general higher than the receding contact angle (after the droplet recedes from a previously wetted surface). The difference between the advancing and receding

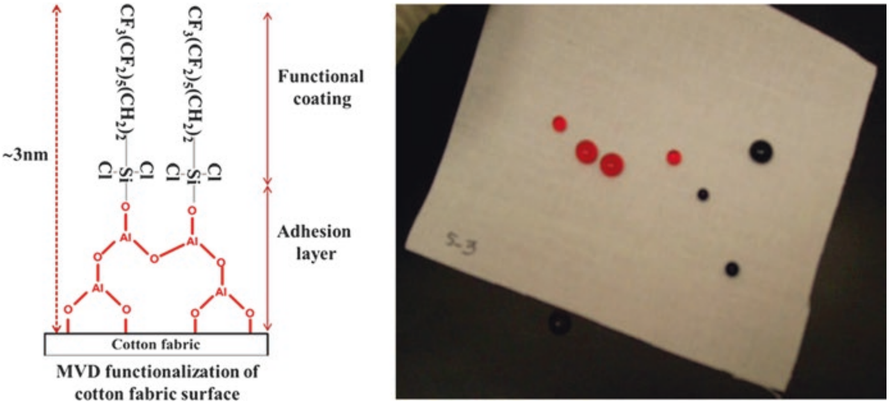

Fig. 5.2 Functionalization of cotton fabric to impart super hydrophobic/oleophobic properties for self-cleaning

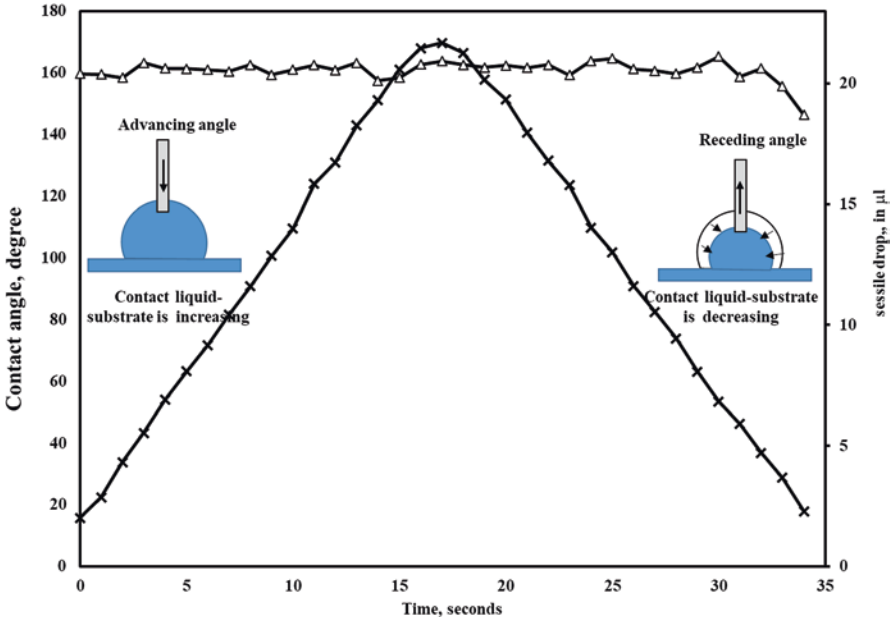

Fig. 5.3 Advancing and receding contact angles

contact angle values is called “hysteresis.” This value can be described as the change in the adsorption of liquid on a solid surface as a consequence of the change in the surface energy or the “roughness of the surface.” Figure 5.3 shows the advancing and receding contact angles of water on cotton fabric after a treatment consisting of N_2-plasma followed by MVD deposition of trimethylaluminum nanoparticles, then MVD deposition of a bifunctional trichlorosilane blend, and finally MVD deposition of a (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane layer (FOTS).

5.4 Antimicrobial Properties

To impart antimicrobial properties, cotton fabrics have been treated with polyethylene glycol (Vigo and Leonas 1999), zirconium complexes (Morris et al. 1981), metallic and organometallic salts (Morris et al. 1981), and natural and inorganic substances such as tea extracts, chitosan, copper, zinc, etc. (Jeon et al. 2003). Silver is widely used as antimicrobial agent. Silver/sodium carboxymethyl cotton for burn dressing was developed by partial exchange of Na^+ by Ag^+ (achieved by treating sodium carboxymethyl nonwoven cotton gauze with $AgNO_3$) (Parikh et al. 2005). The most promising approaches to impart antimicrobial properties are the sol-gel process and cyclodextrins treatment.

5.4.1 Sol-Gel Process

Tarimala et al. used the sol-gel process to impart antimicrobial properties to cotton fabric (Tarimala et al. 2006). The authors used dodecanethiol-capped silver nanoparticles (prepared from silver nitrate, tetraoctylammonium bromide, chloroform, sodium borohydride, and 1-dodecanethiol), tetraethyl orthosilicate, ethanol, and water. Cotton fabric was dipped into the solution, soaked for 5 min, and padded at a speed of 4 yd min^{-1} at 2.76 10^5 Pa. The treated fabrics were dried at 60 °C for 10 min and cured at 150 °C for 5 min. Scanning electron microscopy showed the formation of homogenous and uniform coating on the fiber surface. The measurements of antimicrobial properties against *Escherichia coli* were performed by measuring the optical density of the medium containing the bacteria at 600 nm. Treated fabric showed excellent performance against *Escherichia coli.*

5.4.2 Cyclodextrin Modification

In textile applications, cyclodextrins have been used to impart various functional properties such as UV protection (El-Tahlawy et al. 2007; Scalia et al. 2006a, b), slow release of fragrances (Martel et al. 2002), insecticide delivery (Romi et al. 2005), and antibacterial properties (Wang and Cai 2008). Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) is a broad-spectrum antibacterial and antifungal agent. It is widely used in consumer products, and its reaction with β-cyclodextrin has been reported in previous studies (Lu et al. 2001; Loftsson et al. 2005).

