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Chemical Functionalisation of Cotton Fabric to Impart Multifunctional Properties

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Abstract

A cotton fabric was functionalised using the nanoparticle vapor deposition (NVD) and molecular vapor deposition (MVD) techniques to impart super hydrophobic/oleophobic properties. The NVD method was used to deposit a layer of Al_2O_3 nanoparticles onto the fabric surface. MVD led to the deposition of a functional layer of (tridecafluoro-1,1,2,2,-tetrahydrooctyl)trichlorosilane (FOTS). The nanoparticles deposition increased the surface roughness, leading to higher contact angles when compared with the surfaces functionalised only with FOTS. FTIR spectra showed the presence of peaks corresponding to fluorocarbon chains and Al_2O_3 on functionalised samples. Surface free energies of the samples were calculated. Low hysteresis and dynamic contact angles higher than 150° were obtained for water and organic liquids. Tetrabutyl orthotitanate ($Ti(OC_4H_9)_4$) was used to functionalise fabrics to impart self-cleaning and UV protection properties. Furthermore, the functionalisation with monochlorotriazyl-β-cyclodextrin molecules introduced cavities on the fabric surface, which were used to perform the inclusion of antimicrobial agents.
Keywords: molecular vapour deposition, functionalisation, water repellency, self-cleaning

1 Introduction

Super hydrophobic surfaces are attractive for many applications, where water repellency, anti-sticking, self-cleaning and anti-fouling are desired or required [1–4]. Super hydrophobic surfaces exist in nature, however, various surfaces are fabricated based on natural surface structures [5], e.g. rose petals can be considered super hydrophobic [5, 6]. A surface is said to be hydrophilic when the static water contact angle is below 90°. A surface is hydrophobic when the contact angle is between 90° and 150°. However, a surface is considered super hydrophobic when the contact angle is higher than 150° [7]. On super hydrophobic low adhesive surfaces, a liquid droplet rolls off the surface as the interaction liquid-solid is minimised. This property is called "self-cleaning" or "lotus effect" since the rolling liquid droplet can "clean-up" the surface as it rolls over surface dust or particles [8].

In general, a surface is considered super hydrophobic when exhibiting a static water contact angle greater than 150° and a sliding angle smaller than 10°. Scientists have studied the structures of super hydrophobic surfaces to understand the behaviour of highly hydrophobic surfaces. Natural super hydrophobic surfaces consist of 20–40 μm particles, each covered by smaller-scaled, rough surfaces [9]. The nanoparticle structure and the surface roughness have been reported to lead to a super hydrophobic property. To impart super hydrophobic properties, a surface can be functionalised in two ways. The first approach consists of using low-surface-energy materials (such as fluorocarbons) to create a rough coating. However, preparing rough surfaces with fluorocarbons is difficult to achieve. İn the second approach, a rough surface can be modified with low-surface-energy materials [9]. In this study, a vapour phase reaction is used to form nanoparticles on the fabric surface, which create a rough surface. Other functional properties

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that are of particular interest are antimicrobial property, self-cleaning and UV protection.

2 Experimental

2.1 Materials

Desized, scoured and bleached cotton fabrics (yarn linear density: warp/weft = 16.4 tex/14.7 tex; mass per unit area = 118.7 g/m^2) were used in this study. They were purchased from Testfabrics, Inc. (Testfabrics, West Pittston, PA, USA). Water (deionised in a Milli-Q plus system from Millipore to reach the final resistivity of 18.2 MΩ·cm) and varying volumetric concentrations of isopropyl alcohol (IPA) were used to assess the hydrophobic properties of the treated cotton fabrics.

2.2 Methods

Super hydrophobic treatment

The treatment procedure used was reported in our previous work [10, 11]. The chemicals used for the treatments were: water, (tridecafluoro-1,1,2,2,-tetrahydrooctyl)trichlorosilane (FOTS, $(Cl)_3Si(CH_2)_2(CF_2)_5(CF_2)_3$), a blend of bifunctional trichlorosilanes and trimethylaluminum (TMA, $Al(CH_3)_3$). Three treatments were performed. In the treatment A, the fabric was pretreated with N_2-plasma, followed by the MVD deposition of FOTS (MVD FOTS layer). In the treatment B, the fabric was pretreated with N_2-plasma followed by the ALD deposition of Al_2O_3 and then by the MVD deposition of FOTS (ALD Al_2O_3 + MVD FOTS layer). In the treatment C, the fabric was pretreated with N_2-plasma followed by the MVD deposition of trimethylaluminum nanoparticles, then the MVD deposition of a bifunctional trichlorosilane blend and finally the MVD deposition of a FOTS layer (NVD Al_2O_3 + MVD bifunctional tricholorosilane + MVD FOTS layer).

