Surface Chemical Modification of Bio-mimetic Materials: Underwater Oil / Fouling Repellency

By

Divya Mahendran

20101004

Integrated MS, 5th Year

IISER, Pune, India

Under the supervision of

Dr. Ashish Vaidya

Unilever R & D,

64, Main Road, Whitefield,

Bangalore 560066, India

Certificate

This is to certify that this dissertation entitled "**Surface Chemical Modification of Bio-mimetic Materials: Underwater Oil / Fouling Repellency**" towards the partial fulfillment of the BS-MS dual degree programme at the *Indian Institute of Science Education and Research, Pune* represents original research carried out by **Divya Mahendran** at *Unilever R & D, 64, Main Road, Whitefield, Bangalore 560066, India* under the supervision of **Dr. Ashish Vaidya,** Research Scientist, Skin Form and Function, *Unilever R & D, 64, Main Road, Whitefield, Bangalore 560066*, *India* during the academic year 2014-2015.

Ashish Vaidya

Date: 25/03/2015

Declaration

I hereby declare that the matter embodied in the report entitled "**Surface Chemical Modification of Bio-mimetic Materials: Underwater Oil / Fouling Repellency**" are the results of the investigations carried out by me at the Department of *Skin Form and Function, Unilever R & D, 64, Main Road, Whitefield, Bangalore 560066, India* under the supervision of **Dr. Ashish Vaidya,** Research Scientist, *Unilever R & D, 64, Main Road, Whitefield, Bangalore 560066, India* and the same has not been submitted elsewhere for any other degree.

Divya

Divya Mahendran

Date: 25/03/2015

Acknowledgements

It gives me immense pleasure to thank my mentor **Dr. Ashish Vaidya** for his support and inspiring guidance throughout the period of my work. I am indebted to him for enlightening me on the finer skills of dealing with Polymer chemistry. It would have been impossible to achieve this goal without his constant support and encouragement.

I would like to express my special gratitude to **Mr. Somnath Das** for his encouragement, constructive suggestions, technical value addition and training during the course of this project.

I take this opportunity to thank my **Prof. Britto S Sandanaraj,** for his support during the project.

I wish to express my sincere gratitude to **Dr. Manoj Joshi,** for providing me support and opportunity to do my project at Unilever R & D. I sincerely thank **Dr. Vijay Gadgil** for providing me all the laboratory facilities. I also thank **Dr. Anita Damodaran** and **Dr. Babita Baruwati** for making me part of the students program.

I am also grateful to **Balu K**, **Praful Lahorkar** and **Rajkumar Perumal** for their technical assistance and support during this work.

Last, but not the least, I would like to thank my family for everything they have done for me.

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Abstract

Complementary combination of surface chemical functionality and hierarchical surface topography provides superior and diverse surface properties. We demonstrated under-water oil/fouling repellency on bio-mimetic materials having complementary combination of hydrophilic functionality and hierarchical micro-nano surface topography. Poly(dimethylsiloxane) based bio-mimetic replica (PDMS-replica) was prepared following conventional soft lithography. This PDMS-replica was then functionalized with (3-Aminopropyl)trimethoxysilane to obtain the amino-silane modified PDMS-replica$^{silica/NH_2}$.

Subsequently, epoxy terminated polyalkylene glycol monoallyl ethers (PG-Ep) were synthesized and characterized by the epoxidation of polyalkylene glycol monoallyl ethers (PG/ polyglycol) using MCPBA. Finally, polyglycol modified PDMS-replica (PDMS-replica$^{silica/NH_2/OH}$) was prepared by reacting PDMS-replica$^{silica/NH_2}$ with PG-Ep. The resulted PDMS-replica$^{silica/NH_2/OH}$ showed under-water oil repellency with the oil contact angle, θ_{oil} of ~142° under-water. At each stage of the chemical modification, surface composition was analyzed using X-ray photoelectron spectroscopy and wettability was verified using contact angle measurements.

Introduction

Superhydrophobic materials have emerged in many industrial and biological applications which include anti-fouling[1, 2, 3] and self-cleaning / anti-stick [4, 5, 6, 7] coatings. Most of these materials[8, 9, 10] were designed by mimicking the micro/ nanostructural topographies present on self-cleaning leaf surfaces [11, 12] integrated with surface energy modification. Similarly, researchers have exploited the synergistic effect of $-CF_3$ terminal functionality and structured surface topography for developing superoleophobic surfaces. [13, 14, 15]

Unfortunately under water, these superhydrophobic and superoleophobic surfaces having low solid-air ($\gamma_{\text{solid-air}}$) surface energy attract foulants like oil, stain, proteins etc. This is potentially to be due to the high solid – water ($\gamma_{\text{solid-water}}$) interfacial energy, which they exhibit under water. Fundamentally, for under water fouling repellency, it is essential to have surfaces having low solid – water ($\gamma_{\text{solid-water}}$) interfacial energy [16] along with complementary surface roughness.