Several studies reported on the use of monochlorotriazinyl-β-cyclodextrin (MCT-β-CD) to modify textiles (Rehmann et al. 2003; Scalia et al. 2006b; Romi et al. 2005; Wang and Cai 2008). Monochlorotriazinyl functional groups form covalent bonds with hydroxyl groups in cellulose (Fig. 5.4). Hydroxyl groups in cellulose serve as reactive anchors for reactive dyes (Reuscher and Hirsenkorn 1996). MCT-β-CD is the first reactive cyclodextrin derivative produced industrially for textile applications (Szejtli 1997).

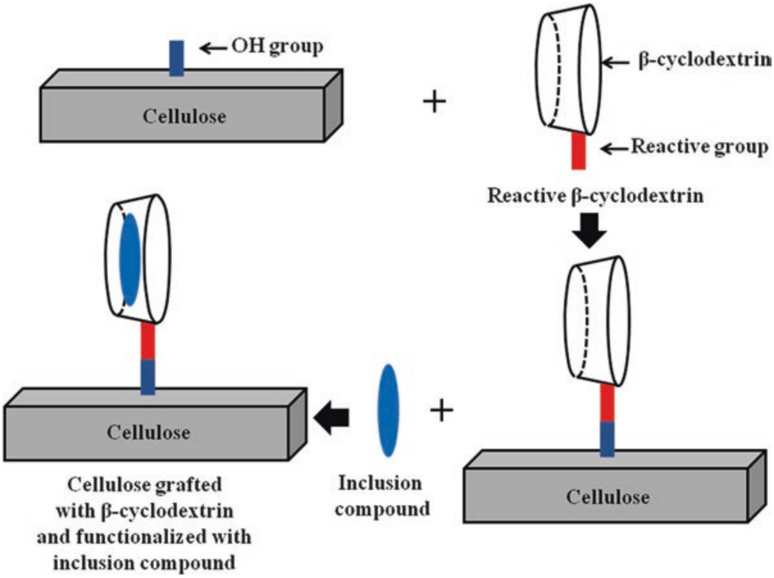

Fig. 5.4 Schematic illustration of the grafting of β-cyclodextrins on cellulose and inclusion of guest compounds in the cavities

MCT-β-CD was grafted to cotton fabrics (Cabrales et al. 2012). MCT-β-CD was stirred for 5 min, and then sodium carbonate (Na_2CO_3) was added to the solution. The amount of Na_2CO_3 was ¼ of the amount of MCT-β-CD. The solution was stirred for 5 min, and the pH of the solution was maintained at 11.5. Cotton fabrics were immersed into MCT-β-CD solution for 5 min and passed through a two-roller laboratory padder (BTM 6-20-190) at a speed of 365 cm/min and an air pressure of 41 kPa. Treated fabrics were dried for 10 min at 50 °C and cured at 150 °C for 10 min in a Ben Dry-Cure Thermosol Oven. Samples were rinsed with water and dried. Figure 5.5 shows an illustration of the chemical reaction between MCT-β-CD and cellulose.

To impart antimicrobial properties, triclosan inclusion in the cavities of cyclodextrins was performed. MCT-β-CD-grafted cotton samples were placed in triclosan solution in ethanol (0.01 mol L^{-1}) for 24 h. Figure 5.6 shows the inclusion of triclosan inside MCT-β-CD cavities. Treated cotton fabrics were dried for 30 min at 40 °C, rinsed with distilled water and with 50% ethanol-water solution, and then dried for 30 min at 40 °C. The 50% ethanolic solution was used due to the low solubility of triclosan in water. Triclosan molecules can be adsorbed also on the fabric surface but not forming inclusion compounds with cyclodextrins. These molecules could interfere with the spectroscopic quantification of the inclusion compounds. Rinsing with alcoholic solutions has been reported to remove adsorbed triclosan molecules on the textile surfaces (Scalia et al. 2006b). Thus, MCT-β-CD-grafted cotton samples were placed in a beaker containing 10 mL of ethanol for 24 h.

To assess the antimicrobial efficiency, colony-forming unit (CFU) of *S. aureus* was measured (Tran et al. 2009; Cabrales et al. 2012). Figure 5.7 shows the CFU of

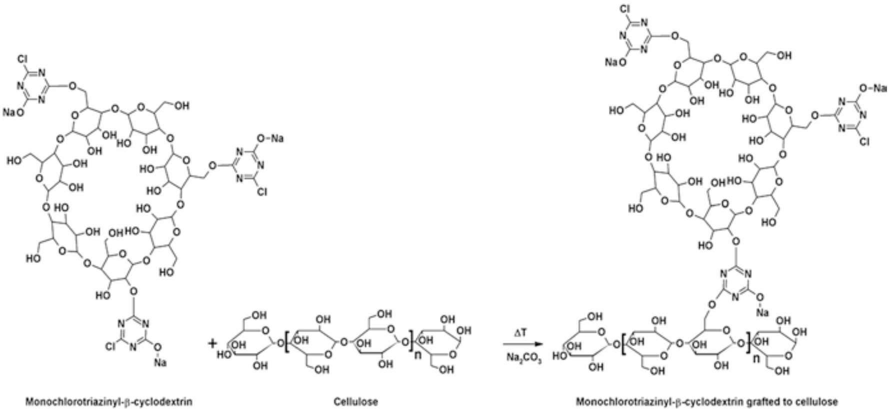

Fig. 5.5 Chemical reaction between monochlorotriazinyl-β-cyclodextrin and cellulose

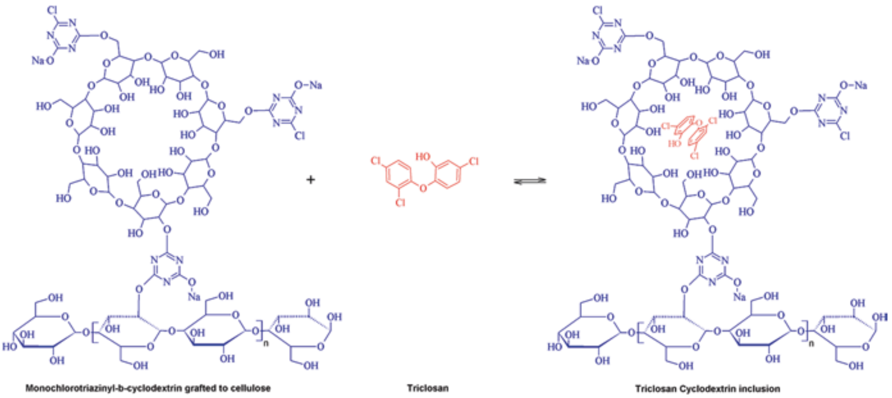

Fig. 5.6 Inclusion of triclosan inside MCT-β-CD cavities

S. aureus of untreated control fabric and MCT-β-CD-grafted cotton fabrics. MCT-β-CD-treated cotton fabric loaded with triclosan molecules exhibited excellent antimicrobial activity against *S. aureus* (100% inhibition efficiency). Upon rinsing the MCT-β-CD-grafted cotton with ethanol, the fabric did not exhibit its antimicrobial property. This indicated that guest compounds in MCT-β-CD cavities can be removed, allowing other guest compounds to be incorporated.

