

# Simple and Eco – Friendly Fabrication of Super hydrophobic PET Foam for Oil /Water Separation

Than ThanAye<sup>1</sup>, Cai-Hong Shen<sup>2</sup>, PhyuPhyu Win<sup>1</sup>

<sup>1</sup>Department of Research and Innovation Ministry of Education Yangon, Myanmar

<sup>2</sup>The Xinjiang Technical Institute of Physics & Chemistry Chinese Academy of Sciences (XJIPC-CAS) Urumqi, China

**Abstract** - Superhydrophobic and superoleophilic PET (polyethyleneterephthalate) foam was successfully prepared by coating of modified silane solution on the surface of PET foam. To prepare superhydrophobic PET foam, raw PET foam was pretreated by alkali to get affinity of -OH group and coated with modified silane solution. The formation of alkali treatment to get rough morphology and then followed modified with silane solution for superhydrophobicity was confirmed with scanning electron microscopy and investigated the wetting behavior and absorption capacity of probing liquids on the superhydrophobic foam. The coated foam showed higher water repellent activity and higher absorption capacity of oil than raw PET foam with 156 °C of water contact angle and absorption capacity of three kinds of probing liquids were 2 times greater than raw PET foam.

**Keywords:** PET, superhydrophobic, SEM, FTIR, probing liquid

## I. INTRODUCTION

The discharge of oil-contaminated water from the daily life of people as well as from industries can result in serious environmental pollution, and the frequent oil spills resulting from oil transport accidents may be destructive for marine and aquatic ecosystems. Therefore, oil/water separation has always been an important and exigent task in the fields of chemical engineering and environmental protection [1, 2]. Although many methods such as chemical and biological treatments, gravity separation, as well as the use of absorbance and electric field, have been developed and successfully employed as oil/water separation technologies, the limitations of low separation efficiency, energy cost, and complex separation instruments have caused difficulty in taking advantage of these methods [3]. Thus, it is necessary to develop effective technologies and new materials for oil/water separation. As a cost-effective and well-established technique, spray coating is capable of achieving superhydrophobic surfaces with different morphologies; it involves the spraying of a low-concentration suspension consisting of a solvent, inorganic particles, and a polymeric binder [4–6]. In

previous studies, our group has reported the simple approach for directly fabricating superhydrophobic polymer coatings with hierarchical micro and nano-structures via spraying polymer solutions on flat substrates with various solvent compositions [7, 8]. Conventionally, by utilizing the spray coating method to fabricate superhydrophobic membranes for oil/water separation, a mesh (metal mesh and fabric) serving as a support is required for improving mechanical properties and rendering a micro-scale porous structure [9, 10, ].

In this work, we prepared a simple method for fabrication of superhydrophobic and superoleophilic poly (ethylene terephthalate) (PET) foam by coating modified silane solution. The PET foam was pretreated by NaOH solution for roughening of the foam surface. Here in, we reported the superhydrophobic PET foam for environmental remediation by using solution – immersion method. The morphology, functional changing, wetting behavior and oleophilic property of raw PET foam, alkali pretreated PET foam and modified superhydrophobic PET foam were studied.

## II. EXPERIMENTAL SET UP

### A. Materials

Poly (ethylene terephthalate) foam, Tetraethoxysilicate (TEOS), methyl trimethoxysilane (MTMS), isopropyl alcohol, ethanol, sodium hydroxide, hydrogen peroxide, concentrated hydrochloric acid, gasoline, lubricating oil, diesel were used directly. Ultrapure water was used throughout all the experiments.

### B. Preparation of Modified Silane Solution

Modified silane solutions were prepared via one pot reaction. In a typical solution (1), 1g of MTMS, 0.7g of TEOS and 14ml of IPA were mixed in a beaker and stirred for 10 minutes in magnetic stirrer. After that 0.4ml of water and 30µl of concentrated hydrochloric acid were added to the mixture solution to adjust pH 4 and then followed by continuous stirring for 3 hours in ambient temperature. Then the modified silane solution was kept for several hours for preservation. 2g of MTMS, 1.4g of TEOS, 0.8ml of ultrapure water and 3g of MTMS,

2.1g of TEOS , 1.2ml of ultrapure water were used for solution (2) and (3) respectively and other reaction conditions were the same as solution(1).