The dynamic contact angle measurements were performed using an FTA 1000 instrument (First Ten Angstroms, Portsmouth, VA). A 26-gauge needle was used to dispense a drop of the liquid (5–8 μL) onto the fabric surface. To calculate the contact angles, the Laplace fit method was used. To measure the advancing and receding angles, the needle was brought into close proximity to the fabric surface and the test liquid was pumped for 20 s until the drop reached the size of approximately 30 μl. Subsequently, the liquid was pumped in at the same rate until the drop detached from the needle or all of the liquid returned to the syringe.

Self-cleaning and UV protection

The cotton fabric samples were also dipped into titania nanosols (prepared from $Ti(OC_4H_9)_4$) and passed through a two-roller laboratory padder (BTM 6-20-190) at the speed of 3.66 m/min and air pressure of 2.76 × 105 Pa. The padded fabric samples were then dried at 60 °C for 10 min and then cured at 150 °C for 5 min. The samples were subjected to a hydrothermal treatment by boiling them in water for 1 h. Afterwards, the samples were dried, ironed and finally conditioned in a laboratory maintained at 65 ± 2% relative humidity and 21 ± 1 °C for at least 24 hours before performing the analysis.

Functionalization with cyclodextrin

MCT-β-CD was grafted to the cotton fabrics. Different MCT-β-CD concentrations in water (5, 10, 15, 20, 25, 30 w/w %) were prepared and stirred for 5 min. Then, Sodium Carbonate (Na_2CO_3) was added to the solution (x/4, x is the amount of MCT-β-CD). The solution was stirred for 5 min. The pH of the solution was around 11.5. The cotton fabric samples were dipped into the solution, soaked for 5 min and passed through a two-roller laboratory padder. The wet pick-up was around 100%. The padded fabric samples were dried at 50 °C for 10 min. The samples were thoroughly rinsed with water and dried.

3 Results and discussion

3.1 Super hydrophobic treatment

Figure 1 shows a droplet of the dye solution, which diffuses inside the fibre when placed on the untreated control cotton fabrics. However, when the fabric is functionalised with the MVD technique, inside the fibres and forms a bead on the surface FOTS (Figure 2), the dye solution does not diffuse

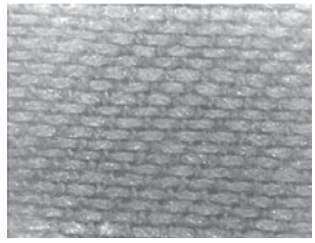

Figure 1: Untreated cotton fabric

(Figure 3). This means that the droplets of water will be easily rolled off the fabric.

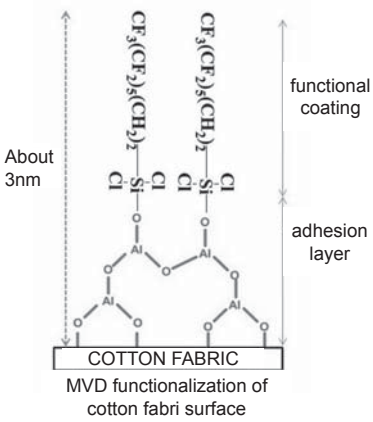

Figure 2: MVD functionalised cotton fabric

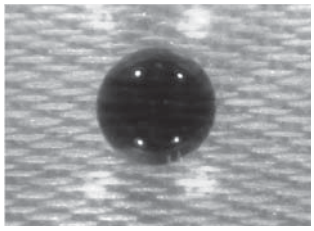

Figure 3: Droplet of water easily rolled off fabric surface

Textile surfaces are not ideal surfaces such as glass slides. Thus, surface roughness and heterogeneity leads to complicated wetting phenomena. On these types of surfaces, the measured contact angles after the liquid droplet advances (called advancing contact angle) is usually greater than the contact angle that results after the droplet recedes (called receding contact angle) from a previously wetted surface. The difference between the advancing and receding contact angles is called "hysteresis" and can be described as the change in the adsorption of liquid on a solid as a consequence of the change in the surface energy [12] or the "roughness of the surface" [13]. Figure 4 shows the advancing and receding contact angles of the cotton fabric after the treatment C, which shows low hysteresis. The treatment B on the same fabric results in high hysteresis (Figure 4). Any heterogeneities, even at the molecular scale (e.g. a different length of the chain), and surface defects will lead to hysteresis in advancing and receding contact angle measurements [8]. The advancing and receding contact angles are also affected by the shape of the tip of the molecule chains that are emerging from the surface. The hysteresis of the samples was measured using distilled water with the above-mentioned procedure.