5.5 UV Protection

Ultraviolet radiation (UVR) is composed of UV-A (ranging between 320 nm and 400 nm), UV-B (ranging between 290 nm and 320 nm), and UV-C (ranging between 100 nm and 290 nm). UV-C is absorbed by the ozone layer; however, UV-A and

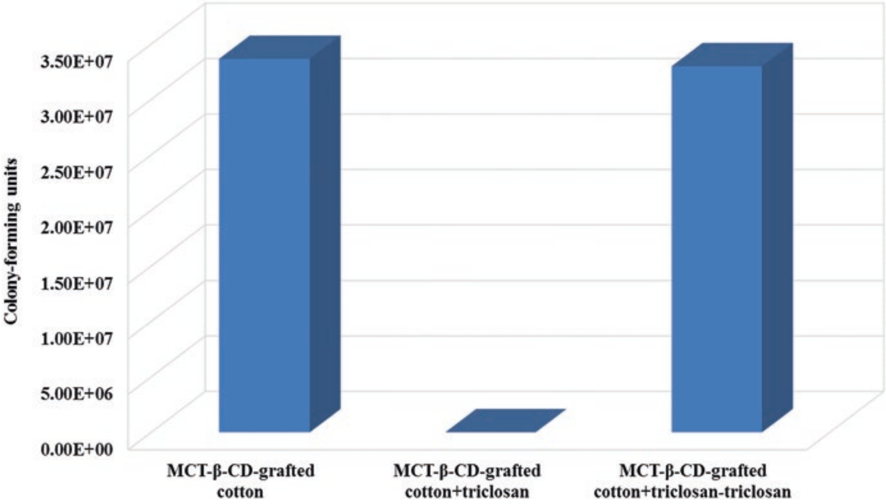

Fig. 5.7 Antibacterial activity test of MCT-β-CD-grafted cotton fabric, MCT-β-CD-grafted cotton fabric with triclosan included in cyclodextrins cavities, and MCT-β-CD-grafted cotton fabric with triclosan included in cavities and then washed with ethanol

UV-B reach the earth surface and can cause various health issues such as skin cancer, sunburn, and photoaging. Special focus has been on UVR transmission of textiles because of the growing demand in the marketplace for lightweight apparel that offers protection from UVR while fostering comfort.

Srinivasan et al. studied the characteristics of the dye and the UV protection provided by the dyed fabrics (Srinivasan and Gatewood 2000). The authors reported that color is not a reliable indicator of the UV protection of the dyed fabrics. Zhou et al. showed that when optical brighteners were added to laundering detergents, the UVR-blocking ability of cotton fabrics and cotton/polyester blends is improved (Zhou and Crews 1998). Eckhardt and Rohwer investigated the factors affecting the UVR transmission of undyed fabrics (Eckhardt and Rohwer 2000). It was concluded that the single best predictor of the ability of undyed woven fabrics to pass the UV-damaging wavelengths was the fabric porosity.

The effect of the concentration of the UV absorber (Rayosan™) was investigated. Scoured and bleached 100% cotton fabrics (typical lightweight summer clothes) were treated using exhaustion method. Figure 5.8 shows the evolution of the UPF as a function of the concentration of the UV absorber. The nonlinear relationship shows that high UV-absorber concentrations result in higher UPF values until a plateau is reached above 8%. The plateau is explained by the saturation of sites (cellulosic OH groups) available for chemical reaction. When the percentage of the UV absorber is greater than 5%, fabric A provides excellent protection from UVR (UPF $\geq$ 40), while fabric B provides only a good protection. This demonstrates that the type of the substrate and the concentration of the UV absorber impact the level of protection provided by the cotton fabric.

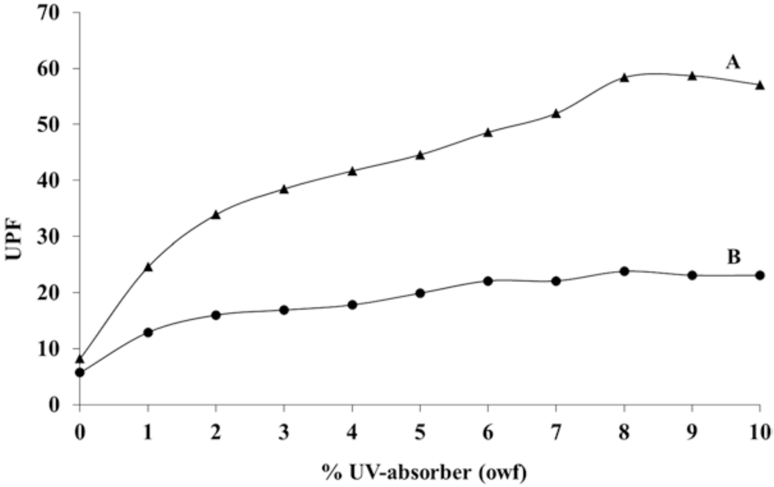

Fig. 5.8 Evolution of the ultraviolet protection factor as a function of UV-absorber concentration. Fabric A: 22.8 Ne, 4.15 oz./yd^2, Fabric B: 40.4 Ne, 3.32 oz./yd^2

