Effect of Different Poly (ethylene terephethalate) Hydrolysis to Manipulate Proper Nano-Surface Structures for Fabricating Ultra hydrophobic Substrate

Akbar Khoddami, Zahra Mazrouei Sebdani and Shadpour Mallakpour

Abstract—**To achieve ultra hydrophobic Poly (ethylene terephthalate), PET substrate, two liquid etching methods of alkaline hydrolysis and aminolysis were applied to influence surface topography. To create low surface energy a layer of fluorocarbon was coated on the surface. The preferences of two methods were investigated by SEM microscopy, 3M water and oil repellency, sliding angle, self-cleaning and tensile properties .The results indicated that both chemical etching methods are able to create proper surface roughness and there is no necessity to apply nano particles which have a lot of side effects. However, the conventional polyester weight reduction process, alkaline hydrolysis, compared to the aminolysis process, presents better procedure for industrial scale manufacturing of ultra hydrophobic polyester substrates, by which the etching effect more or less is limited to the substrate surface.**

Key words: Chemical etching, coatings, hydrophobicity, polyesters, surface roughness.

I. INTRODUCTION

SUPER hydrophobic surfaces are those surfaces on which droplets appear to sit without any significant surface wetting and exhibits contact angles in excess of 150°. In this case the surfaces provide both a nanoscale surface roughness and a low surface energy [1–8].

Many papers and patents are available and considerable amount of research works is in progress on the fabrication of super hydrophobic surfaces and textiles in different ways [1,2,5,9–23]. Many methods have been reported to produce these surfaces by application of nanoparticles that not only penetrate a person's skin by releasing from the finished fabric surface and cause health problems, but also make textiles uncomfortable to wear [15].

As for polymers, there are a whole range of options for texturing surfaces that can be separated into two broad classifications: random and patterned texturing. The random techniques would include the processes such as liquid, plasma or laser etching and generation of hairy surfaces. The production of regular structures would include techniques such as embossing, laser writing or printing. The oldest method is to use the appropriate liquid to etch away the top surface [24]. Many authors investigated the etching of polymer surfaces with different methods for variety of applications [25-28]. Alkaline hydrolysis and aminolysis are two chemical processes that are used for etching polyesters generating some chemical and morphological changes on the polyester substrates [29-35].

In our previous papers [36, 37], it was revealed that there is a possibility to replace the use of nanoparticles, generally used as a simple way to change surface roughness to fabricate lotus type textiles, by chemical etching methods. In this research, alkaline hydrolysis and aminolysis are compared in detail for creating appropriate roughness on the polyester surface in order to find a better and more facile way to change substrate topography with minimum side effects on the fibers' bulk properties.

II. EXPERIMENTAL

A. Materials

Polyester fabric with plain weave (100%, 120 g/m^2) was used as a substrate. Sodium hydroxide, methyl amine, acetic acid and sodium carbonate were prepared from Merck, Germany. The selected fluorocarbon was Rucostar EEE and prepared from Rudolf, Germany. Non-ionic detergent, Sera Wet C-NR, was supplied by DyStar.

B. Fabric treatment

The polyester fabric was firstly washed to remove any possible impurities which can adversely affect the surface treatments by1 mL/L non-ionic detergent and 0.2 g/L sodium carbonate (pH 8–9) with L: R of 30:1 at 50–55 °C for 45 min. Then, the samples were rinsed for 60 min and air dried without any tension.

The scoured polyester fabrics were impregnated in a treatment bath containing 30, 45 and 60 g/L Rucostar EEE, acetic acid (1 mL/L) and propane 2-ol (5 mL/L). Acetic acid and propane 2-ol were used as a pH adjuster and wetting agent, respectively. Subsequently, the sample was passed through a two-roll laboratory padder (Mathis, Switzerland). This treatment gave a wet pickup of 75–80%. After drying (2 min, 100 °C) the fabric was cured for 2 min at 180 °C in a lab dryer (Warner Mathis AG, Niederhasli/Zürich).

Alkaline hydrolysis of scoured polyester samples was carried out with 60 g/L sodium hydroxide, L:R of 20:1, for 15, 30, 45, 60 and90 min at 80 ± 5 °C.

