

Hydrophobic Treatment of Blended Fabric's Surface

Anna BORISOVA^{1*}, Skaidrite REIHMANE^{1,2}

¹ Institute of Textile Materials Technologies and Design, Riga Technical University,

14/24 Azenes Street, LV-1048, Riga, Latvia

² Institute of Polymer Materials, Riga Technical University, 14/24 Azenes Street, LV-1048, Riga, Latvia

crossref <http://dx.doi.org/10.5755/j01.ms.19.2.1139>

Received 30 January 2012; accepted 15 October 2012

The nature-inspired theory of hydrophobic surface is an interdisciplinary subject which involves physics, chemistry, material science, and even biology. Nowadays with more developed equipment, we are able to fabricate man-made hydrophobic surfaces which have significant water-repellence and durability what will make this scientific direction maintaining and long-lasting. The present study covers a method of bringing high hydrophobicity to cotton/polyester fabric. Three different commercially available fluorine containing hydrophobic agents were applied to samples in different concentration and compared by physical properties. According to experimental results the sufficient concentration of agents is ascertained. Samples and recommendations for industrial testing are developed.

Keywords: hydrophobic effect, cotton/polyester fabric.

1. INTRODUCTION

Nowadays the requirements toward quality and competitiveness of textile materials have notably increased, favoring the development of chemicals and technologies toward improvement of properties of textile materials. Since the discovery of the self-cleaning effect of lotus leaves and insect wings in nature, hydrophobic surfaces have received a great scientific and industrial attention because of their wide range of application. Hydrophobicity is one of the most widely-spread textile finishes today, beside a great amount of effort has been put into the research of the mechanism of superhydrophobicity on solid surfaces. Roach et al. noted, if the contact angle is increased by roughness to greater than 120° the term ultrahydrophobicity should be used and if the contact angle is increased to greater than 150° and the contact-angle hysteresis is less than ~10° the term superhydrophobicity should be used [1]. In the cutting edge research, nanotechnologies are effectively used to explore the intrinsic essence of the subject. For instance, these include lithography, templating, plasma treatment, sol-gel process, electrospinning etc. [2–7]. It is also became possible to combine finishes and create multifunctional treated surfaces. Miao et al. reported the grafting of the perfluoroalkyl phosphate acrylates onto a cotton fabric via γ -ray irradiation to improve hydrophobic, oleophobic and flame retardant properties. The contact angle for water was over 150°, the flame retardancy of the fabric was also improved [8]. Tsafack and Levolois-Grutzmacher reported the use of cold plasma technique to reach a single treatment step and provide excellent flame retardant and water-repellent properties of cotton fabrics [9]. Shateri Khalil-Abad and Yazdanshenas reported the modification of cotton textiles with silver nanoparticles with further

treatment with octyltriethoxysilane, reaching a static water contact angle of 151° and antibacterial activity toward both Gram-positive and Gram-negative bacteria [10]. Textor and Mahning reported the preparation of hydrophobic sol-gel coating that simultaneously offer antistatic properties for an appropriate textile finishing and refinement of polymer foils [11].

Among wide choice of hydrophobic agents, fluorochemicals belong to one of the most important water and oil repellent finishes because of their low surface free energy [12]. If the surface tension of the fabric has been altered with a fluorochemical, the fabric will allow a droplet of water (surface tension 72.8 dyne/cm) to bead up and roll off without penetrating the fabric structure [13]. In spite of scientific developments toward new textile (super)hydrophobic agents creation, commercial chemical agents hold a stable market niche. Leading chemical companies (Rudolf Chemicals, Huntsman, BASF, CHT Bezema etc.) offer a wide range of hydrophobic agents but don't disclose their chemical composition completely making its comparison difficult. In practice, having deal with hydrophobic treatment of fabrics on an industrial scale in textile factory, one often has to find a solution regarding the optimal application of technology by experienced handling with real production, i. e. modifying the production process on-site, which requires additional material and economical costs and time. Therefore, there's a necessity to carry out experiments in comparison of agents effectiveness, which are declared by production company as fluorine-containing, to find the most appropriate finishing conditions to achieve the desired result.