Hence, in response to the demand of surfaces which can surmount these limitations, the field of superhydrophilic surfaces attained much attention [17, 18, 19] for under water fouling repellency. These surfaces find useful in diverse applications ranging from maritime fouling, industrial/domestic fouling to biomedical fields. [20]

Researchers have explored the process for developing underwater superoleophobic surfaces utilizing hydrophilic chemistry integrated with various organic and inorganic substrates. Gondal *et al.* [21] developed superhydrophilic as well as underwater superoleophobic TiO_2 nanoparticles-coated steel meshes capable of separating oil from water. Zou *et al.* [22] found that hydrophilic triglyme polymer deposited thin-film composite (TFC) polyamide reverse osmosis (RO) membranes show significantly reduced organic fouling than the untreated commercially obtained RO membranes. Xue *et al.* [23] developed superhydrophilic and underwater superoleophobic polyacrylamide hydrogel-coated stainless steel meshes for separating oil from water. Liu *et al.*[24] developed superhydrophilic and underwater superoleophobic surfaces by grafting zwitterionic poly(sulfobetaine methacrylate) (pSBMA) polymer brushes on the glass fiber for separation of oil from water. Ju *et al.*[25] developed fouling-resistant oil/water separation membrane coating materials by modifing the polysulfone ultrafiltration membrane surfaces with crosslinked poly(ethylene glycol) diacrylate (PEGDA). Venault *et al.*[26] reported that poly(ethylene glycol) methyl ether methacrylate (PEGMA) modified microporous expanded poly (tetrafluoroethylene) (ePTFE) membranes showed anti-fouling properties. Zheng *et al.*[27] have recently developed superhydrophilic and under-water superoleophobic fabrics with under water self-cleaning properties, by fabricating its micrometer and nanometer sized hierarchical structures by coating with scaly titanium oxide, which separated oil/water mixtures.

In most of the previous publications, researchers have attempted fabricating smooth surfaces or randomly patterned surfaces [28, 29] for achieving materials with superhydrophilicity/ superhydrophobicity/ superoleophobicity. Though it is highly desirable, we observed limited attention in “hydrophilic chemical modification” of hierarchical surface patterns. This is because; such attachment chemistries involve rigorous intermediate chemical surface modifications, which tend to spoil/alter the original roughness of the material.

Hence our objective was to develop an underwater oil- repellent bio-mimetic replica possessing tethered poly(alkylene glycol) on the hierarchical micro- nanostructures. Poly(dimethyl siloxane) based biomimetic replica (PDMS-replica) was developed following nanocasting based on soft lithography[30, 31, 32] using natural colocasia leaf template. In this process, a viscous blend of poly(dimethyl siloxane) (PDMS) was applied on the leaf template, subsequently curing it into a solid film. As during the course of solidification, the complementary structures on the leaf’s original surface was transferred onto the replica, the solid negative replica obtained has to be replicated again to get positive polymeric replica with surface patterns similar to the natural leaf template. Hence a subsequent replication of the negative PDMS-replica was performed after vapor depositing an anti-stick monolayer of dodecyltrichlorosilane, following the same procedure. After modifying the positive replica obtained with silica, the resulted PDMS-replica$^{\text{silica}}$ was treated with (3-Aminopropyl) trimethoxysilane to get amino-silane modified PDMS-replica$^{\text{silica/NH}_2}$. The replica was finally tethered with polyglycol by treating the PDMS-replica$^{\mathrm{silica/NH_2}}$ with epoxy terminated polyglycol to get hydrophilic replica$^{\mathrm{silica/NH_2/OH}}$. The epoxy terminated polyglycol was synthesized by the epoxidation of polyalkylene glycol monoallyl ethers using MCPBA. Scanning electron microscopy images of the PDMS-replica was acquired to evaluate the successful replication of the topographical hierarchical pattern, at both the micro and nano scales. The chemical composition of surface modified PDMS replica at each stage was determined using X-ray photoelectron spectroscopy. A flat PDMS control film without the surface pattern; was also synthesized following the same chemical treatments to understand the functional superiority of the surfaces obtained by fabricating hierarchically patterned surfaces. Contact angle measurement studies were performed to analyze the underwater and aerial wetting behavior of the replica at each stage of the chemical modification.

1. Experimental Section

2.1. Materials

Silicone elastomer base and curing agent (Sylgard® 184 Silicone elastomer kit) was purchased from Dow Corning. 3-Chloroperbenzoic acid (MCPBA, 77%), Hydrogen peroxide solution (30%), Dodecyltrichlorosilane (95%), ammonia solution (30%), (3-Aminopropyl)trimethoxysilane (97%) and tetraethyl orthosilicate (98%) were purchased from Sigma-Aldrich. Sodium hydrogen carbonate (98%) was acquired from Merck. Polyalkylene glycol monoallyl ethers $[CH_2{=}CHCH_2(OCH_2CH_2)_n(OCH_2CH(CH_3))_mOH]$ namely Polyglycol A 20-20 (M Wt. 2100), Polyglycol A 11-4 (M Wt. 750), Polyglycol A 350 (M Wt. 350) were procured from Clariant.

2.2. Instrumentation

FT-IR spectroscopy: FT-IR spectra were recorded using a Perkin-Elmer FT-IR spectrometer. The sample was dispersed in potassium bromide powder and was pressed into a pellet for scanning in the range of 400-4000 cm^{-1}.

Nuclear magnetic resonance (NMR) spectroscopy: ^1H & ^{13}C NMR spectra were recorded on 200 MHz Bruker spectrometer using $CDCl_3$ as the solvent. Chemical shifts of various peaks in the ^1H NMR spectra were referred with respect to the $CDCl_3$ peak appearing at δ 7.26.

Thin-layer chromatography (TLC): TLC was performed on silica gel coated on aluminium plates. Hexane/ ethyl acetate (12:7 v/v ratios) was used as the solvent system. The TLC plates were further developed in an iodine chamber.

Scanning electron microscope (SEM)**:** Hitachi S-4700 field emission scanning electron microscope was used to study the surface morphological changes occurred during the chemical treatment of the PDMS-replica, operated at an acceleration potential of 10 kV. Prior to imaging, the samples were attached to an aluminium stub followed by sputter coating with a thin layer of gold.