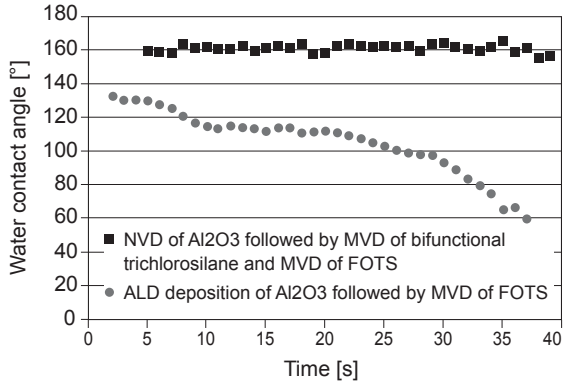

Figure 4: Dynamic water contact angle of functionalised cotton fabric

3.2 Self-cleaning and UV protection

The cotton fabric was successfully modified by titania nanosols prepared by means of the sol-gel process using tetrabutyl orthotitanate ($Ti(OC_4H_9)_4$) as an active ingredient. Scanning Electron Microscopy showed the presence of a titania dioxide film on the fibre surface (Figure 5). The photocatalytic properties of the titania-nanosol-treated cotton fabric were investigated. The results showed that the stains of coffee and red wine were successfully decomposed by the exposure of the stained fabric to UV radiation (Figure 6). The exposure of TiO_2 particles to the photons of energy equal to or greater than the band gap energy results in the promotion of an electron from the valance band to the conduction band of the particle. This creates a region with a positive charge (hole, h+) in the valance band and a free