Aminolysis of scoured polyester samples was carried

A. Khoddami and Z. Mazrouei Sebdani are with the Department of Textile Engineering, Isfahan University of Technology, Isfahan, Iran. S. Mallakpour is with the Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan and Nanotechnology and Advanced Materials Institute of Isfahan University of Technology. Correspondence should be addressed to A. Khoddami (e-mail: khoddami@cc.iut.ac.ir).

out with 30, 32, 34, 36 and 38% methyl amine, L:R of 15:1, for 150 min at 30 °C. After rinsing with much diluted acetic acid and distilled water for 20 min, the sample was air dried without any tension.

All alkaline hydrolyzed and aminolysed samples were finished with the optimum concentration of the fluorochemical, Rucostar EEE 45 g/L, according to the above mentioned conditions.

C. *Evaluation methods*

To study the level of the sample hydrophobicity, both sliding angle [38] and the 3M oil and water repellency tests [39-40] were examined. Details of 3M tests are available in our previous papers [36, 37].

In addition, the re-orientation of fluorocarbon polymer chains after wet processing was evaluated in accordance with AATCC Test Method 61–1994 tests No. 2A by Polymat (AHIBA1000 Datacolor; Zürich) in order to assess how samples keep their performance after washing and hot-pressing at 120 ◦C using an Elnapress/SDL. Scanning electron microscopy (Hitachi S-300N) was applied to study the samples surface structure. Also, the self-cleaning property was evaluated using photographic method by Canon camera model macro70-135 and also MATLAB software in which photographs of samples, uniformly covered with carbon black, were compared before and after water drop movement on the surface. Determination of fabrics tensile properties was carried out according to ASTM: D5035-90 strip method with gauge length of 0.15 m, crosshead speed of 100 mm/min and 10 tests for each sample.

III. RESULTS AND DISCUSSION

A. *Fluorochemical Treatment*

Table I indicates that fluorocarbon finishing is unrelated to the applied concentration and leads to maximum oil and water repellency with 3 M water repellency of 10 and oil repellency of 8 for three samples. The sample treated with 30 g/L fluorochemical showed higher sliding angle than the samples treated with 45 and 60 g/L. The sliding angle of the sample treated with 60 g/L fluorochemical was statistically as the same as the sample treated with 45 g/L. So, there was a slight decrease in the sliding angles when fluorocarbon concentration increased from 30 to 60 g/L and results in well hydrophobic film coverage. In addition, samples treated with 30 and 45 g/L of the fluorochemical had more tenacity than the samples treated with 60 g/L. The effect of treatment with Rucostar EEE was, in general, to increase the fabric strength, but at 60 g/L concentration, the strength reduced maybe due to the imparted sample stiffness attained by higher concentration of fluorochemical. Accordingly, the concentration of 45 g/L was chosen as an optimum concentration for further experiments, while economic aspect was also considered. Furthermore, improving sliding angle can be manipulated by changing surface roughness with a more important role than the fluorochemical concentration.

B. *Effect of alkaline hydrolysis or aminolysis and after-treatment with fluorochemical on the repellent and tensile properties*

Although there are some defects with application of nanoparticles to roughen the surface, many researches have been reported to use these particles to fabricate lotus type textiles. Nanoparticles, because of their very small size could leave the surface and penetrate a person's skin. This is important from this point of view that they may cause health problems. Also, textiles treated with nanoparticles could be uncomfortable for wearing [15]. So, developing a simple method for the manufacture of hydrophobic surfaces on textiles by harmless and flexible materials is necessary. In our previous papers [36,37], in order to create surface roughness, aiming at replacement of nanoparticles, the possible roughening effect of polyester alkaline hydrolysis as well as aminolysis was investigated. The results demonstrated the priority of these two methods instead of the application of nanoparticles. In contrast to the drawback of nanoparticles that could leave the surface, alkaline hydrolysis and aminolysis could create nano structures on the polyester surface by etching the surface via particular manners, Figures 1 and 2. In this paper, two methods of chemical etching, alkaline hydrolysis and aminolysis, were compared [29].Accordingly, the reported data was limited to those samples which were hydrolyzed and then finished with fluorochemical while more details could be found in other papers [36,37].

Repellent properties of alkaline hydrolyzed samples are illustrated in Table II. It should be mentioned that, for each part, separate control sample was tested and repeatability of the results was assessed. The results of 3M tests showed the highest values for oil and water repellency after fluorocarbon finishing. In addition, as can be seen in Table II, the alkali treatments reduced the samples' sliding angles remarkably, less than 10°, in comparison with those samples treated with the fluorochemical. The differences between sliding angles of alkaline hydrolyzed-fluorocarbon treated samples were not statistically significant, except for those samples that were hydrolyzed for 15 and 90 min with more or less higher tilting angle for the longer hydrolyzed sample.

