Nanocomposites fabrication by self-assembly method to modify macroscopic properties

N Lopez-Barbosa[1] and J F Osma[1]

[1] Universidad de los Andes, Bogotá D.C., Colombia

E-mail: jf.osma43@uniandes.edu.co

Abstract. Polymeric nanocomposites have been in the scope of scientists for the last decade due to their multiple applications and simple synthesis. Self-assembly fabrication can be performed through different methods such as layer-by-layer or the controlled growth of nanostructures on a surface. These methods allow fast elaboration of nanocomposites that can be readily integrated in sensors or films. The current work exposes the self-assembly of nanocomposites for the modification of material's macroscopic properties such as hydrophobicity and temperature's resistance on textiles. Hydrophobicity properties of cotton textiles were modified by the application of functionalized silica nanoparticles on their surfaces. Thermal resistance of cotton textiles was achieved by incorporating TiO_2 nanoparticles into the matrix, increasing the scope of their applications. Functionalization was attained by chloro-trimethyl-silane (CTS) and γ-amino(propyl) triethoxy silane (APTES) in organic and inorganic solvents. Wetting phenomena characteristics appeared to highly depend on the synthesis parameters.

1. Introduction

Nanocomposites are an emerging technology used to modify macroscopic properties of different materials. Among others, textiles have been in the scope of researchers to provide them with multifunctional properties such as UV [1], thermal and flame resistance [2], and antibacterial [2–5], antimicrobial and conductive [4,6] properties. Similarly, the need of fabricating hydrophobic surfaces have increased from self-cleaning applications to engineered surfaces for anti-sticking, antifouling and controlled wettability, among others [7]. Superficial hydrophobicity principally depends on the differential interfacial energy between the surface and the water droplet [8], which can be modified by lowering the surface free energy or changing the surface roughens. Several attempts [9–13] have been done to modified the wetting phenomena of cotton textiles by incorporating different nanocomposites onto their surface in the attempt to either decrease the surface energy or simulate structures found on the lotus leaf surface.

Hydrophobic and superhydrophobic surfaces have been used in a great variety of applications such as spray cooling [14], spray painting [15], self-cleaning coatings [16], ink-jet printing and turbines [17], among others. When resting on a solid surface, the shape of a droplet is only determined by the surface tensions acting on the liquid if the effect of inertial forces is negligible. This is the case when the free fall velocity of the droplet is considerably smaller than the surface tension [18]. In such case, the resting droplet can be assumed to have a spherical crown shape [19] and the resting contact angle can be interpreted as the interactions of the solid-liquid, liquid-gas and gas-solid interphases.

In the current study, the wetting phenomena of cotton textiles was modified by SiO_2 nanoparticles functionalization through the attachment of chloro-trimethyl-silane (CTS) and γ-amino (propyl)

triethoxy silane (APTES). In addition, the interaction between functionalized SiO_2 and TiO_2 nanoparticles was also studied. Wetting phenomena was studied by means of the sessile drop static contact angle method.

2. Materials and methods

2.1. Materials
SiO_2 and TiO_2 industrial grade nanoparticles were used. Acetone, chloro-trimethyl-silane (CTS) and γ-amino (propyl) triethoxy silane (APTES) were obtained from Sigma Aldrich. Textiles used were 100% cotton without dyes.

2.2. SiO₂ nanoparticles silanization
A SiO_2 nanoparticles solution in milli Q water of 1.66mg/mL was used. 1mL of CTS 2% (v/v) solution was added and left still overnight. The same procedure was performed with APTES in both milli Q water (APTES-W) and acetone (APTES-A) solvents. Functionalized nanoparticles were dried by solvent evaporation method.

The effective bonding between CTS or APTES with SiO_2 nanoparticles was confirmed by FT-IR measurements in an A250/D FT-IR (Bruker, United States).