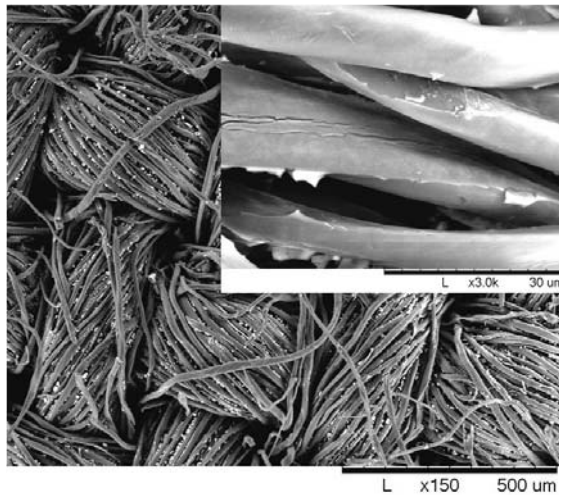

Figure 5: Scanning Electron Microscopy of titania-nanosol-treated cotton fabric

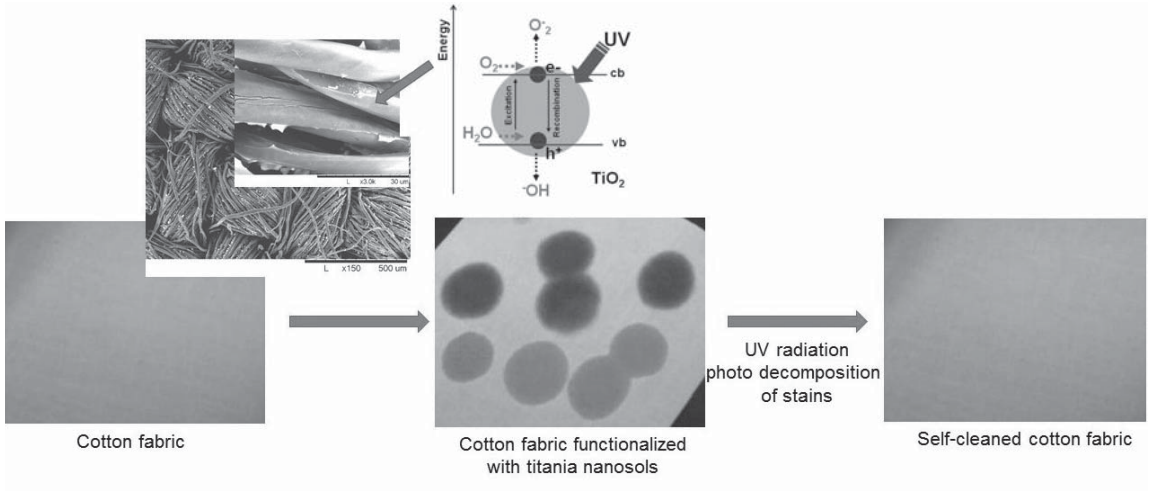

Figure 6: Stains are removed by exposing titania-nanosol-treated fabric to UV radiation

electron (e–) in the conduction band. Hydroxyl and super-oxide groups are very reactive and decompose organic substances by oxidation. Furthermore, the titania nanosol treatment imparted to the cotton fabric a very good protection from UV radiation. This property is largely attributed to the scattering effect of UV radiation by the TiO_2 particles. The durability of the treatment was investigated by performing repeated home laundering and the results showed no effect of laundering on the UV protection efficiency.

3.3 Functionalisation with monochlorotriazyl-β-cyclodextrin

Figure 7 illustrates the reaction mechanism between cellulose macromolecules and MCT-β-CD. The cyclodextrin derivative is fixed to the cotton by a nucleophilic substitution reaction between the hydroxyl groups of the cellulose chain and the chlorotriazine ring. The hydrochloric acid is released as a byproduct of the reaction.

Phenolphthalein forms inclusion compounds with cyclodextrin. When phenolphthalein is included in the CD cavity in alkaline solutions, it is transformed from the red-coloured dianion form to its colourless form. This characteristic makes phenolphthalein a very effective colorimetric indicator to confirm that cyclodextrin cavities are available to form inclusion compounds. The control and treated samples were immersed into a solution containing phenolphthalein. The maximum absorbance of phenolphthalein in an alkaline solution is at 552 nm. As shown in Figure 8, when the amount of grafted MCT-β-CD on the fabric is increased, the absorbance at 552 nm is decreased.

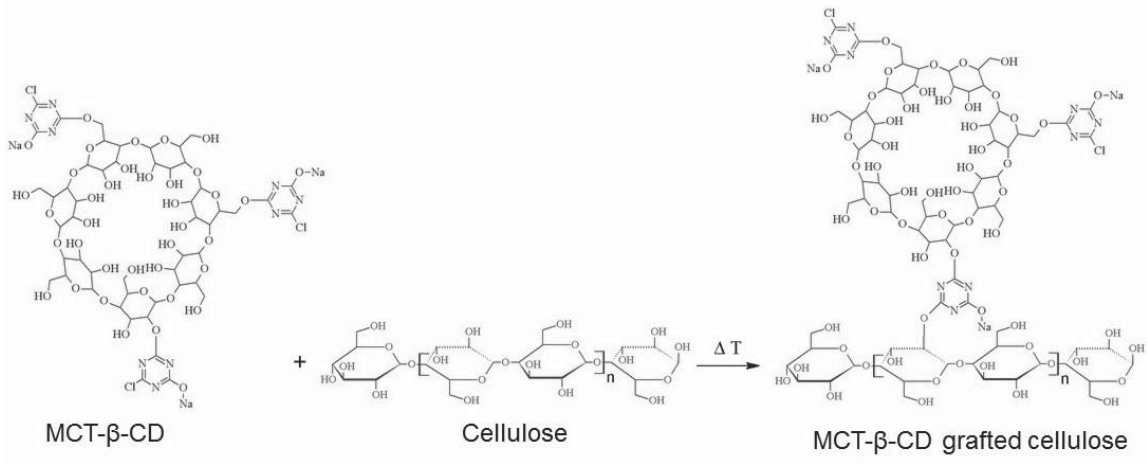

Figure 7: Reaction between MCT-β-CD and cellulose

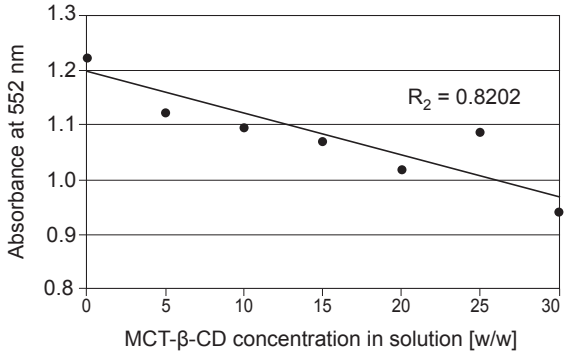

Figure 8: Phenolphthalein inclusion – absorbance at 552 nm as function of MCT-β-CD concentration in solution expressed in w/w %