TABLE I
WATER REPELLENCY AND PHYSICAL PROPERTIES OF FLUOROCHEMICAL-TREATED POLYESTER FABRICS

Fluorochemical (g/L)	Sliding angle (°)	Tenacity change[a] (%)	Water and oil repellency 3M test					
			Before wash		After wash		After wash & hot pressing	
			Water	Oil	Water	Oil	Water	Oil
30	19.1±0.5	12.1±3.4	10	8	2	0	9-10	7-8
45	17.9±0.7	12.8±2.5	10	8	2	0	10	8
60	16.1±0.5	-5.3±1.6*	10	8	2	0	10	8

[a] Minus shows the tenacity loss, compared to untreated sample

TABLE II
WATER REPELLENCY OF ALKALINE HYDROLYZED SAMPLES TREATED WITH FLUOROCHEMICAL

Hydrophobic treatment	Alkaline hydrolysis time(min)	Sliding angle (°)	3M water and oil repellency test: Before wash water	Before wash oil	After wash water	After wash oil	After wash & hot pressing water	After wash & hot pressing oil	Change of tenacity (%)[a]
Fluorochemical	-	17.5±0.6	10	8	2	0	10	8	+12.8±2.8
	15	7.3±0.4	10	8	2	0	10	8	+1.1±0.8
	30	9.0±0.3	10	8	2	0	10	8	+4.1±0.9
	45	8.7±0.2	10	8	1-2	0	10	8	+6.8±1.6
	60	8.7±0.5	10	8	2	0	10	8	+11.5±2.7
	90	9.9±0.3	10	8	2	0	10	8	-40.3±3.3

[a]Minus and plus show the tenacity decrease and increase, respectively, compared to untreated sample

Figure 1 shows SEM micrographs of pits created on the alkaline hydrolyzed samples for 15 and 90 min [36]. Polyester fibres are susceptible to bases depending on their ionic character. Ionizable bases like caustic soda affect the outer surface of polyester filaments. It was assumed that a random attack of the base on the carboxyl groups of the surface polymer molecules took place in amorphous regions more than crystalline ones. So, the regions around the TiO_2 particles are more hydrolyzed by the base [29] and polymer chains are more degraded around them because these regions are more amorphous compared to other parts of the surface. This action leaves axially oriented, elliptical voids around the TiO_2 particles, delusterant agents, forming entry points for the alkaline solution to attack polymer under the original fiber surface. Development of the pits in both depth and length occurs with continued exposure to alkaline solution and leaving of TiO_2 particles from the surface [30], Figure 1(D) and (E).In other words, although the surface of polyester is etched by the alkaline solution and the fibers appear thinner in diameter, nano and micro pits are created on the surface just in the presence of TiO_2 particles.

However, the best result (sliding angle of ~7°) was achieved by 15 min moderate alkaline treatment which was economically and industrially applicable.

Accordingly, as can be seen at Table III, amine-treated samples after fluorocarbon finishing showed the highest values for 3M oil and water repellency. Evaluating sliding angle of the samples showed a gradual increase with the increase of methyl amine concentration so that the sliding angle of aminolysed sample with a concentration of 30% was less than those treated with a higher concentration. Generally, the differences between the sliding angles of amine-treated samples were not statistically significant except for the treated sample with 30% amine.

Furthermore, the results indicated that aminolysis and alkaline hydrolysis processes can create proper roughness on the surface and replace the use of nanoparticles [36, 37].

Figure 2 shows SEM micrographs of methyl amine treated samples after treatment with fluorochemical and nanoparticles [37]. Amine reaction is selective, and amorphous regions are degraded in the initial stage of treatment leading to cracks on the surface of fibers [34,35]. Different etchings in amorphous and crystalline regions as well as internal stress that remained in the fibers are the factors that lead to cracks on the surface [35].