2.3. Nanoparticles immobilization on textiles
Seven different solutions were attained for immobilization over cotton textiles. All solutions were prepared in milli Q water with a concentration of 1mg/mL. Solution TiO_2 was prepared by dissolving TiO_2 nanoparticles. Solution CTS-W was prepared by dissolving CTS-silica complexes. Solution APTES-W was prepared by dissolving APTES-silica complexes prepared in water. APTES-A was prepared by dissolving APTES-silica complexes prepared in acetone. Solution CTS-TiO_2 was prepared by dissolving both TiO_2 nanoparticles and CTS-silica complexes. Solution APTES-W-TiO_2 was prepared by dissolving both TiO_2 nanoparticles and APTES-silica complexes prepared in water. Finally, solution APTES-A-TiO_2 was prepared by dissolving both TiO_2 nanoparticles and APTES-silica complexes prepared in acetone.

Five 100% cotton textiles were placed in each solution and left still for 10 minutes. Textiles were removed from the solution and dried at room temperature (25°C) overnight. Each of the textiles had a superficial area of 50×50mm.

2.4. Wetting phenomena measurements
Wetting phenomena was analysed through sessile drop static contact angle measurement. 2.5μL of milli Q water were dropped at a height of 3cm on the surface of each textile. Tangential and perpendicular video of the drops was registered for later image processing. Static contact angle measurements were taken 5, 10 and 15 seconds after the droplet touched the textile surface through video analysis by means of the software Tracker. When the three static angle measurements differed considerably, measurements of the contact angle were performed every second for 15 seconds. The experimental setup is shown in Figure 1.

Textiles were placed on a hotplate and heated at 80°C for 1h to study the effect of the presence of TiO_2 nanoparticles. Wetting phenomena measurements were repeated afterwards.

All contact angle measurements were repeated three times in each textile, giving a total of thirty measurements per solution, fifteen prior to heating and fifteen afterwards.
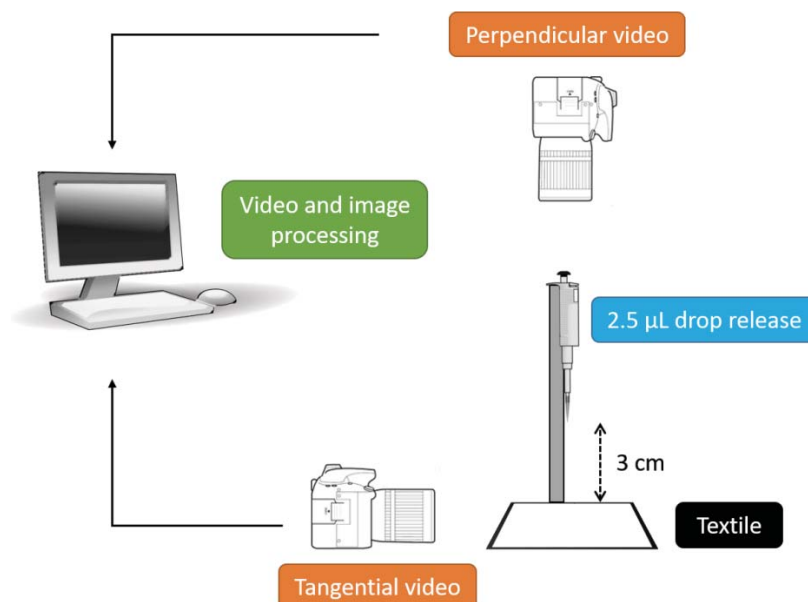
Figure 1. Experimental setup for static contact angle measurements.