The aim of this study is to approve early developed finishing technology's effectiveness in the case of different chemical agents, investigate and compare properties of commercially available hydrophobic agents, determine an optimal finishing technology for specific cotton/polyester fabric. The present study covers the sequence of testing procedures and scientific approach for estimation and comparison of different commercial hydrophobic agents

*Corresponding author. Tel.: +371-29984599; fax.: +371-67615765.
E-mail address: a.borisova@inbox.lv (A. Borisova)

for more rapid introduction in manufacturing process in a textile factory.

2. MATERIALS AND METHODS

The range of mixed fiber composition goods expands nowadays. Cotton/polyester fabrics are among the most popular ones. In the present study applied twill weave cotton/polyester (50/50) fabric (surface density 203 g/cm²; 24 tex/warp, 42.7 Tex/weft; average thickness 0.42 mm) is used for Latvian army uniform production.

Three commercially available fluorine containing hydrophobic agents were selected for its effectiveness comparison: Tubicoat HP 27 (CHT Bezema), Rucostar DDD (Rudolf Chemicals) and Oleophobol ZSR (Huntsman).

Fabric's pre-treatment. Fabric samples were washed in non-ionic liquor (1 g/L) of Felosan NOF (CHT Bezema) at 60 °C for 60 min.

Hydrophobic treatment of fabric. Samples' treatment technology was chosen during previous studies of water-repellency finish of cotton [14] and examined practically in the case of the blended fabric. Fabric samples were immersed into the agent's liquid with 5 different concentrations (10; 20; 30; 40 and 50 g/L) for 15 min at 40 °C. According to manufacturer's recommendation the addition of CH₃COOH 60 % (1 g/L) was necessary in the case of Tubicoat HP 27. Padded samples with wet pick-up of 70 %–80 % were dried at 100 °C–105 °C for 15 min and cured at 160 °C for 3 min.

Tests. In order to evaluate properties of hydrophobic agents according to international and national standards the following testing procedures were applied to samples:

- capillarity [15];
- surface contact angle by sessile drop method;
- resistance to water penetration (EN 20811);
- surface wetting resistance (LVS EN 24920);
- air permeability (LVS EN ISO 9237:2001);
- laundering durability (EN ISO 105-A01).

3. RESULTS AND DISCUSSION

Capillarity. A sample's edge was immersed into a solution of potassium dichromate (5 g/L), fixing the penetrated liquid's height after 0.5; 1; 2; 3; 5; 10; 15; 20; 30 and 60 min. The capillarity action wasn't observed for all samples except 10 g/L-treated ones with capillarity of 1 cm/h. The capillarity of untreated sample was 17 cm/h.

Surface contact angle. In general, contact angles are measured for the evaluation of the surface tension and wettability. Although it is hard to measure the surface tension of a solid directly, it is easy to measure its contact angles [16]. Young equation, Wenzel equation, and Cassie–Baxter equation are the fundamental theories to describe the wetting phenomena on hydrophobic surfaces. They are necessary and useful, but not sufficient to fit all situations. When a liquid drop wets a hydrophobic surface, its state depends on the particular surface property and the wetting process [2]. The sessile drop method is an optical contact angle technique used to estimate the wetting properties of a localized region on a solid surface. The

angle between the baseline of the drop and the tangent at the drop boundary is measured [17].

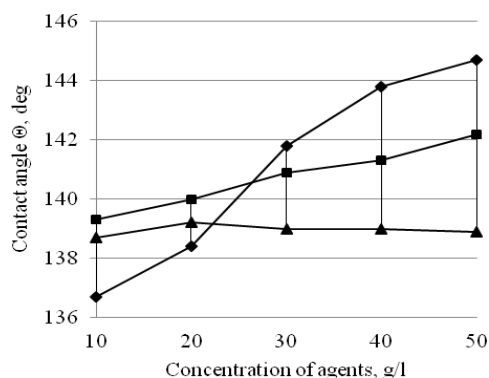


Fig. 1. Treated samples (◆ – Tubicoat HP 27; ■ – Rucostar DDD; ▲ – Oleophobol ZSR) surface contact angle values measured by sessile drop method

Based on analysis of treatment technology of cotton textiles with fluorochemicals described in [14, 18] with contact angle > 150°, it was deduced that application of particular agents by immerse method may result superhydrophobization of the textile surface. Unfortunately, we didn't achieve superhydrophobicity – the greater value ($\theta = 144.7^\circ$) belongs to Tubicoat HP 27 treated sample (50 g/L) (Fig. 1). That can be related to fabric's mixed (cotton/polyester) composition. The comparison of surface morphology of treated samples (Fig. 2) hasn't shown significant changes in fabric's structure. It was reported in [1, 19], in order to reach a superhydrophobic state it is needed to create a surface roughness with a set of different characteristic scale, for textiles these are fiber diameters and fiber separation, determined by the braiding density. The invariable surface morphology with a combination of rather high contact angle values in our case could be considered as a positive factor with position of consumers and possibility to apply those agents to ready-made technical garments.