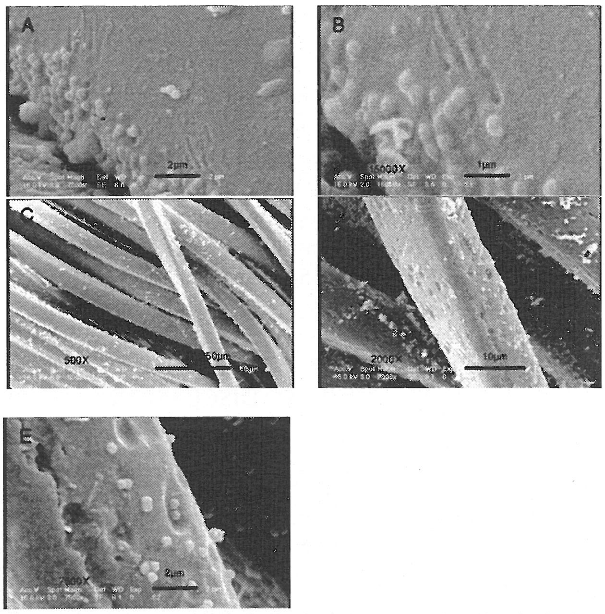

Fig. 1. SEM micrographs of alkaline hydrolyzed samples. (A, B) 15 min, and (C–E) 90 min, after finishing with fluorochemical–nanoparticles [36].

If sliding angle of the samples is compared, it can be demonstrated that alkaline hydrolysis treatment, with sliding angles range of less than 10°, was preferably better than aminolysis, with sliding angles range of more than 12°. Chemical hydrophobicity of the fluorocarbon film on the topmost surface layer, coupled with created pits and

TABLE III
WATER REPELLENCY OF AMINOLYSED SAMPLES TREATED WITH FLUOROCHEMICAL

Hydrophobic Treatment	Amine concentration (%)	Sliding angle (°)	3M water and oil repellency test: Before wash Water	Before wash Oil	After wash Water	After wash Oil	After wash & hot pressing Water	After wash & hot pressing Oil	Change of tenacity (%)[a]
Fluorochemical	-	17.5±0.6	10	8	2	0	10	8	+12.8±2.8
	30	12.9±0.6	10	8	1-2	0	10	8	-47.3±3.8
	32	14.5±0.4	10	8	2	0	10	8	-77.5±3.5
	34	15.4±0.5	10	8	2	0	10	8	-76.9±1.4
	36	16.4±0.6	10	8	W-1	0	10	8	-91.7±1.7
	38	16.7±1.0	10	8	1	0	10	8	-88.5±1.0

[a]Minus and plus show the tenacity decrease and increase, respectively, compared to untreated sample

rough surface, of the alkaline hydrolysis produced super hydrophobicity, with the best result (sliding angle of 7°) achieved by 15 min alkaline hydrolysis treatment in comparison with the best result of aminolysis by sliding angle of 12.5°.

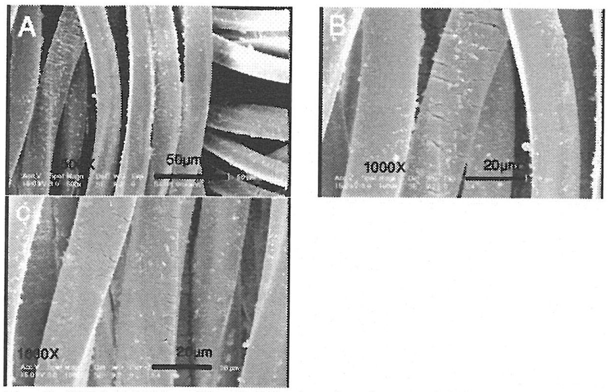

Fig. 2. SEM micrographs of aminolysed polyester fabrics finished with fluorochemical-nanoparticles (A) 500X, and (B, C) 1000X [37].

The decrease in sliding angle is attributed to the introduction of double roughness with the original roughness appearing from the fabric structure itself and the next from the special shapes on the surface created by chemical etching. The effect of fabric structure on hydrophobicity can be proved by comparing the sliding angle of fluorochemical treated smooth polyester film, Melinex, (30.5±1.9°) with the fabric (17.9±0.7°) [36].

It seems that the double-scale topography (pits or cracks/fabric structure) of the polyester surface is simulating the lotus leaf effect which is compatible with previous finding about the binary length scale topography (2 μm fiber/50 μm woven bundles) of the microfiber polyester. So, polyester fabrics made from microfibers are more water repellent as compared to conventional polyester fabrics [41,42].Also, some other reports showed importance of roughness at two length scales kinetically and thermo dynamically [14,43,44].