3. Results and discussion

3.1. SiO₂ silanization

SiO_2 effective silanization was confirmed through FT-IT measurements of the resulting powder. Results for solutions CTS is shown in Figure 2. Among the peaks, there is a dominant peak at $1059cm^{-1}$. This peak is associated to the O-Si-O bond that appears between the SiO_2 nanoparticle and the CTS. The presence of the peak confirms that the silanization was effective.
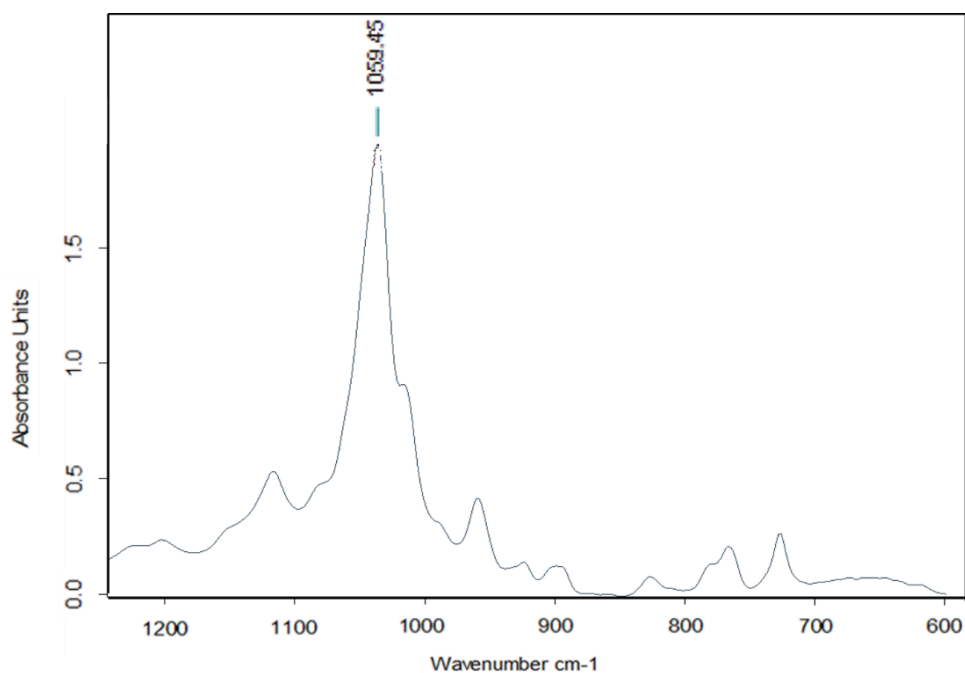

Figure 2. FT-IR spectre for solution CTS.

Figure 3 shows the FT-IR spectre of solution APTES-W. The spectre contains two main groups of peaks; one between 1100 and 1000cm^{-1}, and one around 800cm^{-1}. The first group is attributed to the O-Si-O bond that appears between the nanoparticles and APTES, which proves the correct silanization of the sample. The second group corresponds to the Si-CH$_3$ rocking characteristic of silane. This means that there is an excess of silane in the sample.
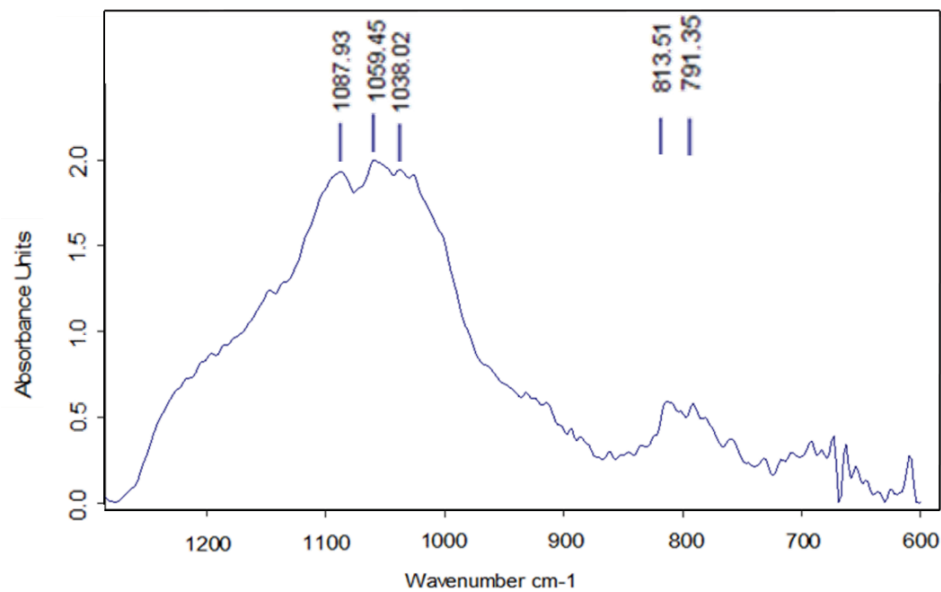
Figure 3. FT-IR spectre for solution APTES-W.