Resistance to water penetration. During this experiment we were fixing the penetrometer's water column height when first three water droplets appeared on the textile material's surface with a constant water column's pressure. With the increase of concentration of agents, the resistance to water penetration of samples increases (Table 1). The water resistance to penetration of untreated sample is 15 mm H₂O. The better results belong to Rucostar DDD treated samples. It was noticed that during experiments Oleophobol ZSR treated samples wet out completely. On the contrary, Tubicoat HP 27 and Rucostar DDD samples don't wet up and preserve its hydrophobic properties.

Surface wetting resistance. Dynamic wettability of impacting droplets on the treated samples was ascertained according to spray test method. The water repellency rating (W.R.R.) is used to denote the extent of the wetting. The higher rating indicates fewer wetting. Results in Table 2 show that samples treated with Tubicoat HP 27 and Rucostar DDD possess high hydrophobicity for imparting droplets with W.R.R. = 5. Untreated sample W.R.R. is 1.

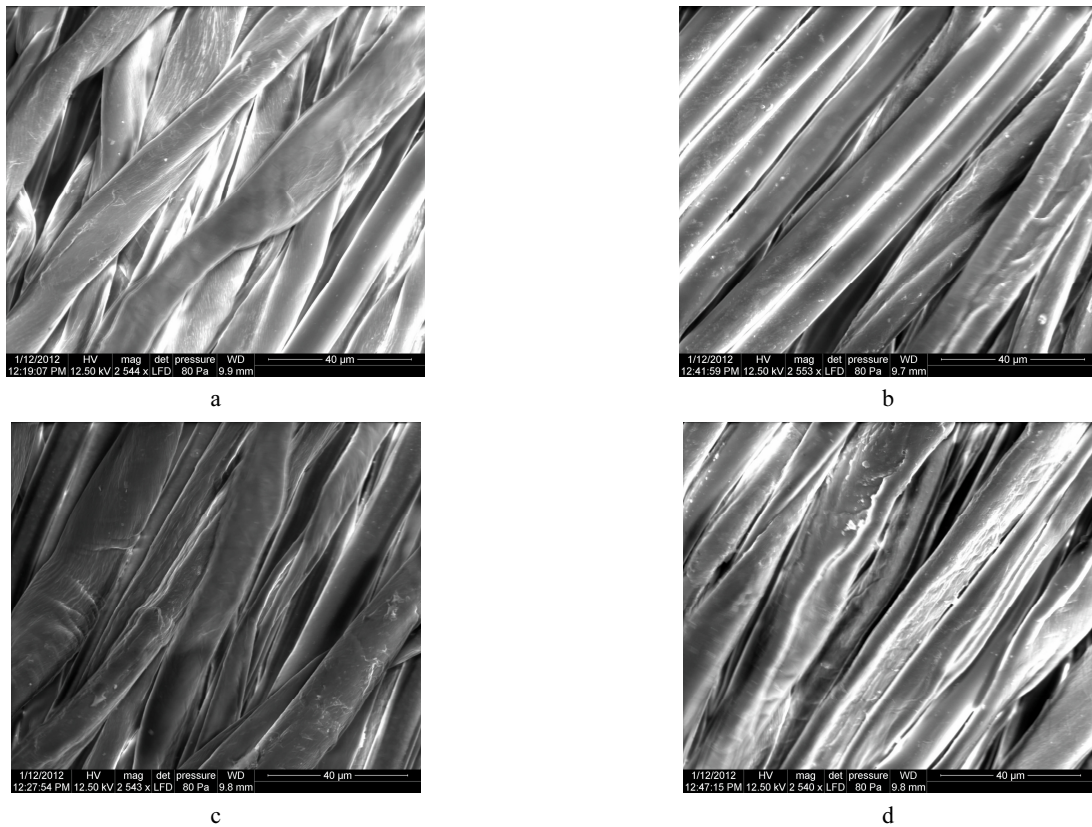


Fig. 2. Microphotograph of cotton/polyester fabric obtained by FEI Quanta 200, the variable pressure scanning electron microscope (SEM): a – washed and untreated; b – washed and treated with Tubicoat HP 27 (30 g/L); c – washed and treated with Rucostar DDD (30 g/L); d – washed and treated with Oleophobol ZSR (30 g/L)