Since tensile strength plays an important role in service ability of fabrics in industrial scale, the tenacity of aminolysed and alkaline hydrolyzed samples were evaluated. The effect of treatment with Rucostar EEE was, in general, to increase the fabric strength. This effect may be because that the Rucostar EEE increases fiber lubricity and associated ease to accommodate deformation forces. It is clear that alkaline hydrolysis and aminolysis decrease the tenacity of samples, compared to the only fluorocarbon treated sample, via chain breakages throughout the fibers [30], but the decrease in the samples strength due to the alkaline hydrolysis is very negligible. So, alkaline hydrolyzed-fluorocarbon finished samples resulted in tenacity improvement in comparison with the untreated fabrics, except for 90 min, Table II.

On the other hand, Primary and secondary bases and ammonia can diffuse into polyester fiber and attack in depth resulting in breaking of polyester chain molecules by amide formation [29]. So, significant tenacity loss by aminolysis process may be due to more penetration of amine to the fibers because of smaller molecular size as compared with NaOH, Table III.

C. Re-orientation of fluorochemical chains during wash

The required surface energy in air or in an aqueous environment can be obtained by applying a polymer containing both hydrophobic and hydrophilic segments [45]. Thus the hybrid fluorochemical functions effectively as a stain repellent in air and also as an effective oily soil release finish in washing. After washing, the re-orientation of Rocustar EEE during air drying was incomplete, Tables I–III. Therefore, the repellent properties showed remarkable decrease in both oil and water repellency due to the dual action of the fluorochemicals resulted from the re-orientation of hydrophobic chains. Hydrophobic moieties present at the air/polymer interface moved away from the surface into the bulk of the polymer by immersing into water [46]. Alkaline hydrolyzed- fluorochemical or aminolyzed- fluorochemical treated samples showed the same tendencies as the only fluorochemical treated samples and similar deficiency of molecular re-orientation after washing. Decay of the repellency after wet treatment is not due to removing of the hydrophobic moieties, because they retrieve their original repellency performance after heating at 120 °C. So, migrations of hydrophobic moieties caused by the water are at least partially reversible. The buried fluorine containing moieties migrate toward the surface on heat treatment [47]. In spite of the decay of hydrophobicity after washing, all treated samples show minimum 3M water repellency of 1–2 which is fair enough for water repelling and obtaining self-cleaning effect. In addition, there are no practical differences between aminolysed and alkaline hydrolyzed-fluorochemical treated samples.

D. Self-cleaning properties of the repellent finished samples

Qualitative and quantitative evaluation of the samples self cleaning was carried out using photographs of the samples coated with thin layer of carbon black before and after passing water droplets on the surface (Figure 3). A water droplet, from the distance of about 2 cm above the surface, was placed on the surface with a dropper and the surface was tilted until the droplet could slide. The droplet moved over the repellent finished fabrics, gathered the black powder and cleaned the fabrics.

In quantitative analysis by MATLAB software, the ratio of white pixels to the all pixels was calculated in the binary pictures before and after passing the water droplet. The results, Table IV, indicate that the extent of surface cleaning was increased with the following order for samples finished with the: fluorochemical <fluorocarbon finished aminolysed fabric <fluorocarbon finished hydrolyzed fabric.

The increase in self-cleaning effect is quite clear with alkaline hydrolysis and aminolysis. However, the best result was acquired on alkaline hydrolyzed sample in which proper surface roughness was created.

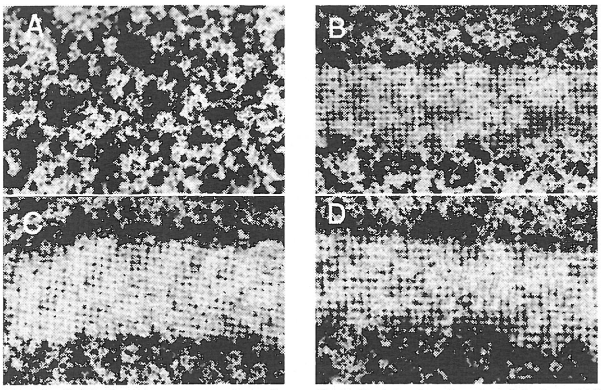

Fig. 3. Self-cleaning properties of repellent finished polyester fabrics, (A) covered by carbon black and (B–D) after movement of water droplet. (B) Fluorochemical, (C) alkaline hydrolysis-fluorochemical and (D) amine-fluorochemical treated sample.