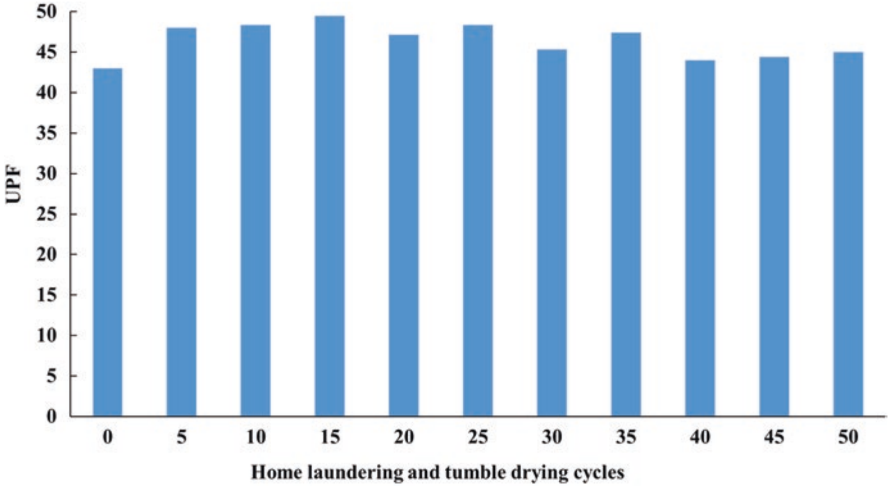

Fig. 5.9 Woven cotton fabric treated with UV absorber: UPF vs. washing cycles

The durability of the treatment was tested after 40 cycles of laundering and tumble drying. Figure 5.9 shows that repeated laundering and tumble drying have no effect on the level of the UVR protection. There is actually a slight increase after 40 cycles, which is attributed to optical brighteners present in commercial detergent used during laundering. The durability of the treatment is attributed to the chemical constitution of this UV absorber. It is a “colorless” reactive dye, formulated from chlorotriazine functional groups, which reacts with cellulose hydroxyl groups through nucleophilic substitution and establishes covalent bonds with cellulose.

5.6 Wrinkle Recovery

Cotton fibers are composed of cellulose macromolecules with repeating anhydroglucose units. The degree of polymerization (number of anydroglucose units) can very between 8000 and 15,000 depending on the cotton cultivar. On each anydroglucose unit, there are three available hydroxyl groups (–OH), which serve as sites for water molecule absorption by establishing many hydrogen bonds with cellulose macromolecules (Fig. 5.10).

When subjected to a deformation, fabrics made of cotton have the tendency to wrinkle. In this process, hydrogen bonds between cellulosic chains in the amorphous regions of fibers break, which allows the chains to slip past one another. Because of the presence of many hydroxyl groups, the hydrogen bonds then reform in new places holding creases and wrinkles in the fiber and fabric. By preventing or restricting cellulosic chain slippage, cotton fabric can resist to the deformation, and wrinkles are not formed or minimized (Perkins 1996). The fabric appears smooth and free of surface deformation. Replacing weak hydrogen bonding by strong covalent bonding in the amorphous regions of the fibers, using appropriate chemical treatment, can restrict the chain slippage of the cellulosic chains (Fig. 5.11).

N-methylol-based products with very low formaldehyde release have been used by the textile industry for many years as cross-linking agent. Other promising compounds are polycarboxylic acids such as 1,2,3,4-butanetetracarboxylic acids and citric acids (Dehabadi et al. 2013). The traditional method for imparting wrinkle-free property is based on the pad-dry-cure process. It consists of impregnating the sample in an aqueous solution containing the cross-linking agent and the appropriate catalyst, padding the impregnated fabric to reach a wet pickup of 90–100%,

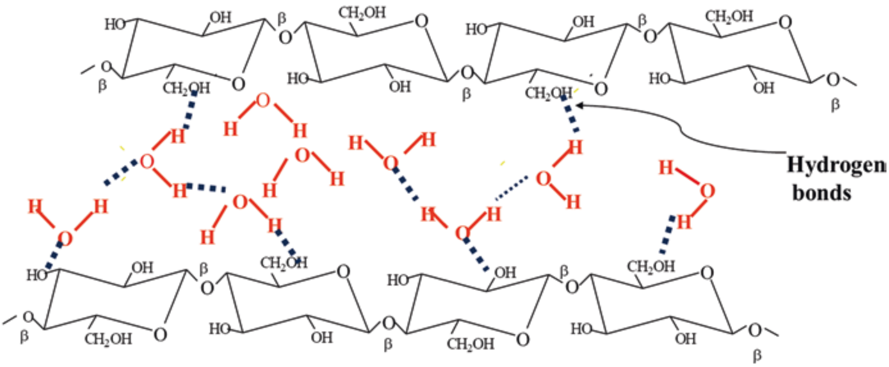

Fig. 5.10 Hydrogen bonding in cellulose

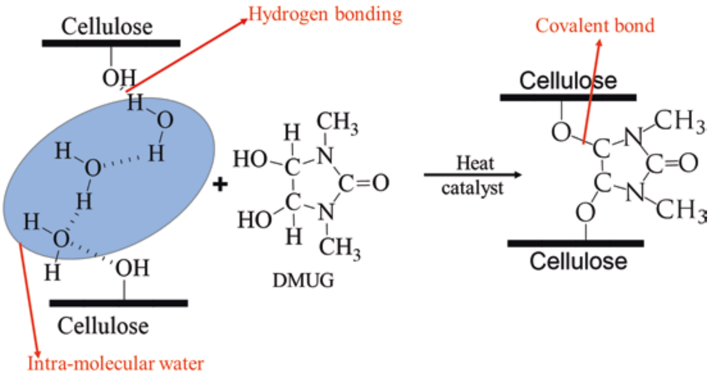

Fig. 5.11 Chemical cross-linking of cellulose chains in cotton fabric to prevent the appearance of wrinkles

drying at 100 °C to remove water, and then curing at 150 °C to establish covalent links between cellulose chains and the cross-linking agent.

The term durable press refers to the smoothness of the fabric. This term is used to describe textile apparels which possess certain wrinkle-resistance properties during daily wear and which require little or no ironing after home laundering and tumble drying.