Goniometer: Wettability of the surface was studied using contact angle measurements under ambient conditions. The contact angles were measured on the surfaces of pristine positive PDMS-replica, PDMS-flat, PDMS-replica^{OH}, PDMS-replica^{silica}, PDMS-replica$^{silica/NH_2}$, PDMS-flat$^{NH_2/OH}$ and PDMS-replica$^{silica/NH_2/OH}$ using a Kruss DSA100 contact angle measuring system and were analyzed using drop shape analysis software. Sessile-drop technique was used to perform the advancing and receding water contact-angle measurements on the replica surfaces. The underwater oil-repellency of the surfaces was studied using captive bubble method with light liquid paraffin oil.

X-ray photoelectron spectroscopy (XPS): XPS (ESCA-3000 instrument, VG Scientific Ltd. England) was used for studying the surface chemical compositions of pristine PDMS-replica, PDMS-replica$^{silica/NH_2}$ and PDMS-replica$^{silica/NH_2/OH}$. Al-Kα radiation source was used to generate the X-rays for exciting the samples, at a power of 150 W. The high-resolution spectra of the replica films were achieved with pass energy of 50 eV and 90° electron takeoff angle. Spectra were deduced using the Scienta ESCA300 database [33, 34]. The Gaussian peak deconvolution analyses were carried out using Origin Pro 8 (OriginLab Corporation, Northampton, MA).

2.3. Synthesis of functional polymers

Synthesis of epoxy terminated polyglycol

The epoxidation of polyalkylene glycol monoallyl ether using MCPBA was carried out in toluene. 5.0 g of Polyglycol A 20-20 (1 equivalent) was dissolved in 90 mL of toluene taken in a 100 mL two-necked dry round bottom flask attached to a Dean Stark apparatus which was connected to a water condenser. Nitrogen was continuously purged to the reaction mixture using Schlenk line. The reaction mixture was stirred at 140^{o}C for 3 h to remove moisture. After making the reaction mixture completely dry, the temperature of the system was brought down to 25^{o}C. 0.639 g (1.5 equivalents) of 3-Chloroperbenzoic acid (MCPBA) was then added to the reaction mixture and was stirred at 25^{o}C for about 60 h. The progress of epoxidation reaction was monitored using thin layer chromatography. After completion of the reaction, the solvent was evaporated using a rotary evaporator and a yellow viscous liquid was obtained. Synthetic scheme is shown in **Figure 1.** The product was purified using 5% aqueous solution of $NaHCO_3$, in which the by-product m-chlorobenzoic acid is soluble. The organic layer was washed with hexane/ ethyl acetate (12:7 v/v ratios) solvent mixture. The solvent was evaporated under vacuum after treating it with sodium sulfate and a colorless viscous liquid was obtained. The polymer was characterized using FT-IR and NMR.

Product characterization: Colorless viscous liquid; FT-IR peaks at ~1110 cm^{-1} (ether, C-O str); ~3500 cm^{-1} (O-H str) (broad peak); 1723 cm^{-1} (C=O str). ^{1}H NMR ($CDCl_3$, ppm) peaks at δ 2.62 and 2.78, 3.159 (epoxy-O-C-$\underline{\mathbf{H}}$), 3.65 (linear ether-O-C-$\underline{\mathbf{H}}$). ^{13}C NMR (CDCl3, ppm) peaks at δ 17.36 (CH ($\underline{\mathbf{C}}H_3$)), 44.26 (epoxy-O-$\underline{\mathbf{C}}$-$H_2$) and 50.89 (epoxy-O-$\underline{\mathbf{C}}$-H), 68.58 (C-$\underline{\mathbf{C}}H_2$-O), 70.62 ($CH_2$-$\underline{\mathbf{C}}$H ($CH_3$)-OH), 72.97, 73.35 and 75.22(O-$\underline{\mathbf{C}}H_2$). Refer **Figures 2, 3 and 4.**

The same synthetic strategy and characterization methods were used for the synthesis and characterization of epoxy terminated polyglycols of various grades from polyalkylene glycol monoallyl ethers of different molecular weights.

2.4. Surface modification of biomimetic replica (PDMS-replica)

(1) Synthesis of negative PDMS replica

PDMS elastomer was used for the texture replication of a dried colocasia leaf template. The PDMS blend was prepared by hand mixing the components in 10: 1 ratio [35] with mixing ten parts by weight of PDMS prepolymer and one part by weight of the curing agent. The viscous blend was then applied on a colocasia leaf (bottom part) placed in a polystyrene petridish. It was kept undisturbed under ambient conditions for about 20 h in a dust free chamber. During the course of solidification, the complementary topography of the leaf's original surface was expected to be copied on the solid negative replica. It was then heat cured at 60^{o}C for 1 h. After solidification, the negative PDMS- replica was peeled off from the leaf, rinsed with distilled water and was dried with nitrogen gas.

(2) Synthesis of positive PDMS-replica

Negative PDMS-replica was used as the template for preparing the positive replica. Firstly, 4.0 mL of light liquid paraffin oil (LLPO or white mineral oil) is allowed to stand in a degassing system of vacuum desiccator for about 20 minutes to remove the volatile impurities present in it. 3.0 mL of dodecyltrichlorosilane is then added to the LLPO in vacuum. The negative PDMS replica was placed above that, facing the textured portion towards the oil, after about 15 minutes. It was left undisturbed for 4 h under vacuum. The dodecyltrichlorosilane modified negative replica was removed from the vacuum and was heat cured at 60^{o}C for 1 h. The viscous silicone elastomer blend of prepolymer and curing agent (10:1 ratio) was applied on the negative PDMS-replica modified with dodecyltrichlorosilane placed in a petridish. It was kept at ambient temperature for about 20 h. It was then heat cured at 60^{o}C for 1 h. After solidification, the positive PDMS-replica was peeled off from the negative replica. Synthetic scheme is given in **Figure 7.**