The hydrolyzed sample with more amounts of washed particles away, shows cleaner surface than the comparable samples. These effects coupled with sliding angle less than 10°. It was demonstrated that there is a direct relationship between sliding angle and self-cleaning effect [15]. It is obvious that the interaction between the droplet and the black particles had been adequate to overcome the low adhesion between the fabric and the particles similar to lotus leaf [48] (Figure 3). In fact, the particles stuck to the water drop rolling across the surface (Figure 4).Some black particles, which are stuck among the woven bundles, could not be removed by the water droplet which moves on the pinnacle of the rough surface.

TABLE IV
INCREASE OF WHITE PIXELS OF HYDROPHOBIC FABRICS AFTER PASSING THE DROPLET, COMPARED TO THE SAME BEFORE PASSING THE DROPLET

Treatment	White pixels increase (%)	Sliding angle (°)
Fluorochemical (45 g/L)	6.5	17.9±0.7
Alkaline hydrolysis (15 min) & Fluorochemical (45 g/l)	15.9	7.3±0.4
Aminolysis (30%) & Fluorochemical (45 g/L)	8.5	12.9±0.6

However, in order to remove almost all the particles between fabric structures, passing the droplet gently back and forth for several times is adequate (Figure 5).

In addition, it is revealed in Figure 6 that each place where the water drop touches the surface at first, the contamination will be collected by the drop surface which aids the surface cleaning by rain. These experiments indicate the parameters affecting self-cleaning properties, and pave the way to effective measurement of the level of biomimetics of lotus leaf effect on textile.

IV. CONCLUSION

Super hydrophobic surfaces can be achieved by two main necessities: low surface energy and the appropriate degree of roughness. In this work, artificial lotus leaf structures were fabricated on the polyester substrate using chemical etching by alkaline hydrolysis and aminolysis. It was demonstrated that the weave construction of the substrate coupled with pits (created by alkaline hydrolysis) or cracks (created by aminolysis) remarkably affect the dual scale surface roughness to fabricate super hydrophobicity.

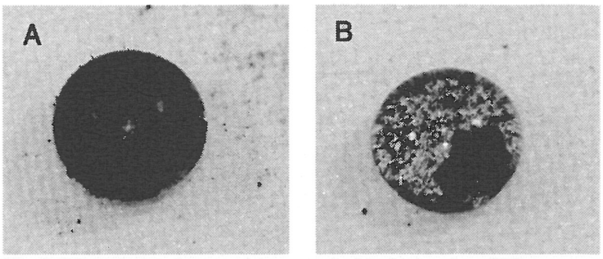

Fig. 4. Water drops after transition over the blacked surface [37].

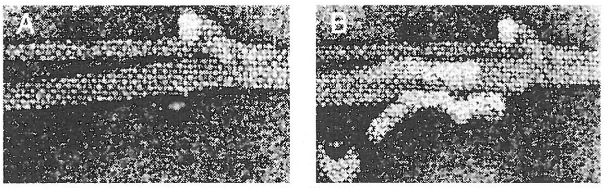

Fig. 5. Cleaning of the surface under the drop movement, (A) one and (B) several times [37].

Alkaline hydrolysis method indicated more proper surface roughness leading to decrease of sliding angles. Objective and subjective comparison of the self-cleaning properties of the samples treated with both methods recognized the higher efficiency of the alkaline hydrolyzed-fluorocarbon treated samples. The influence of the applied etching method on the physical properties was so different. While aminolysed- fluorocarbon treated samples illustrated loss of tenacity, the alkaline hydrolyzed-fluorocarbon treated samples showed an increase in the sample tenacity. In addition, it was clarified that, the decay of hydrophobicity after washing in all tested methods is not at that level to diminish self-cleaning properties. Therefore, it was demonstrated that both methods can replace application of the nanoparticles with possible harmful effects and difficult application process, but according to the results, the alkaline hydrolysis with high feasibility in textile industries presents a simple and facile method to engineer super hydrophobic surface.

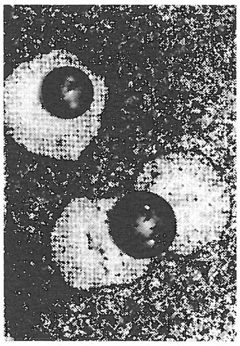

Fig. 6. Collection of contamination at the drop surface when it contacts superhydrophobic surface [37].

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