The American Association of Textile Chemists and Colorists (AATCC) Test Method (TM) 124 outlines the protocol for ascertaining a smoothness grade to a fabric. This test is designed to evaluate the smoothness appearance of fabric specimens after five cycles of repeated home laundering and tumble drying. In general, three trained observers visually evaluate the appearance of the cross-linked fabrics by laying the specimen on a solid surface standing at an incline of 5° from the vertical under specified lighting conditions. The specimen is then compared to six standard replicas (3-D plastic models) showing varying degrees of smoothness and having grades 1 (very wrinkly), 2, 3, 3.5, 4, and 5 (very smooth). The specimen is assigned the grade of the replica it most closely resembles.

Abidi et al. reported on the cross-linking of cotton fabric with DMUG (Abidi et al. 2005). The authors reported an increase in the durable press and wrinkle recovery angle (Fig. 5.12) and drastic decrease in abrasion resistance and breaking force (Fig. 5.13). Overall, there is 50% decrease in breaking strength of the treated fabric and 90% decrease of the abrasion resistance. Cellulose cross-linking in cotton fabric results in stiff material, which can break easily. Furthermore, because chemical cross-linking occurs between OH groups of cellulose and the cross-linking agent, drastic decrease is also observed in the amount of adsorbed water and amount of fixed dye molecules. Wrinkle-free-treated cotton fabrics are often white or light shade color.

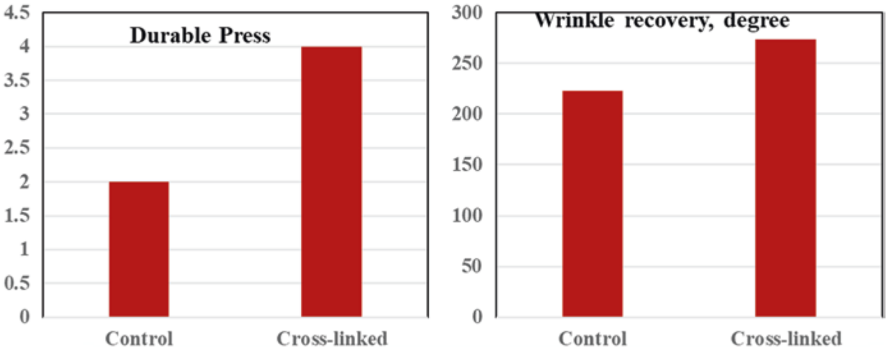

Fig. 5.12 Durable press and wrinkle recovery angle (sum of the warp and filling) of the control and cross-linked cotton fabric

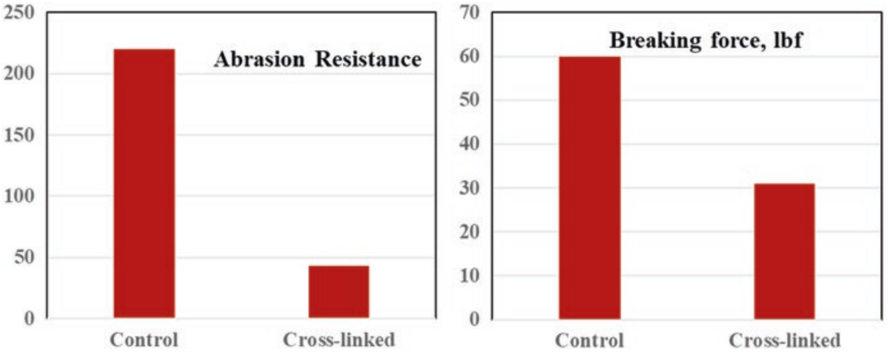

Fig. 5.13 Flex abrasion resistance (in cycles) and breaking for of the control and cross-linked cotton fabric

5.7 Water Repellency Combined With Wrinkle-Free Treatment

Abidi et al. reported that cotton fabric can be easily functionalized with vinyltrimethoxysilane ($H_2C{=}CH{-}Si(OCH_3)_3$) to impart water repellency and wrinkle recovery (Abidi et al. 2007). Functionalization with vinyltrimethoxysilane introduces reactive surface vinyl groups ($-CH{=}CH_2$), which can be used to graft monomers through addition polymerization (Fig. 5.14). The presence of vinyl groups on the surface of the fabric was confirmed by universal attenuated total reflectance FTIR (UATR-FTIR) spectrum of the treated fabric (vibrations 1410 cm^{-1} and 1600 cm^{-1} assigned to C=C stretch and the vibration 756 cm^{-1} assigned to Si-O-Si symmetric stretch).

Figure 5.15 shows the water contact angle and wrinkle recovery angle values as a function of the concentration of vinyltrimethoxysilane. For low concentration of VTMS (<1 mol/L), the treated fabric is hydrophilic. However, the increase of the

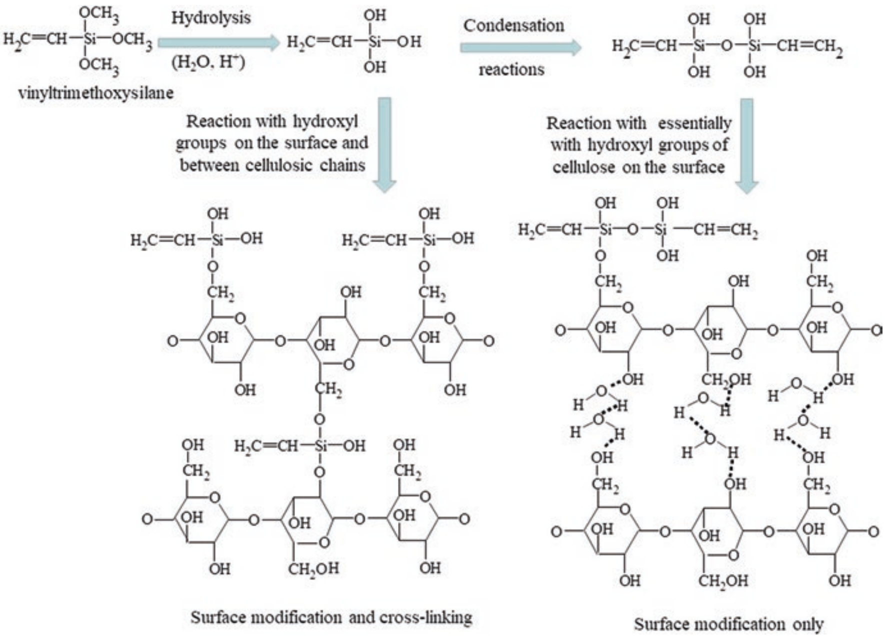

Fig. 5.14 Functionalization of cotton cellulose with vinyltrimethoxysilane (Adapted from (Abidi et al. 2007))