(3) Synthesis of amine terminated replica

PDMS-replica was treated with an oxidizing mixture [36] of hydrochloric acid (35%, 4 mL), hydrogen peroxide (30%, 4 mL) and water (8 mL) for 10 minutes to get the oxidized PDMS-replica (PDMS-replica^{OH}). It was rinsed with distilled water and purged with nitrogen gas. The dry PDMS-replica^{OH} was then instantly submerged in a sol-gel mixture with the patterned surface facing the solution, by supporting it using a needle. The sol-gel mixture for depositing silica nanoparticles was prepared by mixing tetraethyl orthosilicate (2 parts), ammonia (2 parts), and ethanol (15 parts). It was made sure that the replica dangles inside the container and would not touch the bottom. The solution was kept undisturbed for 15 minutes to get the silica-modified positive replica (PDMS-replica^{silica}). The PDMS-replica^{silica} was rinsed with ethanol and dried with nitrogen.

After drying, it was immediately transferred into a container with (3-Aminopropyl) trimethoxysilane in solution. The solution was prepared by dissolving 0.5 mL of (3-Aminopropyl) trimethoxysilane in 10 mL of methanol. After about 20 minutes of contact time, the amino-silane was presumed to be reacted with the surface silanol groups present on the PDMS-replica^{silica} to obtain the $–NH_2$ terminated silica-modified positive replica (PDMS-replica$^{silica/NH_2}$). The amine functionalized replica was washed with methanol and dried under vacuum. Synthetic scheme is shown in **Figure 10.**

(4) Synthesis of polyglycol terminated replica

The silica-modified PDMS-replica activated by tailoring (3-Aminopropyl)trimethoxysilane (PDMS-replica$^{silica/NH_2}$) is used for the covalent attachment of epoxy functionalized polyglycol. PDMS-replica$^{silica/NH_2}$ was immersed in polyalkylene glycol monoepoxy ether containing solution for 4 h at room temperature. The solution was prepared by dissolving 0.25 mL of epoxy polyglycol in 10 mL of THF. After 4 h treatment, the replica was kept under vacuum for 1 h and was assumed that the amine has reacted with the epoxy functionality to yield PDMS-replica$^{silica/NH_2/OH}$. It was then washed with THF and dried under nitrogen gas. Synthetic scheme is shown in **Figure 13.**

(5) Synthesis of PDMS- flat $^{NH_2/OH}$

The PDMS- flat $^{NH_2/OH}$ was also prepared following the same procedure used for PDMS-replica$^{silica/NH_2/OH}$. Firstly, the flat PDMS substrate was prepared by applying the viscous PDMS blend, made by mixing the PDMS base and the curing agent in 10:1 ratio, onto a polystyrene petridish. After keeping it undisturbed under ambient conditions for 20 h, it was heat cured at 60^{o}C for 1 h and was peeled off. The surface hydroxyls (Si-OH) were generated by treating it with an oxidizing mixture of hydrochloric acid (35%, 4 mL), hydrogen peroxide (30%, 4 mL) and water (8 mL) for 10 minutes (PDMS- flat^{OH}). It was washed with distilled water and purged with nitrogen gas. The PDMS- flat^{OH} was not modified with silica to avoid the roughness, silica nanoparticles would create. Hence, the dry PDMS-flat^{OH} was directly transferred into a container with 0.5 mL of (3-Aminopropyl) trimethoxysilane dissolved in 10 mL of methanol. After about 20 minutes, the amino-silane was presumed to react with the surface silanol groups on the PDMS-flat^{OH} to give –NH_2 terminated PDMS-flat^{NH_2}. It was washed with methanol and dried under vacuum. Finally, the polyglycol tethered flat PDMS (PDMS-flat$^{NH_2/OH}$) was obtained by treating PDMS-flat^{NH_2} with PG-Ep dissolved in THF for 4 h at 25°C. After 4 h, it was kept under vacuum for 1 h and was washed with THF and dried under vacuum.

3. Results and Discussion

3.1 Epoxy terminated polyglycol

Various grades of epoxy terminated polyglycols were synthesized using polyalkylene glycol monoallyl ethers of different molecular weights. **Figure 1** shows the synthetic scheme of epoxy terminated polyglycol. The polymer of interest was synthesized by the epoxidation of polyglycol using MCPBA. The progress of the reaction was monitored at different time intervals using TLC. **Figures 2-6** shows the characterization spectra obtained for pure epoxy terminated polyglycol (PG-Ep) using FT-IR, ^{1}H and ^{13}C NMR**.** The purity of the sample was inferred from the disappearance of the C=O peak at 1723 cm^{-1} in the FT-IR spectrum (**Figure 2c**). The formation of the epoxy ring is confirmed from the peaks at δ 2.62 and 2.78, 3.159 in the ^{1}H NMR spectrum (**Figure 3**).