Table 1. Water resistance to penetration of treated samples

Agent's trade name	Water resistance to penetration, mm H ₂ O				
	Agent's concentration, g/L				
	10	20	30	40	50
Tubicoat HP 27	150	210	230	240	260
Rucostar DDD	220	255	270	290	340
Oleophobol ZSR	120	130	145	155	165

Table 2. Surface wetting resistance of treated samples

Agent's trade name	W.R.R.				
	Agent's concentration, g/L				
	10	20	30	40	50
Tubicoat HP 27	5	5	5	5	5
Rucostar DDD	5	5	5	5	5
Oleophobol ZSR	5	5	4	4	5

Air permeability. Textiles material air permeability has influence on human heat-exchange processes in clothes service conditions. Large majority of textile after-treatment technologies have influence on this material's property. In comparison with untreated samples ($R = 67.8$ mm/sec) different concentration of agents almost doesn't have influence on air permeability coefficient's values because of fabric's compact structure (Fig. 3).

The difference of the air permeability between examined agents could be related to its possible unequal

chemical composition. The greatest air permeability values (greater than untreated samples' value) belong to Olephobol ZSR agent, what could be explained with its weak hydrophobic action, proved during above-mentioned experiments, and chemical composition.

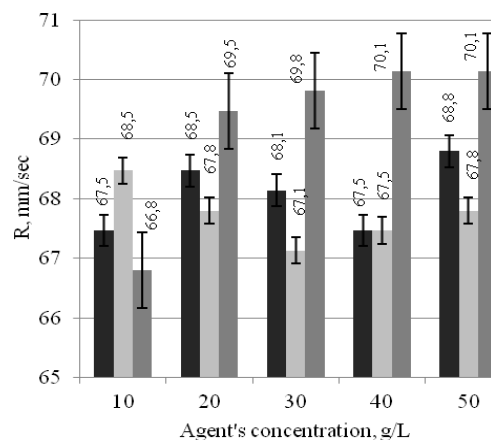


Fig. 3. Air permeability coefficient of treated samples (■ – Tubicoat HP 27, ■ – Rucostar DDD, ■ – Oleophobol ZSR)

Laundering durability. A standard laundering condition, 2 g of detergents in 400 ml of distilled water while stirring at 40 °C for 30 min for each cycle [20]. With an increase in the number of laundry cycles, the values of contact angle decrease. In average, the total decrease is 7% in the case of Tubicoat HP 27 and Rucostar DDD

(Figs. 4, 5). Also increasing the concentration of agents, the contact angle value increases.

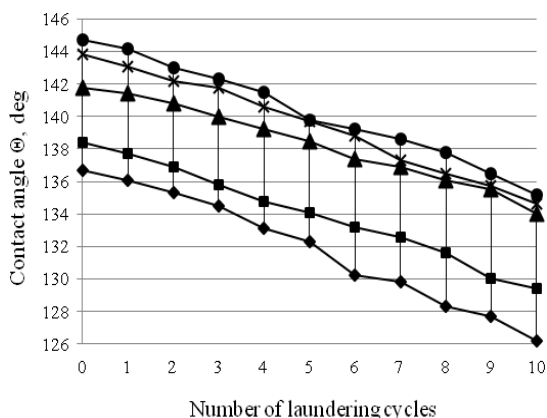


Fig. 4. Laundry durability of Tubicoat HP 27 treated samples (♦ – 10 g/L; ■ – 20 g/L; ▲ – 30 g/L; x – 40 g/L; ● – 50 g/L)

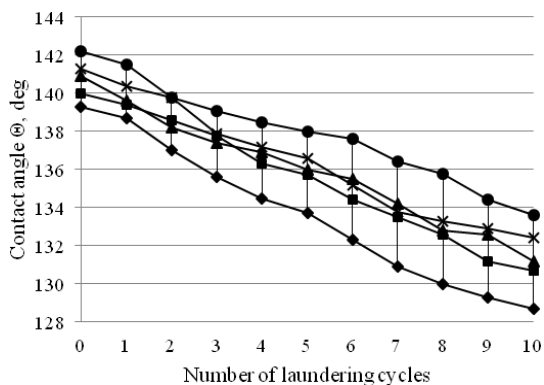


Fig. 5. Laundry durability of Rucostar DDD treated samples (♦ – 10 g/L; ■ – 20 g/L; ▲ – 30 g/L; x – 40 g/L; ● – 50 g/L)

In the case of Olephobol ZSR an average total decrease is 8 %; however the contact angle dependence on agent's concentration can be hardly distinguished in this particular case (Fig. 6).