Figure 4 shows two peaks that correspond to the O-Si-O bonding (1087.30cm^{-1}) and the Si-CH$_3$ rocking of silane (805.29cm^{-1}) in the FT-IR spectre of solution APTES-A. In contrast with the APTES-W spectre, peaks are easier to identify in this sample.
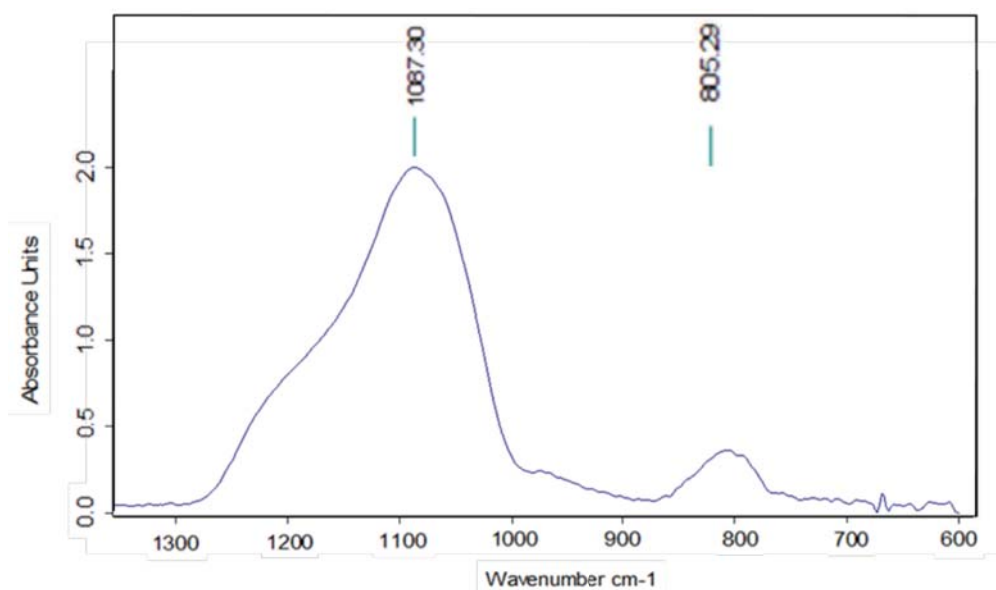

Figure 4. FT-IR for solution APTES-A.