### C. Alkali Treatment of PET Foam

Firstly, 2.9812g of PET foam was washed by deionized water to remove the impurities and immersed in sodium hydroxide solution containing 6g of sodium hydroxide and 6g of hydrogen peroxide in 600ml of water and heated at 90°C for one and half hours. And then the foams were washed by abundant distilled water until the pH of the washing solution got pH7 and , dried in oven at 80°C for 1 hours.

### D. Coating PET Foam with Modified Silane Solution

A piece of pretreated PET foam ( 2.5cm x 2.5cm x 1.8cm ) were immersed in original modified silane solutions and diluted modified silane solutions (1) , (2) and (3) with the ratio of 1:1,1:2 and 1:3 in v/v with isopropyl alcohol for 2 hours and the samples were dried in oven at 150°C for 45 minutes.

### E. Characterization

The morphological change of fabrics were observed by using a scanning electron microscope (SEM, Zeiss Supra VP55, Germany). Chemical changes between raw PET foam, alkali treated PET foam and

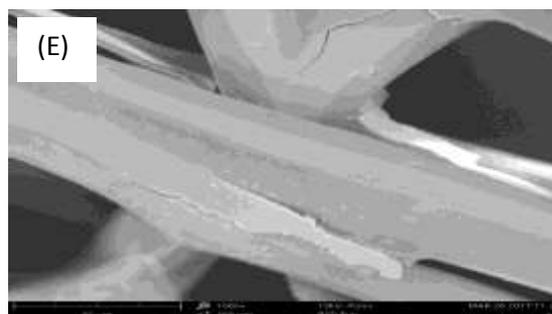
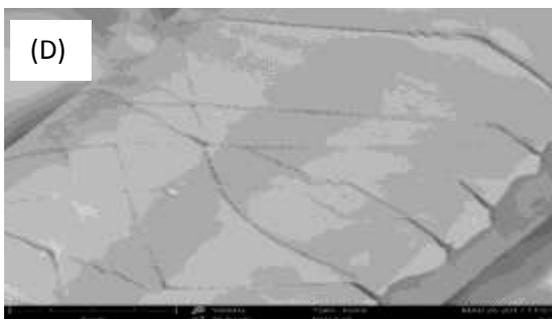
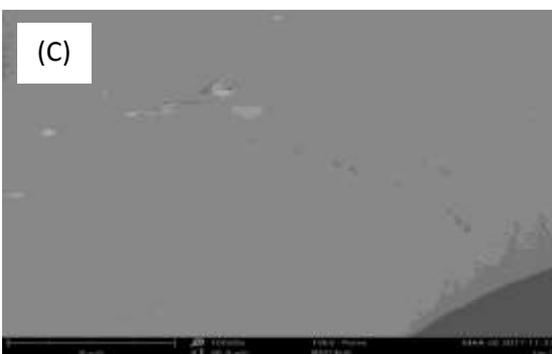
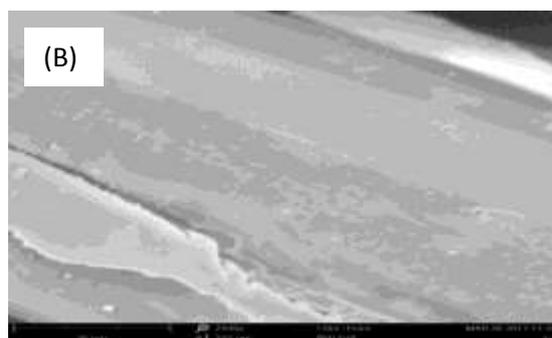
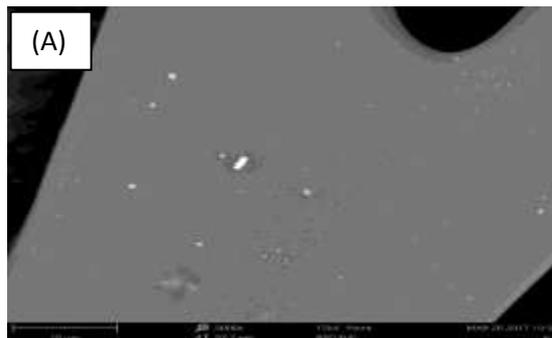
silane coated PET foam were analyzed by Fourier-transform infrared spectrometer ( FT-IR, FTS-165,BIO-RAD). Contact angles (CAs) were measured with 4μL deionized water droplet on a Goniometer (XGCAMA, Shanghai Xuanyichuangxi Company) at ambient temperature. At least three measurements were made within 60s of water droplet formation on the sample, and the average value was reported.