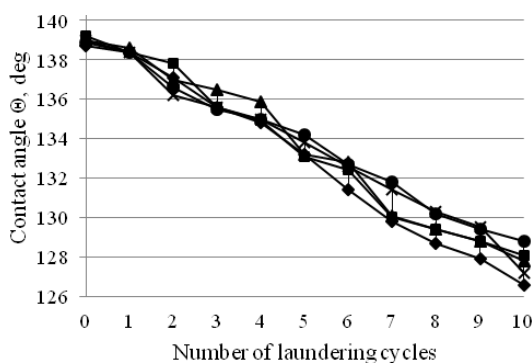


Fig. 6. Laundry durability of Olephobol ZSR treated samples (♦ – 10 g/L; ■ – 20 g/L; ▲ – 30 g/L; x – 40 g/L; ● – 50 g/L)

According to AATCC test method, specimens subjected to this test should sustain five typical careful

hand launderings at a temperature of $40\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$ [21, 22]. The descending nature of contact angle values, depending on increase of laundering cycles, corresponds to the previous studies [22–24]. Hence, the laundering durability of examined agents which were used for present fabric's modification with described method, meets the common case of hydrophobic treatment of textiles.

4. CONCLUSION

According to the experimental results of the study it was concluded that:

1. different concentration of agents (10; 20; 30; 40; 50 g/l) almost doesn't have influence on capillarity, surface wetting resistance and air permeability properties of the fabric;

2. the increase of concentration of agents increases resistance to water penetration, contact angle and laundering durability values;

3. in comparison, more effective are Tubicoat HP 27 (CHT Bezema) and Rucostar DDD (Rudolf Chemicals);

4. the sufficient concentration of examined agents for bringing high water-repellent properties to the present cotton/polyester fabric is 30 g/L, which could be recommended for industrial testing.

In continuation of investigation toward blended fabric's durable water-repellency and possible achievement of superhydrophobicity, also receiving evidence of the positive effect on complex properties of material, some further experiments of cotton/polyester fabric's modification are needed in order to develop a method for probable adaptation at the textile manufacture.

Acknowledgments

This work has been supported by the European Social Fund within the project "Establishment of interdisciplinary research groups for a new functional properties of smart textiles development and integrating in innovative products" (ESF Nr. 2009/0198/1DP/1.1.1.2.0./09/APIA/VIAA/148).

REFERENCES

1. Roach, P., Shirtcliffe, N. J., Newton, M. I. Progress in Superhydrophobic Surface Development *Soft Matter* 4 2008: pp. 224–240. <http://dx.doi.org/10.1039/b712575p>
2. Yan, Y. Y., Gao, N., Barthlott, W. Mimicking Natural Superhydrophobic Surfaces and Grasping The Wetting Process: A Review on Recent Progress in Preparing Superhydrophobic Surfaces *Advances in Colloid and Interface Science* 169 2011: pp. 80–105.
3. Guo, Z., Liu, W., Su, B. L. Superhydrophobic Surfaces: From Natural to Biomimetic to Functional *Journal of Colloid and Interface Science* 353 2011: pp. 335–355.
4. Ma, M., Hill, R. M. Superhydrophobic Surfaces *Current Opinion in Colloid & Interface Science* 11 2006: pp. 193–202. <http://dx.doi.org/10.1016/j.cocis.2006.06.002>
5. Stanssens, D. et al. Creating Water-repellent and Superhydrophobic Cellulose Substrates by Deposition of Organic