3.2. Wetting phenomena measurements

Contact angle measurements were performed by video analysis in the software Tracker, from three five different textiles from each solution. Tangential videos were used to determine the contact angle between the textile surface and the droplet of water. Perpendicular videos were used to monitor the contact area between the droplet and the textile. The mean contact angle of three measurements per textile prior to heating are shown in Figure 5 and after heating in Figure 6.
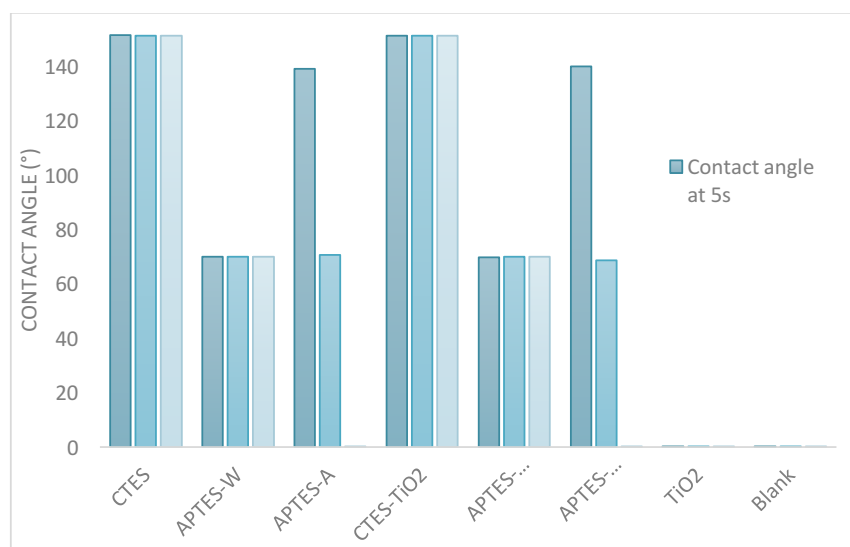
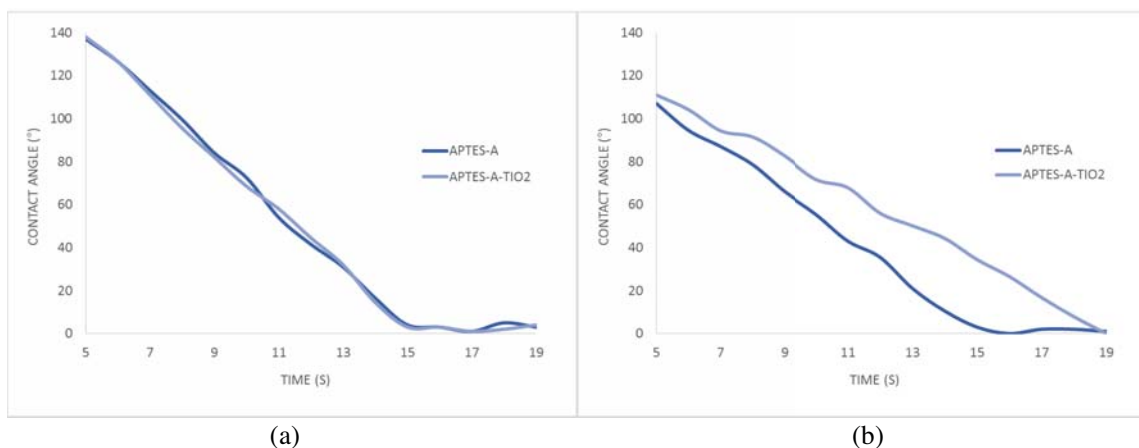**Figure 5.** Mean contact angle measurements before heating.
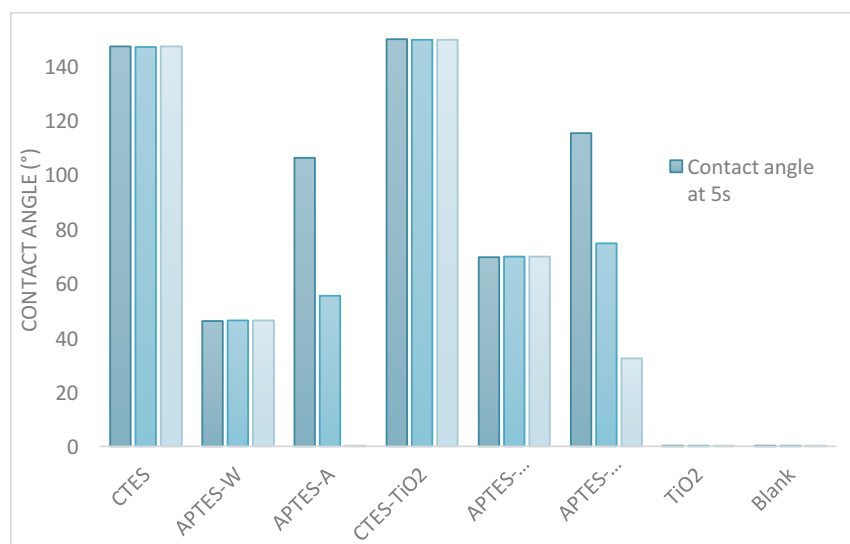
Figure 6. Mean contact angle measurements after heating.