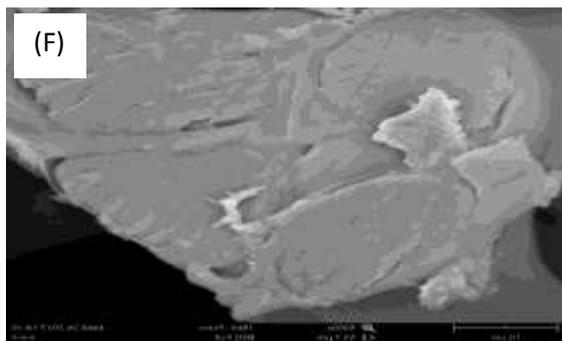
## III. RESULTS AND DISCUSSION

### A. Coating PET Foam with Modified Silane Solution

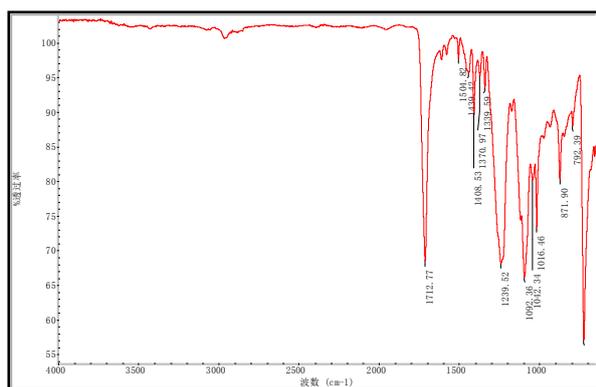
The morphology of raw PET foam, pretreated PET foam and silane coated PET foam were investigated by using a scanning electron microscope (SEM, Zeiss Supra VP55, Germany). . It can be seen in Fig .1 A , a little impurity was found in the surface of the raw PET foam .It may be due to some dust or some crystal of organic compound in polymerization of PET foam. In order to improve the compatibility of PET foam with modified silane solution, the PET foam was treated with NaOH solutions to generate chemical and morphological changes in the PET foam. This treatment can generate chemical and morphological changes in PET foam [ 11 , 12 , 13 ]. As shown in Fig. 1 ( B ) , morphological changes of pretreated PET foam roughened the foam surfaces and increasing the contact area with modified silane solutions .Modified silane solutions coated to pretreated PET foam

tightly on the foam surface and roughened the foam surface very much shown in SEM images Fig. 1 (C) to (F) [14].





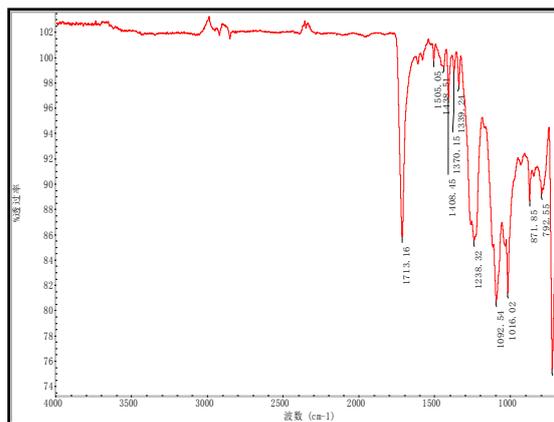
**Fig.1** Morphology of PET foam at different steps (A: Raw PET Foam ; B: Pretreated PET Foam ; C:D: E: Silane Coated PET Foam ; F: Cross section of Silane Coated PET Foam