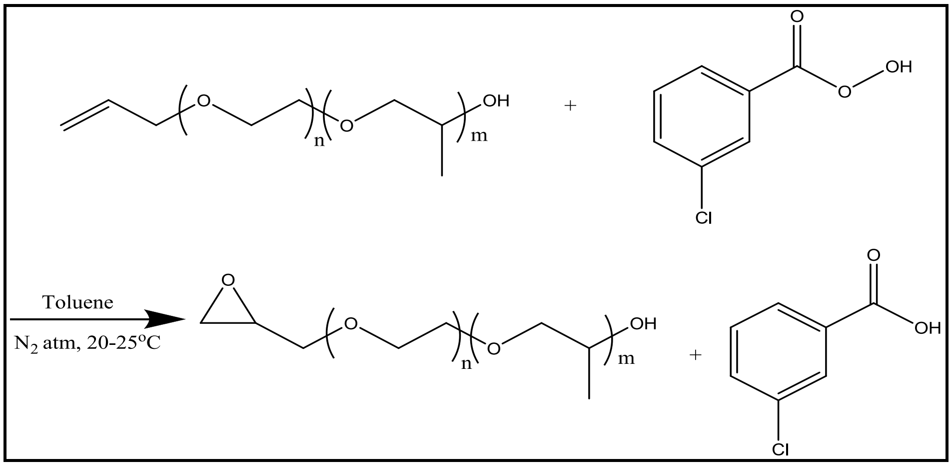

Figure 1: *Synthesis of epoxy terminated polyglycol*

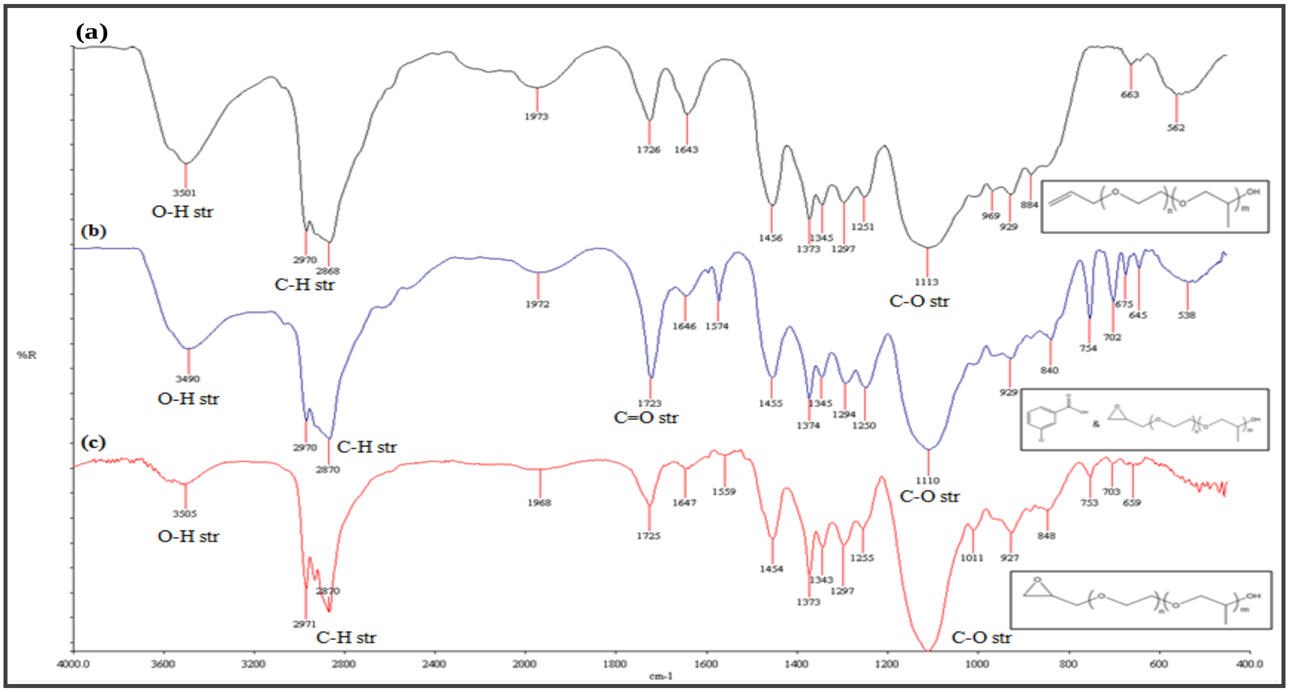

Figure 2: *FT-IR spectrum of (a) polyglycol, (b) epoxy terminated polyglycol with m-chlorobenzoic acid impurity and (c) purified epoxy terminated polyglycol*

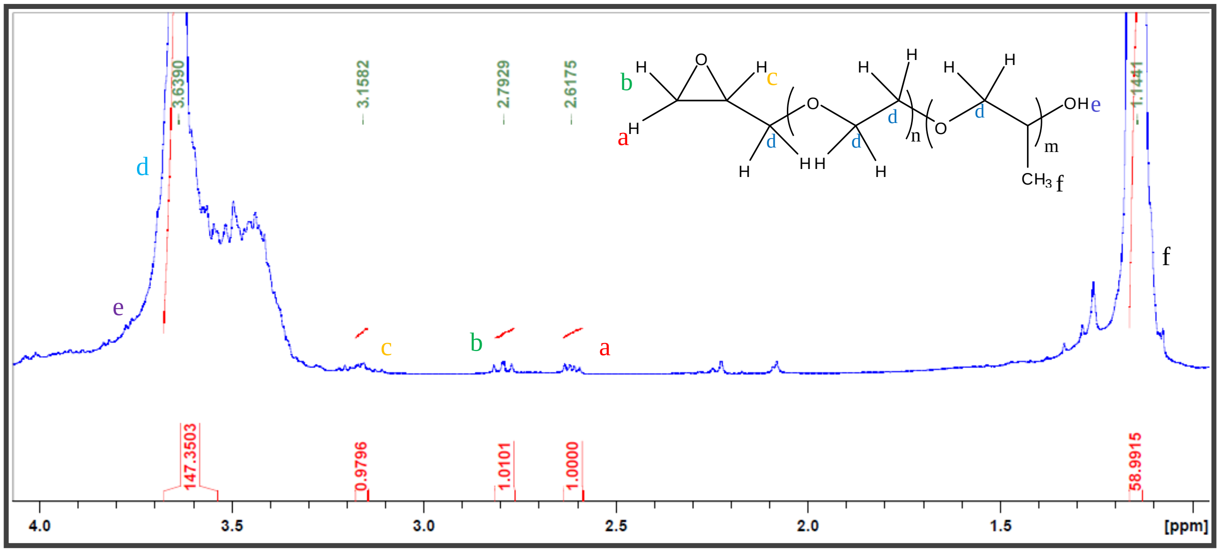

Figure 3: *^{1}H NMR of polyalkylene glycol monoepoxy ether (polyglycol A 20-20,* M Wt. 2100*)*