Regardless of the presence of TiO_2 nanoparticles in the treatment, textiles functionalized with solutions CTES and CTES-TiO_2 exhibited a superhydrophobic wetting phenomena with no significant variation after the heating process, as stated in [15]. In contrast, textiles from solutions APTES-W and APTES-W-TiO_2 exhibited a hydrophilic behaviour before the heating process. This is attributed to the hydrogen bonds formed between the water droplet molecules and the APTES superficial amino groups. However, after heating, there is a greater decrease in the contact angle between the droplet and

the surface in textiles treated with solution APTS-W than those treated with solution APTS-W-TiO$_2$. This is attributed to two different phenomena. For instance, it is known that TiO$_2$ nanoparticles absorb part of the heat before it is transferred to the textile. This allows a greater number of bonds between the silane and the SiO$_2$ nanoparticles to remain unchanged regardless of the heating process, which is translated in a smaller diminishment upon the contact angle between the water droplet and the textile surface. On the other hand, silanization processes were performed at room temperature. Aissaoui et al. [20] showed that room temperature silanization of SiO$_2$ surfaces results in a more or less homogeneous layer covered by silane aggregates. Nevertheless, aggregation is sustained by only one chemical anchoring point, which is easily detached during the heating treatment, contributing to the decrease of the contact angle between the droplet and the functionalized surface.

During the video processing, it was observed that the contact angle between the textile surface and the water droplet of textiles from solutions APTES-A and APTES-A-TiO$_2$ was neither constant before or after the heating process. Because of this, contact angle measurements were performed for fifteen seconds every second after the first five seconds of being the droplet in contact with the textile. The obtained measurements are shown in Figure 7.

Figure 7. Contact angle measurements every second after five seconds of being the droplet in contact with the textile surface in textiles from solution APTES-A and solution APTES-A-TiO$_2$ (a) before and (b) after heating at 80°C for 1 hour.

Although the contact angle between the droplet and the textile surfaces from solutions APTES-A and APTES-A-TiO$_2$ decreased with time, the contact area between the droplet and the textile was always constant at 10.18mm^2. If the contact angle decreases, but the contact area remains constant, there must be a loss in the volume of the droplet. A diminishment of the droplet volume is usually attributed to a loss due to evaporation [19]. However, since the textile is a porous surface, a decrease of the droplet volume may be attributed to water going through the textile.

In an ideal system, static contact angles appear because of the presence of three surface tensions between the three phases of the system; solid, liquid and gas. If the three phases in the system exhibit a force balance, there is a chemical potential matching attributed to all components, and there is a temperature matching such that the gas phase represents the saturated vapour of the liquid phase, the system is said to be in thermodynamic equilibrium [18]. Under this circumstance, a decrease of the volume of the droplet would break down the thermodynamic equilibrium, and a resultant force towards the centre of the droplet would arise [19]. As a consequence, the solid-liquid interphase would shrink until the three surface tensions reach a new equilibrium, i.e. a decrease of the volume of the droplet translates in a reduction of the contact area under a steady contact angle. In contrast, a reduction of the droplet volume was translated in a decrease of the contact angle, rather than the contact area.