**Fig.2** FT – IR Spectrum of Raw PET foam

**Table.1.** FT-IR Absorption Band Assignment of Raw PET Foam

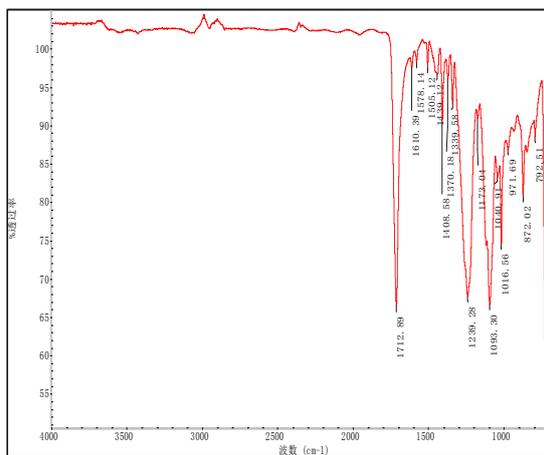
Band position (cm <sup>-1</sup> )	Assignment
2980.34	-aromatic and aliphatic –CH- stretching
1712.77	-C=O- stretching of ester
1504.82	-C=O- asymmetric stretching vibration
1432.42	-CH stretching vibration of aromatic
1408.53	-C=O- stretching of ester
1370.97	-CH <sub>2</sub> trans wagging
1339.59	-CH <sub>2</sub> cis wagging
1239.52	-C=O- stretching vibration of ester
1092.36	-CH <sub>2</sub> asymmetric stretching vibration
1042.34	-anti symmetrical C-O stretching of ester
1016.48	-in plane bending of C-H



**Fig.3** FT-IR Spectrum of Alkali treated PET Foam

**Table.2.** FT-IR Absorption Band Assignment of Alkali treated PET Foam

Band position (cm <sup>-1</sup> )	Assignment
2980.34	-aromatic and aliphatic –CH- stretching
1713.16	-C=O- stretching of ester
1505.05	-C=O- asymmetric stretching vibration
1438.51	-C=H stretching vibration of aromatic
1408.45	-C=O- stretching of ester
1370.5	-CH <sub>2</sub> - wagging
1334.34	-CH <sub>2</sub> trans wagging
1239.32	-C=O- stretching vibration of ester
1092.54	-CH <sub>2</sub> asymmetric stretching vibration
1016.02	-anti symmetrical C-O- stretching
878.6	-CH <sub>2</sub> rocking
792.55	-out of plane bending of C-C bond



**Fig.4.**FT-IR Spectrum of Silane Coated PET Fibre

Table.3.FT-IR Absorption Band Assignment of Silane Coated PET Fibre

Band position (cm <sup>-1</sup> )	Assignment
2980.34	-aromatic and aliphatic -CH- stretching
1718.89	-C=O- stretching of ester
1610.89	- C=C stretching of $\alpha,\beta$ unsaturated ketone
1578.14	-asymmetric -CH <sub>2</sub> - , stretching vibration
1505.12	-C=O- asymmetric stretching vibration
1434.12	-C=H stretching vibration of aromatic
1408.58	-C=O- stretching of ester
1370.18	-CH <sub>2</sub> - wagging
1339.58	- CH <sub>2</sub> trans wagging
1239.28	-C=O- stretching vibration of ester
1173.94	-Si-C- stretching vibration
1093.30	-CH <sub>2</sub> asymmetric stretching vibration
1040.41	- CO-O-CO stretching of ester
1016.56	-anti symmetrical C-O- stretching
971.89	-C=C bending of alkene
872.02	-CH <sub>2</sub> rocking
792.51	-out of plane bending of C-C bond