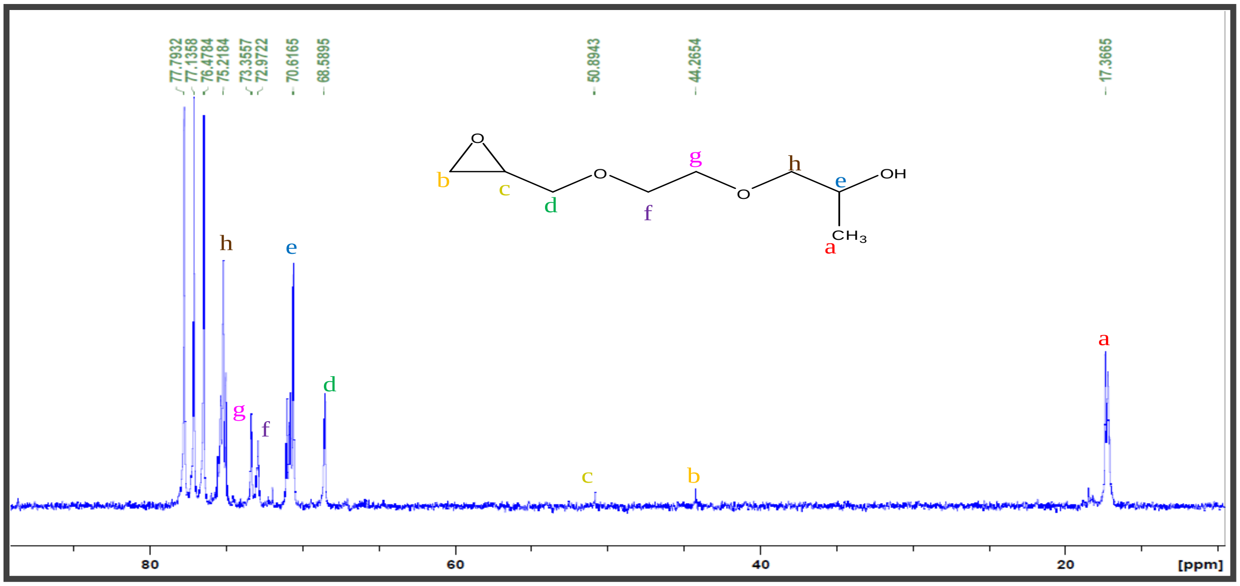

Figure 4: *^{13}C NMR of polyalkylene glycol monoepoxy ether (polyglycol A 20-20)*

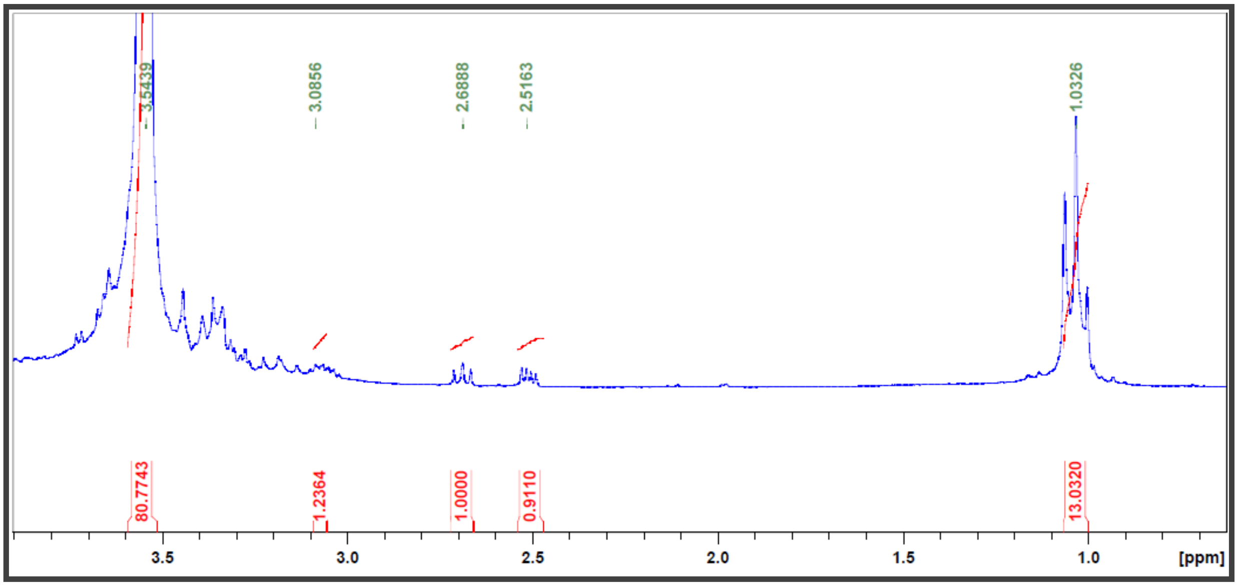

Figure 5: *^{1}H NMR of polyalkylene glycol monoepoxy ether (polyglycol A 11-4, M Wt. 750)*