Triclosan has very powerful antimicrobial properties. The measurement of the released amount of triclosan was performed as follows: first, triclosan was included in the cavities and then the amount of molecules released in ethanol was monitored by the UV absorbance of the solution. Figure 9 shows the results of the release of triclosan in ethanol by measuring the absorbance at 282 nm as a function of the MCT-β-CD concentration in the solution. The results show that triclosan molecules are present in the control after rinsing. This is due to the low solubility of triclosan in water and ethanol-water solution. It is important to point out that the amount of triclosan released by the MCT-β-CD treated samples is higher than the untreated sample. For example, the average amount of triclosan released in ethanol by the samples treated with 30% MCT-β-CD concentration in the solution is enough to achieve a molar concentration by 3.5 times higher than the control.

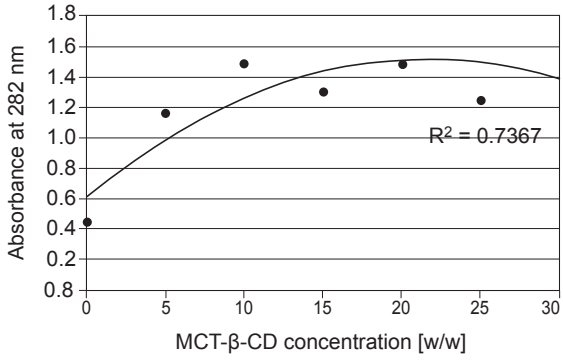

Figure 9: Triclosan release – absorbance at 282 nm as function of MCT-β-CD concentration in solution expressed in w/w%

MCT-β-CD treated cotton fabrics were immersed in triclosan solutions and rinsed. To test the ability to remove triclosan that is included in the cavities, the samples were washed in ethanol. Figure 10 shows the Colony Forming Unit of S. aureus of the control and treated cotton fabrics. The untreated cotton fabric (Sample A) does not exhibit any antimicrobial properties. However, the cotton fabric treated with MCT-β-CD and loaded with triclosan molecules (Sample B) has a very strong antimicrobial activity against S. aureas. When the fabric is washed with ethanol to remove triclosan (Sample C), the fabric does not retain its antimicrobial performance. This indicates that triclosan can be easily removed from the cavity, which allows the cavities to be available for other guest compounds.

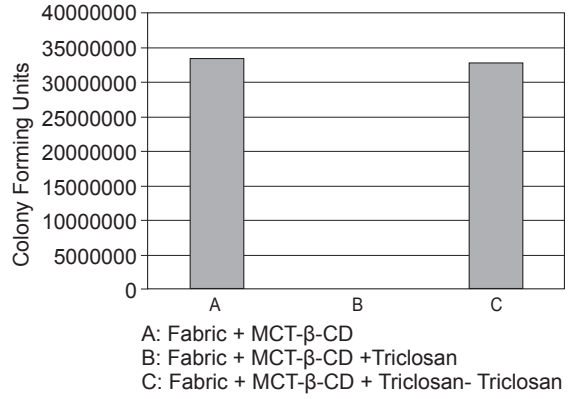

Figure 10: Antibacterial test of (A) untreated cotton (control), (B) MCT-β-CD-30% treated samples with triclosan included, and (C) MCT-β-CD-30% treated with triclosan and washed with ethanol to remove triclosan

4 Conclusion

A cotton fabric was successfully functionalised to impart multifunctional properties. Super hydrophobic properties could be imparted using the NVD and MVD techniques. The self-cleaning and UV protection properties could be imparted using tetrabutyl orthotitanate by means of the sol-gel process. The self-cleaning property was due to the photocatalytic properties of TiO_2 particles formed on the fabric surface. The UV protection was attributed to the scattering effect of the TiO_2 particles. The cotton fabric was also functionalised with β-cyclodextrins. This created free cavities on the

fabric surface that could be used for inclusion of different compounds that do not in general exhibit affinity to cellulose.

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