**B. Wetting Behavior of Modified PET Foams**

In order to investigate the influence of concentration of modified silane solutions to wetting behavior, we prepared three modified silane coated PET foams with solutions (1), (2) and (3). These silane coated PET foams were named as P1 , P2 and P3 according to concentration from dilute to high respectively and water contact angles were measured .The datum were shown in Fig 5a .It was found that P2 has the highest water contact angle with 146 °C . And then original solutions (1) ,(2) and (3) were diluted with IPA in volume ratio of 1: 1 , 1:2 and 1:3 and coated in alkali treated PET foams and detected the water contact angles. It was shown in Fig. 5 b. According to the results of CA, contact angle of the silane coated PET foam diluted with modified silane solution (2) in the volume ratio of 1:2 with IPA is the highest water contact angle about 156 °C .

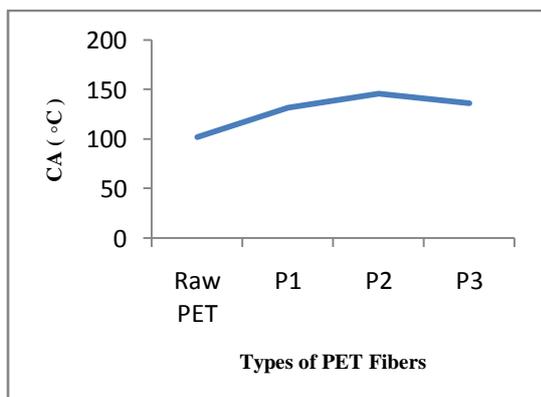


Fig.5.(a) CA changes with different types of PET Fibers( raw PET foam and modified PET foam)

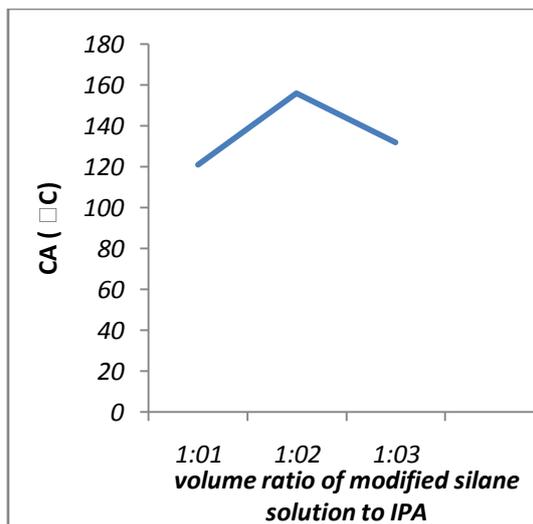


Fig.5.(b) CA changes with the volume ratio of IPA solvent with modified silane solutions

**C. Hydrophobic and Oleophilic Properties of Silane Coated PET Foams**

The adsorption capability of silane coated PET foams were conducted by using a strip sample (2.5cm in length, 2.5 cm in width and 1.8 cm in thickness). The samples were put into contact with water and a specific liquid for the adsorption within 10 minutes. The adsorption capacity of the silane coated PET foams were defined by Q, a ratio between the weight change of the material after liquid adsorption and the initial weight. Q was calculated using the equation:

$$Q = ( M_0 - M_s ) / M_s \times 100\%$$

where  $M_s$  and  $M_0$  are the weights of the material before and after the liquid sorption test. In a typical adsorption experiment, the silane coated PET foam was put into a specific liquid and suspended for 10 minutes to reach the adsorption equilibrium. During the weight measurement, the sample was collected from the liquid using tweezers and led to the edge of the liquid container to remove the excessive oil droplet. All adsorption experiments were conducted two times and an average value were reported in Table ( 4 , 5) and Fig ( 5 , 6 ).The relation between absorptivity of probing liquids and density of raw PET foam and silane coated PET foam were also investigated and the results were shown in table (5).