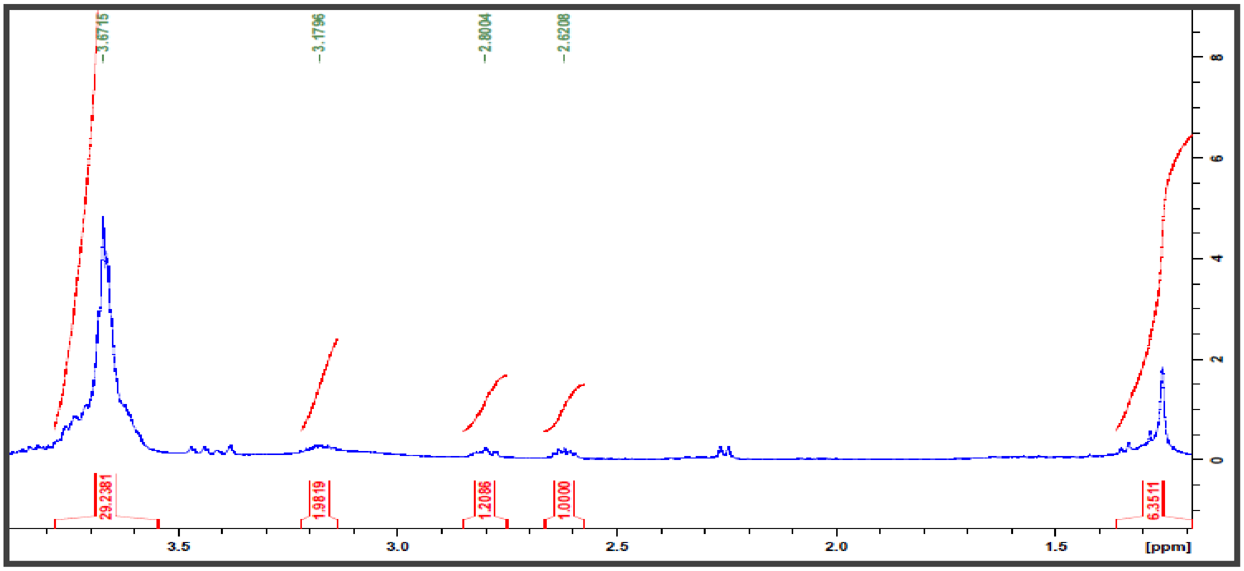

Figure 6: *^{1}H NMR of polyalkylene glycol monoepoxy ether (polyglycol A-350, M Wt. 350)*

Calculation of molar mass, M_n for *Polyglycol A 20-20 using ^{1}H NMR spectrum:*

^{1}H NMR shows signals for both the poly(ethylene glycol) (PEG) and the poly(propylene glycol) (PPG) groups present in the polyglycol copolymer.

By integrating the signal for the methyl protons of the PPG group, the length of PPG (m) could be calculated.

From the integration of the peak at 1.14 ppm (signal from the methyl Hs present in the PPG group), the number of PPG group was found to be around 20.

i.e., # of repeating PPG monomer units, m= 20

So, the molecular weight corresponding to 20 PPG groups= 1160

The integration of peak at 3.63 ppm corresponds to the signals from the protons of the –CH_2 and –CH groups of PPG and –CH_2 groups of PEG

Hence, # of PEG repeating units, n= (total # of signals - # of signals from PPG)/ (# of protons in PEG) = 21

Molecular weight corresponding to 21 PEG groups= 924

Hence, total molecular weight, M_n calculated from the 1H NMR spectrum= Mass of repeating units + Mass of the end groups = 1160+ 924+ 17+ 43= 2144 g mol^{-1}

Therefore, the calculated M_n of polyglycol A 20-20 is approximately 2144 g mol^{-1}.

The calculated molecular weight (2144) is found to be in good correlation with the theoretical value (2100).

Similarly, the molar masses of Polyglycol A 11-4 and Polyglycol A 350 were calculated. Molecular weight control studies carried out for different polyglycols are tabulated in **Table 1**.

Table 1: *Molar mass (M_n), n and m values calculated from ^1H NMR spectra*

Polyglycol	Molar mass, M_n (g/mol) [37]	Calculated molar mass, M_n (g/mol)	n	m
A 20-20	2100	2144	21	20
A 11-4	750	1040	19	5
A 350	350	410	5	2

3.2. PDMS-replica

Biomimetic replica (PDMS-replica) of natural colocasia leaf possessing hierarchical surface roughness was prepared following the conventional nanocasting based on soft lithography. **Figure 7** outlines the procedure followed for the preparation of positive PDMS-replica using the colocasia leaf template. The comparative study of the SEM images obtained for the colocasia leaf **(Figure 8)** and the replicas **(Figure 9)** confirmed the successful replication of the patterns present on the leaf's surface onto the replica.

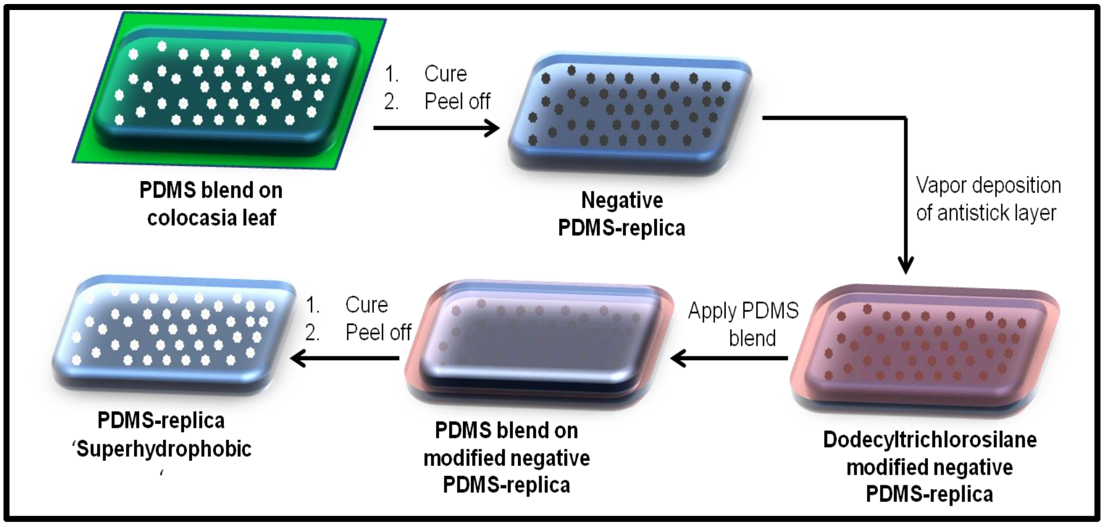

Figure 7: *Synthesis of positive PDMS-replica using colocasia leaf template (PDMS-replica)*