There are at least three factors that might have been involved in this phenomena. For instance, APTES-A and APTES-A-TiO$_2$ solutions were prepared with acetone as a solvent. Pan et al. [21] showed through NMR measurements of silica nanoparticles in acetone solution, that additional hydroxyl groups are given to the SiO$_2$ nanoparticles by the presence of acetone molecules in form of hydrogen bonds. This implies that there is a greater number of bonding sites on SiO$_2$ nanoparticles immerged in acetone than there is when immerged in water. A higher number of APTES bonds with the nanoparticles could be the reason why, at time 0, APTES-A and APTES-A-TiO$_2$ appear to be hydrophobic rather than hydrophilic. However, since the hydroxyl groups that result from the presence of acetone are not covalently bonded, they are easily detached from the surface of the nanoparticle when the droplet enters in contact with the textile surface, which results in a decrease of the contact angle. However, if this was the only difference between APTES-W and APTES-A solutions, the contact angle of the last one should stabilized to the contact angle of the first one with time, which did not happen. This can be attributed to the other two factors present in the system. Firstly, the interactions between the water molecules of the droplet and the hydrogen atoms of the amino group are translated in a more hydrophilic behaviour. Finally, there is a possibility that due to the higher density of hydroxyl groups in SiO$_2$ nanoparticles in acetone solution than those in water, a steric impediment of the APTS groups is created, resulting in a different organization than the one encountered when silanized in water. The change in organization can be translated in non-homogenous distributions that led to non-compact structures, which produces additional surface forces [19]. Also, Choi et al. [22] showed that an incorrect distribution, especially when hydrophobic chains are short, can allow water penetration, which may induce a deformation of the organic layer. This phenomenon is coherent with the fact that the volume reduction is not due to evaporation but because of water going through the textile.

4. Conclusions

Different combinations of functionalized SiO$_2$ and TiO$_2$ nanoparticles were tested as mechanisms to modify the wetting phenomena of 100% cotton textiles. It was found that while CTS produced constant hydrophobic surfaces, APTES produced a final hydrophilic behaviour. However, there was a direct relation between the behaviour of the textiles and the solvent in which silica nanoparticles were functionalized when using APTES. This allowed us to create surfaces where the contact angle between the droplet and the textile was constantly steady and hydrophilic, or presented a short-term hydrophobic property that changed to a hydrophilic behaviour with time, depending on the solvent used for the functionalization of the silica nanoparticles. Variable contact angles were attributed to a loss in volume due to the fact that the contact area remained constant. This loss in volume was a result of the droplet going through the textile.

The fact that the contact area of the droplet remained constant with a decreasing contact angle translated in a greater diffusion time of the droplet through the textile when compared with an untreated one. This could be exploited in applications in which interactions between the textile surface and the passing liquid are more efficient if contact time is increased.

In the combined presence of TiO$_2$ and functionalized silica nanoparticles, the thermal properties of TiO$_2$ protected the silane bonds of the functionalized silica nanoparticles, therefore preserving the hydrophobic properties of the heated textiles. This showed that it was possible to integrate multiple types of nanoparticles in the same textile to obtain multipurpose textiles.

References

[1]   G Broasca, G Borcia, N Dumitrascu and N Vrinceanu 2013 Characterization of ZnO coated polyester fabrics for UV protection *Appl. Surf. Sci.* **279** 272–278

[2]   A El-Shafei, M ElShemy and A Abou-Okeil 2015 Eco-friendly finishing agent for cotton fabrics to improve flame retardant and antibacterial properties *Carbohydr. Polym.* **118** 83–90

[3]   A Hebeish, M K El-Bisi and A El-Shafei 2015 Green synthesis of silver nanoparticles and their application to cotton fabrics *Int. J. Biol. Macromol.* **72** 1384–1390

[4]   W-G Kwak, M H Oh and M-S Gong 2015 Preparation of silver-coated cotton fabrics using silver

carbamate via thermal reduction and their properties *Carbohydr. Polym.* **115** 317–324

[5]   Z A Raza, A Rehman, M Mohsin, S Z Bajwa, F Anwar, A Naeem and N Ahmad 2015 Development of antibacterial cellulosic fabric via clean impregnation of silver nanoparticles *J. Clean. Prod.* **101** 377–386