Table (4) Adsorption Capacity of Water with Different Types of PET Fibre

Type of Sample	Density of Sample ( mg/cm <sup>3</sup> )	Adsorption Capacity of Water (%)
Raw PET	16.7	3750.3
P1(1:1)	17.88	632.1
P2(1:2)	21.5	594.8
P3(1:3)	24.74	632.1

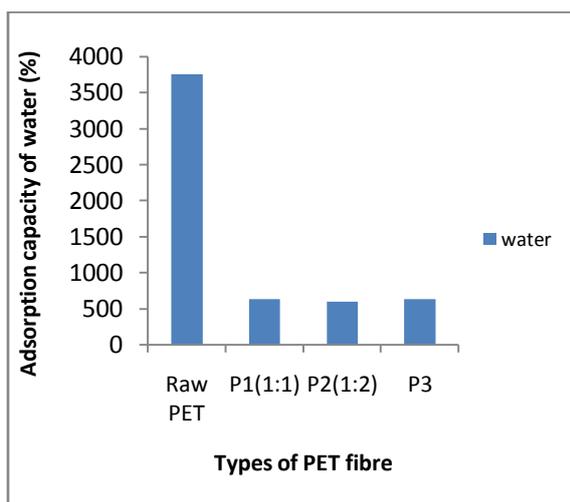


Fig 6. Adsorption behavior of different samples to water in air.

Table (5) Adsorption Capacity of Various Oils with Different Types of PET Foams

Type of Samples	Adsorption Capacity (%)		
	Type of oils		
	Lubricating oil	diesel	Gasoline
Raw PET	2385.3	1125.86	1345.14
P1(1:1)	2989.32	2717.15	2301.899
P2(1:2)	4232.9	3929.52	2668.25
P3(1:3)	2700.22	3134.552	1929.85

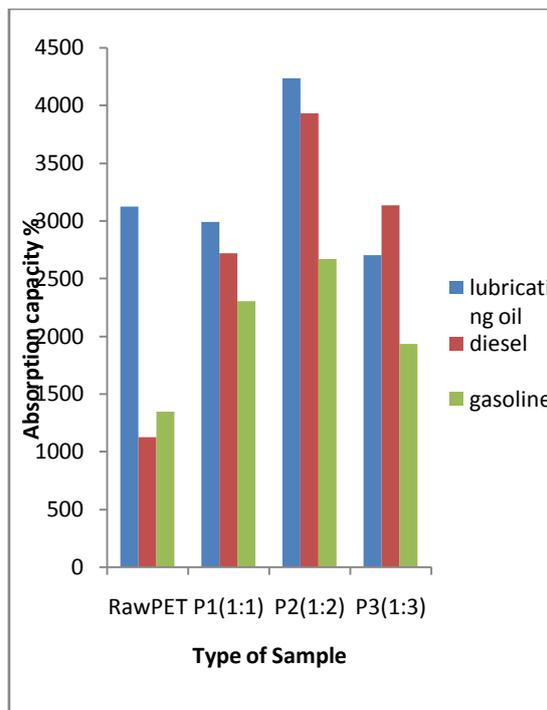


Fig.7. Adsorption behavior of different samples to oil in air

Oil absorption capacities of three kinds of PET foams, under optimal conditions are shown in Fig. 7. It can be seen that the adsorption capacity of oil with Superhydrophobic PET foam P2 (1:2) was approximately larger than 2 times of raw PET foam for three types of oils. The absorptivity of water and oil with raw PET and silane coated PET foams were concerned with density and viscosity of water and specific liquids. The absorption capacities of silane coated PET foam with optimized condition for lubricating oil, diesel, and gasoline oil were 4232.9%, 3929.52% and 2668.25 %, respectively. The reason for this was that the three kinds of oil had different viscosities. Lubricating oil was high density, so it was not easy for it to leak out after absorption, while the viscosity of diesel oil was relatively low, thus it leaked out easily from foam.