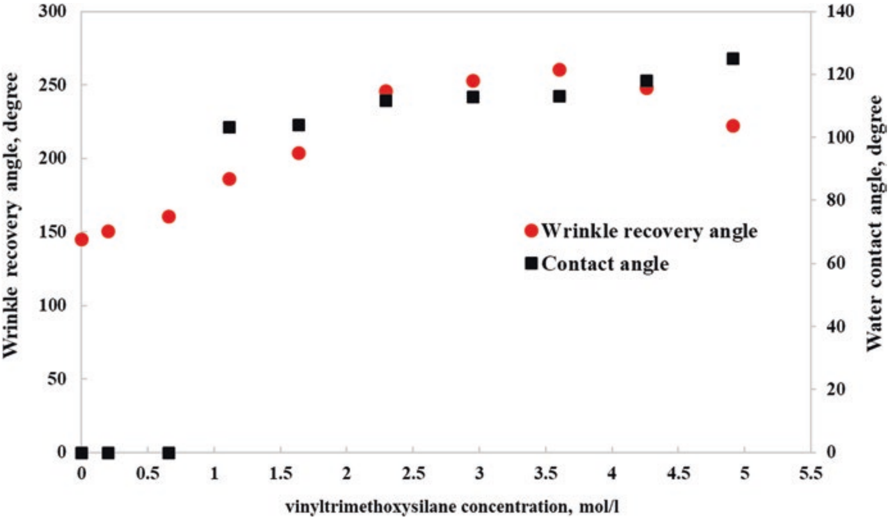

Fig. 5.15 Effects of vinyltrimethoxysilane concentration on the wrinkle recovery and water contact angle

concentration of VTMS increases the contact angles as well as the wrinkle recovery angle values (Fig. 5.15). This demonstrated that the coverage of the surface with (Si-O-Si chains) as well as cross-linking of cellulosic chains occurs.

5.8 Other Finishes

5.8.1 Softening Finish

During the preparation of cotton fabrics for dyeing and finishing, natural waxes are removed by means of scouring and bleaching processes (Schindler and Hauser 2004). Textiles can become embrittled. Treatment with softeners can overcome this deficiency and impart softness. Softening finishes are among the most important of textile chemical after treatment. Applying chemical softeners to textiles imparts soft hand, some smoothness, flexibility and better drape, and pliability. Softeners provide their main effects on the surface of the fibers. Small softener molecules penetrate between fibers and act as internal plasticizer. The physical arrangement of the softener molecules on the fiber surface is important and depends on the ionic nature of the softener molecule and the relative hydrophobicity of the fiber surface. Cationic softeners (e.g., $R_1R_2N(CH_3)_2^+Cl^-$) orient themselves with their positively charged ends toward the partially negatively charged fiber, creating a new surface of hydrophobic carbon chains that provide excellent softening and lubricity seen with cationic softeners. However, anionic softeners (R_1–O–SO_3^- Na^+) orient themselves with their negatively charged ends repelled away from the negatively charged fiber surface, which leads to higher hydrophilicity but less softening than with cationic softeners.

Cationic softeners provide the best softness and are reasonably durable to laundering. They can be applied using exhaustion method to all fibers from a high liquor to goods ratio. The finished textile products acquire hydrophobic surface. Anionic softeners are generally stable to heat at normal textile processing temperatures and compatible with other components of dye and bleach baths.

5.8.2 Flame-Retardant Finishes

The resistance of textile apparels to fire is imparted to textiles using flame-retardant finishes (Schindler and Hauser 2004). Protecting consumers, firefighters, and emergency personnel requires protection from flames. Floor coverings, mattresses, furniture, and drapery also require flame-retardant treatment, especially when used in public buildings. Military and airline industries have multiple needs for flame-retardant textiles. Commercially efficient flame-retardant agents should have little or no adverse effect on the textiles' physical and aesthetic properties, should be produced by a simple process with conventional equipment and inexpensive chemicals, and should be durable to repeated home laundering/tumble drying and dry cleaning.

The mechanism of combustion should be explained in order to understand the mechanisms of effective flame retardants. Combustion is an exothermic process that requires three components: Source of heat, source of oxygen, and suitable fuel. Combustion can be self-catalyzing and can continue as long as oxygen, fuel supply, or excess heat is available. When textiles are exposed to heat, the temperature of fibers increases until the pyrolysis temperature (*Tp*) is reached. At this temperature, fibers are subjected to irreversible chemical changes leading to the production of nonflammable gases, char, liquid condensates, and flammable gases. If the temperature continues to increase until it reaches the temperature of combustion (*Tc*), flammable gases are generated. The combustion process can generate additional heat needed to continue the pyrolysis. Therefore, flame-retardant chemicals applied to textile should disrupt this cycle. Several approaches have been proposed (Schindler and Hauser 2004). Providing a heat sink on or in the fiber by using materials that, when subjected to heat, thermally decompose through strongly endothermic reactions. When enough heat is absorbed by these reactions, the pyrolysis temperature of the fiber is not reached, and no combustion takes place. Examples of these chemical compounds include the use of aluminum hydroxide three hydrate (Al_2O_3 $3H_2O$) and calcium carbonate ($CaCO_3$) as fillers in polymers and coatings. When subjected to heat, Al_2O_3 $3H_2O$ changes to Al_2O_3 and $3H_2O$, while $CaCO_3$ changes to CaO and CO_2. Another approach consists of applying a material (such as boric acid and its hydrate salts) which is able to form an insulating layer around the fiber at temperatures below the pyrolysis temperature of the fiber. When subjected to heat, treated textiles with boric acid and its hydrate salts, boric acid-based compounds release water vapor and produce a foamed glassy surface on the fiber, insulating the fiber from the applied heat and oxygen. Other approaches to achieve flame retardancy consist of influencing the pyrolysis reaction to produce less flammable volatiles and more residual char. This class of chemical compounds is based on phosphorous-containing flame retardants. This class of compound, after they produce phosphoric acid through thermal decomposition, cross-links with hydroxyl-containing polymers which alter the decomposition and yield less flammable by-products.