[6]   K Kardarian, T Busani, I Osório, H Domingos, R Igreja, R Franco and J Cortez 2014 Sintering of nanoscale silver coated textiles, a new approach to attain conductive fabrics for electromagnetic shielding *Mater. Chem. Phys.* **147(3)** 815–822

[7]   C Neinhuis and W Barthlott 1997 Characterization and Distribution of Water-repellent, Self-cleaning Plant Surfaces *Ann. Bot.* **79(6)** 667–677

[8]   N D Tissera, R N Wijesena, J R Perera, K M N de Silva and G A J Amaratunge 2015 Hydrophobic cotton textile surfaces using an amphiphilic graphene oxide (GO) coating *Appl. Surf. Sci.* **324** 455–463

[9]   A Berendjchi, R Khajavi and M E Yazdanshenas 2011 Fabrication of superhydrophobic and antibacterial surface on cotton fabric by doped silica- based sols with nanoparticles of copper *Nanoscale Res. Lett.* **6(1)** 1–8

[10]   N Gogoi, D Rastogi, M Jassal and A K Agrawal 2014 Low-surface-energy materials based on polybenzoxazines for surface modification of textiles *J. Text. Inst.* **105(11)** 1212–1220

[11]   M Shateri-Khalilabad and M E Yazdanshenas 2013 Preparation of superhydrophobic electroconductive graphene-coated cotton cellulose *Cellulose* **20(2)** 963–972

[12]   L F Hao, Q F An, W Xu and Q J Wang 2010 Synthesis of fluoro-containing superhydrophobic cotton fabric with washing resistant property using nano-SiO2 sol-gel method *Advanced Materials Research* **121** 23–26

[13]   C-H Xue, S-T Jia, H-Z Chen and M Wang 2008 Superhydrophobic cotton fabrics prepared by sol–gel coating of TiO2 and surface hydrophobization *Sci. Technol. Adv. Mater* 9(3) 035008

[14]   W M Grissom and F A Wierum 1981 Liquid spray cooling of a heated surface *Int J. Heat Mass Transf.* **24(2)** 261–271

[15]   A Nakajima, T Miyamoto, M Sakai, T Isobe and S Matsushita 2014 Comparative study of the impact and sliding behavior of water droplets on two different hydrophobic silane coatings *Appl. Surf. Sci.* **292** 990–996

[16]   E Gutierrez-Miravete, E J Lavernia, G M Trapaga, J Szekely and N J Grant 1989 A mathematical model of the spray deposition process *Metall. Trans. A* **20(1)** 71–85

[17]   C Mundo, M Sommerfeld and C Tropea 1995 Droplet-wall collisions: Experimental studies of the deformation and breakup process *Int. J. Multiph. Flow* **21(2)** 151–173

[18]   N Lopez-Barbosa, N Zuluaga, S Jumah and J F Osma 2015 Fabrication of folding polymeric thin films with hydrophilic properties *Novos Saberes* **2(2)** 71–83

[19]   X Zeng, G Xu, Y Gao and Y An 2011 Surface Wettability of (3-Aminopropyl)triethoxysilane Self-Assembled Monolayers *J. Phys. Chem. B* **115(3)** 450–454

[20]   N Aissaoui, L Bergaoui, J Landoulsi and P Vi 2012 Silane Layers on Silicon Surfaces: Mechanism of Interaction , Stability and Influence on Protein Adsorption *Langmuir* **28(1)** 656–665

[21]   V H Pan, T Tao, J-W Zhou and G E Maciel 1999 Hydrogen Bonding between Acetone and Silica Gel, as Studied by NMR *J. Phys. Chem. B* **103(33)** 6930–6943

[22]   H Choi and H Liang 2016 Wettability and spontaneous penetration of a water drop into hydrophobic pores *J. Colloid Interface Sci.* **477** 176–180