#### IV. CONCLUSION

In conclusion, we have developed a new type of PET foam through a simple method using the poly ethylene foam as starting material. The obtained superhydrophobic / superoleophilic PET foam can selectively remove the oil phase from an oil/water mixture at room temperature. With such advantages of good phase-selectivity, the modified PET foam was demonstrated its remarkable potency as an effective oil collector in oil spill clean up.

#### ACKNOWLEDGEMENTS

The author is grateful to the laboratory and technical staff of the The Xinjiang Technical Institute of Chem. & Phys., for the support rendered in

carrying out the work. The author would like to thank deeply the deputy director general of Chemical Technology Research Centre, DrPhyuPhyu Win and Director of Department of Research and Innovation, SayarGyi U Win Khaing Moe, , for permitting to attend TYSP in the The Xinjiang Technical Institute of Physics&Chemistry. The author also would like to express sincerely and deeply thanks to Professor Peng-Cheng Ma, The Xinjiang Technical Institute of Phys.&Chem, Chinese Academy of Sciences (XJIPC-CAS), Urumqi, for laboratory facility and financial support.

### REFERENCES

- [1] Kota AK, Kwon G, Choi W, Mabry J M, Tuteja A (2012) Hygro responsive membranes for effective oil-water separation. *Nat Commun* 3:1025–1032
- [2] Tao M, Xue L, Liu F, Jiang L (2014) An intelligent super wetting PVDF membrane showing switchable transport performance for oil/water separation. *Adv Mater* 26:2943–2948
- [3] Gondal MA, Sadullah MS, Dastageer MA, McKinley GH, Panchanathan D, Varanasi KK (2014) Study of factors governing oil-water separation process using TiO<sub>2</sub> films prepared by spray deposition of nanoparticle dispersions. *ACS Appl Mater Interfaces* 6:13422–13429
- [4] Levkin PA, Svec F, Fréchet JM (2009) Porous polymer coatings: a versatile approach to superhydrophobic surfaces. *AdvFunct Mater* 19:1993–1998
- [5] Shirtcliffe NJ, McHale G, Newton MI (2011) The superhydrophobicity of polymer surfaces: recent developments. *J Polym Sci Part B* 49:1203–1217
- [6] Hwang HS, Kim NH, Lee SG, Lee DY, Cho K, Park I (2011) Facile fabrication of transparent superhydrophobic surfaces by spray deposition. *ACS Appl Mater Interfaces* 3:2179–2183
- [7] Li H, Zhao Y, Yuan X (2013) Facile preparation of superhydrophobic coating by spraying a fluorinated acrylic random copolymer micelle solution. *Soft Matter* 9:1005–1009
- [8] Li H, Zhao X, Chu G, Zhang S, Yuan X (2014) One-step fabrication of a superhydrophobic polymer surface from an acrylic copolymer containing POSS by spraying. *RSC Adv* 4:62694–62697
- [9] Tu CW, Tsai CH, Wang CF, Kuo SW, Chang FC (2007) Fabrication of superhydrophobic and superoleophilic polystyrene surfaces by a facile one-step method. *Macromol Rapid Commun* 28:2262–2266
- [10] Rohrbach K, Li Y, Zhu H, Liu Z, Dai J, Andreasen J, Hu L (2014) A cellulose based hydrophilic, oleophobic hydrated filter for water/oil separation. *Chem Commun* 50:13296–13299
- [11] C.-H. Xue, P. Zhang, J.-Z. Ma, P.-T. Ji, Y.-R. Li, S.-T. Jia, Long-lived superhydrophobic colourful surfaces, *Chemical Communications* 4 (2013) 3588–3590
- [12] B.M. Latta, Improved tactile and sorption properties of polyester fabrics through caustic treatment, *Textile Research Journal* 54 (1984) 766 – 775.
- [13] H. Tavanai, A new look at the modification of polyethylene terephthalate by sodium hydroxide, *Journal of the Textile Institute* 100 (2009) 633–639
- [14] B. Leng, Z. Shao, G. de With, W. Ming, Superoleophobic Cotton Textiles, *Langmuir* 25 (2009) 2456–2460.