The thermal degradation of cellulose fibers leads to the formation of small depolymerization products such as levoglucosan. Levoglucosan volatile pyrolysis products are extremely flammable materials and are the main contributors to cellulose combustion. Therefore, chemical compounds designed to act as flame retardants for cellulose should prevent levoglucosan formation. Phosphoric acid acts as an effective flame-retardant agent by reducing levoglucosan generation and catalyzes the dehydration and the carbonization. Chemical compounds which can lead to phosphoric acid formation during early stages of fiber pyrolysis can act as successful flame retardants for cellulose.

5.8.3 *Enzymatic Modification*

The use of enzymes for cellulosic textiles treatment can produce permanent effects (Schindler and Hauser 2004). This process is termed as bio-finishing or bio-polishing. This process removes protruding fibers and slubs from the fabric surface, which can significantly affect the appearance of the fabric by reducing pilling and providing softness and smoothness to the fabric. In the denim process, bio-finishing is used to reduce the abrasive stones and the aggressive chlorine chemistry to impart the desired "worn" look that the consumers desire. The bio-finishing process suffers from several disadvantages such as formation of fiber dust, reproducibility of the effect, and loss of strength. The enzymes used for cellulose treatment are high molecular weight proteins having complex three-dimensional structures composed of long chains of amino acids. The enzyme and substrate form "lock and key" complex that requires the enzyme to have a specific molecular alignment in order to act as a catalyst. The enzymes that hydrolyze cellulose are found in nature in both *Trichoderma* and *Humicola* fungi. *Cellulases* can catalytically hydrolyze the β(1–4) linkages between adjacent repeating glucose units in cellulose. Enzymes contain multiple components that work synergistically to yield glucose from cellulose. At least four components have been identified as being important in providing efficient glucose production. Endo-glucanases hydrolyze cellulose at random locations. Beta-glucanases hydrolyze cellulose polymers from the nonreducing end producing glucose and leaving cellulose chain with one less repeating unit. Cellobiohydrolases produce cellobiose. Cellobiases convert cellobiose into glucose.

It is generally accepted that the mechanism of cellulase interactions with cellulose is via first an adsorption of endo-glucanase, beta-glucanase, or cellobiohydrolase components onto the fiber surface followed by complex formation with the cellulose polymer chain and water. The action of enzymes on cellulose is affected by several factors such as pH, temperature, time, and mechanical agitation. Because enzymes are true catalysts and are not consumed during the chemical reaction, cellulose hydrolysis will continue until the conditions of the reaction are changed (change of the pH or temperature) or until cellulose is removed from the solution.

5.9 Conclusions

Cotton fabric finishing is the most important final step to impart the required functional properties that the consumers desire. The term finishing is often broadly used to describe any treatment to improve the quality of the fabric. This chapter reviewed the most important treatment to impart functional properties. Wrinkle-resistance treatment is performed to prevent the formation of wrinkles on the fabric surface after home laundering and tumble drying. Water and oil repellency treatment is performed to limit liquid or oil diffusion inside the fabric. Antimicrobial treatment is performed to protect against the growth of microorganisms. Flame-retardancy treatment is applied to protect consumers from unsafe textiles. UV protection treatment is required to protect sensitive skins from harmful effects of sunlight ultraviolet radiation.

References

Abidi N, Aminayi P, Cabrales L et al (2012) Super-hydrophobic cotton fabric prepared using nanoparticles and molecular vapor deposition methods. In: Functional Materials from Renewable Sources, vol 1107. American Chemical Society, Washington, pp 149–165

Abidi N, Cabrales L, Hequet E (2009) Functionalization of a cotton fabric surface with Titania Nanosols: applications for self-cleaning and UV-protection properties. ACS Appl Mater Interfaces 1:2141–2146

Abidi N, Hequet E (2004) Cotton fabric graft copolymerization using microwave plasma. I. Universal attenuated total reflectance-FTIR study. J Appl Polym Sci 93:145–154

Abidi N, Hequet E (2005) Cotton fabric graft copolymerization using microwave plasma. II. Physical properties. J Appl Polym Sci 98:896–902

Abidi N, Hequet E, Tarimala S (2007) Functionalization of cotton fabric with vinyltrimethoxysilane. Text Res J 77:668–674

Abidi N, Hequet E, Turner C et al (2005) Objective evaluation of durable press treatments and fabric smoothness ratings. Text Res J 75:19–29

Aminayi P, Abidi N (2013) Imparting super hydro/oleophobic properties to cotton fabric by means of molecular and nanoparticles vapor deposition methods. Appl Surf Sci 287:223–231

Aminayi P, Abidi N (2015) Ultra-oleophobic cotton fabric prepared using molecular and nanoparticle vapor deposition methods. Surf Coat Technol 276:636–644

Cabrales L, Abidi N (2012) Microwave plasma induced grafting of oleic acid on cotton fabric surfaces. Appl Surf Sci 258:4636–4641

Cabrales L, Abidi N, Hammond A et al (2012) Cotton fabric functionalization with cyclodextrins. J Mater Environ Sci 3:561–574

Cocinero EJ, Gamblin DP, Davis BG et al (2009) The building blocks of cellulose: the intrinsic conformational structures of cellobiose, its epimer, lactose, and their singly hydrated complexes. J Am Chem Soc 131:11117–11123

Dehabadi VA, Buschmann HJ, Gutmann JS (2013) Durable press finishing of cotton fabrics: an overview. Text Res J 83:1974–1995

Di Mundo R, De Benedictis V, Palumbo F et al (2009) Fluorocarbon plasmas for nanotexturing of polymers: a route to water-repellent antireflective surfaces. Appl Surf Sci 255:5461–5465

Dillon AC, Ott AW, Way JD et al (1995) Surface chemistry of Al_2O_3 deposition using $Al(CH_3)_3$ and H_2O in a binary reaction sequence. Surf Sci 322:230–242

Eckhardt C, Rohwer H (2000) UV protector for cotton fabrics. Text Chem Color Am Dyestuff Rep 32:21–23