- Nanoparticles *Materials Letters* 65 (12) 2011: pp. 1781–1784.
6. **Su, C., Li, J.** The Friction Property of Super-hydrophobic Cotton Textiles *Applied Surface Science* 256 2010: pp. 4220–4225.
 7. **Wang, X., Ding, B., Yu, J., Wang, M.** Engineering Biomimetic Superhydrophobic Surfaces of Electrospun Nanomaterials *Nano Today* 6 2011: pp. 510–530.
 8. **Miao, H. et al.** Cotton Fabric Modification for Imparting High Water and Oil Repellency Using Perfluoroalkyl Phosphate Acrylate Via γ -ray-induced Grafting *Radiation Physics and Chemistry* 79 2010: pp. 786–790.
<http://dx.doi.org/10.1016/j.radphyschem.2010.01.017>
 9. **Tsafack, M. J., Levalois-Grutzmacher, J.** Towards Multifunctional Surfaces Using Plasma-Induced Graft-Polymerization (PIGP) Process: Flame and Waterproof Cotton Textiles *Surface & Coating Technology* 201 2007: pp. 5789–5795.
<http://dx.doi.org/10.1016/j.surfcoat.2006.10.027>
 10. **Shateri Khalil-Abad, M., Yazdanshenas, M. E.** Superhydrophobic Antibacterial Cotton Textiles *Journal of Colloid and Interface Science* 351 2010: pp. 293–298.
<http://dx.doi.org/10.1016/j.jcis.2010.07.049>
 11. **Textor, T., Mahltig, B.** A Sol-Gel Based Surface Treatment for Preparation of Water Repellent Antistatic Textiles *Applied Surface Science* 256 2010: pp. 1668–1674.
 12. **Yu, M. et al.** Superhydrophobic Cotton Fabric Coating Based on a Complex Layer of Silica Nanoparticles And Perfluorooctylated Quaternary Ammonium Silane Coupling Agent *Applied Surface Science* 253 2007: pp. 3669–3673.
 13. **Easter, E. P., Ankenman, B. E.** A Comparison of Soil Repellent vs. Dual Action Fluorocarbon Finishes on Cotton Blends *AATCC Review* 5 (11) 2005: pp. 27–31.
 14. **Reihmane, S., Baltina, I.** The Water Repellent Finishes For Cellulosic Textiles *Scientific Journal of Riga Technical University* 16 2008: pp. 18–23.
 15. **Volkov, V. A. et al.** Capillarity and Water Repellency of Fabrics *Fibre Chemistry* 42 2011: pp. 249–253.
<http://dx.doi.org/10.1007/s10692-011-9263-x>
 16. **Lee, H. J., Michielsen, S.** Lotus Effect: Superhydrophobicity *Journal of The Textile Institute* 97 (5) 2006: pp. 455–462.
<http://dx.doi.org/10.1533/joti.2006.0271>
 17. **Wei, Q., Huang, F., Cai, Y.** Textile Surface Characterization Methods *Surface Modification of Textiles* The Textile Institute, Woodhead Publishing in Textiles, 2009: pp. 26–57.
<http://dx.doi.org/10.1533/9781845696689.26>
 18. **Ivanova, N. A., Zaretskaya, A. K.** Simple Treatment of Cotton Textile to Impart High Water Repellent Properties *Applied Surface Science* 257 2010: pp. 1800–1803.
 19. **Extrand, C. W.** Super Repellency *Encyclopedia of Surface and Colloid Science* Taylor and Francis, 2002: pp. 2414–2429.
 20. **Bae, G. Y. et al.** Superhydrophobicity of Cotton Fabrics Treated With Silica Nanoparticles And Water-Repellent Agent *Journal of Colloid and Interface Science* 337 2009: pp. 170–175.
<http://dx.doi.org/10.1016/j.jcis.2009.04.066>
 21. AATCC Test Method 61–2006: Colorfastness to Laundering, Home and Commercial: Accelerated.
 22. **Deng, B. et al.** Laundering Durability of Superhydrophobic Cotton Fabric *Advanced Materials* 22 2010: pp. 5473–5477.
 23. **Gao, Q. et al.** Formation of Highly Hydrophobic Surfaces on Cotton and Polyester Fabrics Using Silica Sol Nanoparticles and Nonfluorinated Alkylsilane *Industrial and Engineering Chemistry Research* 48 2009: pp. 9797–9803.
 24. **Huang, W. et al.** Enhanced Washing Durability of Hydrophobic Coating on Cellulose Fabric Using Polycarboxylic Acids *Applied Surface Science* 257 2011: pp. 4443–4448.