El-Tahlawy K, El-Nagar K, Elhendawy AG (2007) Cyclodextrin-4 Hydroxy benzophenone inclusion complex for UV protective cotton fabric. J Text Inst 98:453–462

Eren HA, Anis P, Davulcu A (2009) Enzymatic one-bath desizing - bleaching - dyeing process for cotton fabrics. Text Res J 79:1091–1098

Favia P, Cicala G, Milella A et al (2003) Deposition of super-hydrophobic fluorocarbon coatings in modulated RF glow discharges. Surf Coat Technol 169–170:609–612

Hsieh C-T, Cheng Y-S, Hsu S-M et al (2010) Water and oil repellency of flexible silica-coated polymeric substrates. Appl Surf Sci 256:4867–4872

Jeon HJ, Yi SC, Oh SG (2003) Preparation and antibacterial effects of Ag-SiO_2 thin films by sol-gel method. Biomaterials 24:4921–4928

Klemm D, Heublein B, Fink HP et al (2005) Cellulose: fascinating biopolymer and sustainable raw material. Angew Chem Int Ed 44:3358–3393

Kulinich SA, Farzaneh M (2005) On wetting behavior of fluorocarbon coatings with various chemical and roughness characteristics. Vacuum 79:255–264

Lee I, Evans BR, Woodward J (2000) The mechanism of cellulase action on cotton fibers: evidence from atomic force microscopy. Ultramicroscopy 82:213–221

Liu D, Li W, Feng Z et al (2009a) Plasma enhanced CVD of fluorocarbon films by low-pressure dielectric barrier discharge. Surf Coat Technol 203:1231–1236

Liu YH, Wang XK, Luo JB et al (2009b) Fabrication and tribological properties of superhydrophobic surfaces based on porous silicon. Appl Surf Sci 255:9430–9438

Loftsson T, Ossurardottir IB, Thorsteinsson T et al (2005) Cyclodextrin solubilization of the antibacterial agents triclosan and triclocarban: effect of ionization and polymers. J Incl Phenom Macrocycl Chem 52:109–117

Lu J, Hill MA, Hood M et al (2001) Formation of antibiotic, biodegradable polymers by processing with Irgasan DP300R (Triclosan) and its inclusion compound with beta-cyclodextrin. J Appl Polym Sci 82:300–309

Martel B, Morcellet M, Ruffin D et al (2002) Capture and controlled release of fragrances by CD finished textiles. J Incl Phenom Macrocycl Chem 44:439–442

Maxwell JM, Gordon SG, Huson MG (2003) Internal structure of mature and immature cotton fibers revealed by scanning probe microscopy. Text Res J 73:1005–1012

Morris CE, Vigo TL, Welch CM (1981) Binding of organic anti-microbial agents to cotton fabric as zirconium complexes. Text Res J 51:90–96

Bhat NV, Benjamin YN (1999) Surface resistivity behavior of plasma treated and plasma grafted cotton and polyester fabrics. Text Res J 69:38–42

Nakajima A, Hashimoto K, Watanabe T (2001) Recent studies on super-hydrophobic films. Monatsh Chem 132:31–41

Parikh DV, Fink T, Rajasekharan K et al (2005) Antimicrobial silver/sodium carboxymethyl cotton dressings for burn wounds. Text Res J 75:134–138

Park S, Baker JO, Himmel ME et al (2010) Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance. Biotechnol Biofuels 3:10

Perkins WS (1996) Textile coloration and finishing. Carolina Academic, Durham

Peterlin A, Ingram P (1970) Morphology of secondary wall fibrils in cotton. Text Res J 40:345

Pierson HO (1999) Handbook of chemical vapor depostion [ie deposition] (CVD): principles, technology, and applications. William Andrew, New York

Rehmann L, Yoshii H, Furuta T (2003) Characteristics of modified beta-cyclodextrin bound to cellulose powder. Starch-Starke 55:313–318

Reuscher H, Hirsenkorn R (1996) BETA W7 MCT - new ways in surface modification. J Incl Phenom Mol Recognit Chem 25:191–196

Rivlin J (1992) The dyeing of textile fibers theory and practice. Joseph Rivlin, Philadelphia

Romi R, Lo Nostro P, Bocci E et al (2005) Bioengineering of a cellulosic fabric for insecticide delivery via grafted cyclodextrin. Biotechnol Prog 21:1724–1730

Scalia S, Tursilli R, Bianchi A et al (2006a) Incorporation of the sunscreen agent, octyl methoxycinnamate in a cellulosic fabric grafted with beta-cyclodextrin. Int J Pharm 308:155–159

Scalia S, Tursilli R, Sala N et al (2006b) Encapsulation in lipospheres of the complex between butyl methoxydibenzoylmethane and hydroxypropyl-beta-cyclodextrin. Int J Pharm 320:79–85

Schindler WD, Hauser PJ (2004) Chemical finishing of textiles. Woodhead, Cambridge

Spicka N, Tavcer PF (2013) Complete enzymatic pre-treatment of cotton fabric with incorporated bleach activator. Text Res J 83:566–573

Srinivasan M, Gatewood BM (2000) Relationship of dye characteristics to UV protection provided by cotton fabric. Text Chem Color Am Dyestuff Rep 32:36–43

Szejtli J (1997) Utilization of cyclodextrins in industrial products and processes. J Mater Chem 7:575–587

Tarimala S, Kothari N, Abidi N et al (2006) New approach to antibacterial treatment of cotton fabric with silver nanoparticle-doped silica using sol-gel process. J Appl Polym Sci 101:2938–2943

Tran PL, Hammond AA, Mosley T et al (2009) Organoselenium coating on cellulose inhibits the formation of biofilms by Pseudomonas aeruginosa and Staphylococcus aureus. Appl Environ Microbiol 75:3586–3592

Vigo TL, Leonas KK (1999) Antimicrobial activity of fabrics containing crosslinked polyethylene glycols. Text Chem Color Am Dyestuff Rep 1:42–46

Wang JH, Cai ZS (2008) Incorporation of the antibacterial agent, miconazole nitrate into a cellulosic fabric grafted with beta-cyclodextrin. Carbohydr Polym 72:695–700

Zhou Y, Crews PC (1998) Effect of OBAs and repeated launderings on UVR transmission through fabrics. Text Chem Color 30:19–24