The SEM images of the hierarchical micro- nano sized patterns present on the lower part of the colocasia (*Alocasia macrorrhiza*) leaf are shown in **Figure 8 A-C**. As shown in **Figure 8 A,** the SEM micrograph captured for the lower surface of dry colocasia leaf showed the existence of a periodic arrangement of flower-shaped protuberances. A more magnified SEM image in **Figure 8 B** revealed that each of these protuberances possess a characteristic diameter of 12 μm with about 20 μm spacing between them. **Figure 8 C** demonstrates a further magnified SEM image, where the fiber-like network structures, possessing an average fiber width of not as much as a micrometer, present on each these flower-shaped protuberances are evident. **Figure 8 D** shows a colored water drop on the undersurface of the colocasia leaf. **Figure 9 C-D** shows the images obtained for the positive PDMS-replica developed using the colocasia leaf.

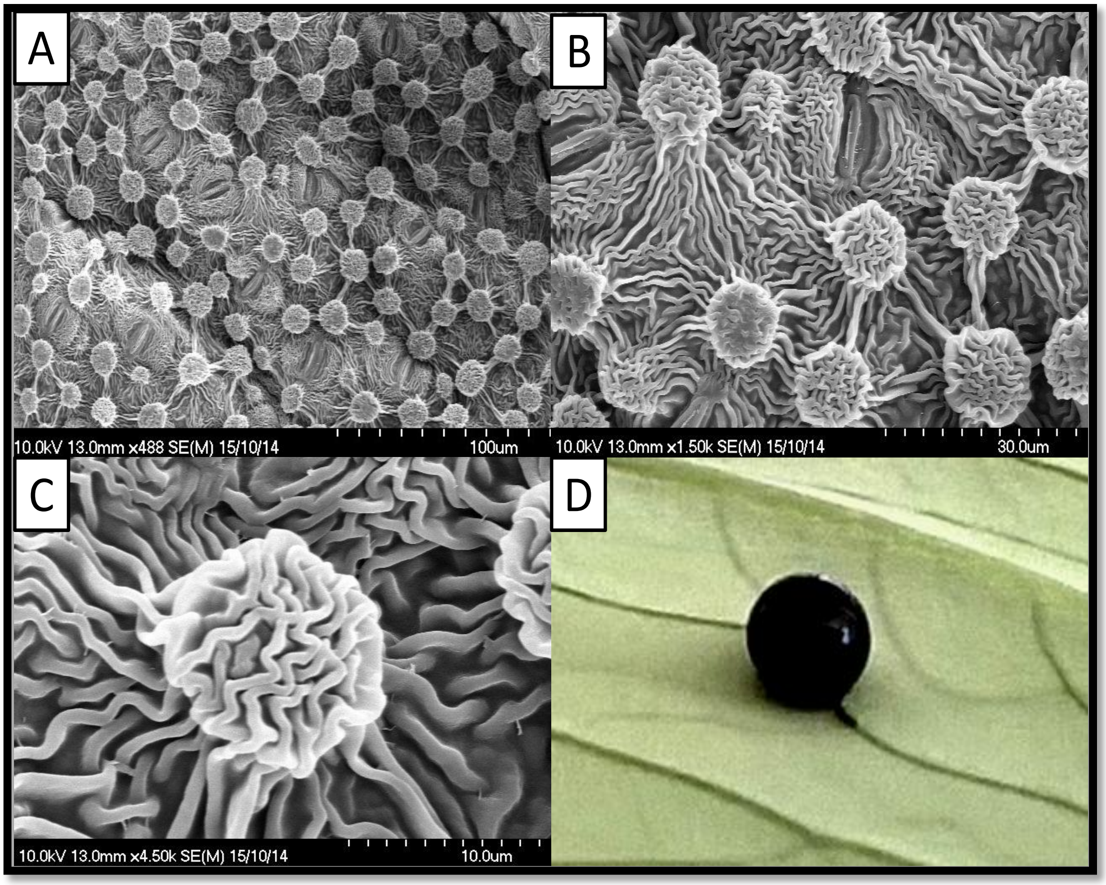

Figure 8: *SEM micrographs of the undersurface of a dry colocasia leaf depicting (A) flower-structured protuberances present in an array (scale bar = 100 μm), (B) magnified image of the protuberances (scale bar = 30μm), (C) fiber-like network present on individual protuberances (scale bar = 10 μm) (D) Image of a drop of aqueous stain on the undersurface of a colocasia leaf.*

The hierarchical array of pits present on the negative PDMS-replica derived from the flower-shaped protuberances present on the leaf surface (**Figure 8 B)** are shown in **Figure 9 A**. The diameter of each pit was found to be around 10 *μ*m with a spatial distance of about 25 *μ*m between each pit. **Figure 9 B** showing the magnified SEM image of the pit wall and its surrounding area revealed the spatial arrangement of channels with a width of less than a micrometer, which would have originated from the fiber-like mesh structure present on the protuberances of the leaf (**Figure 8 C**).

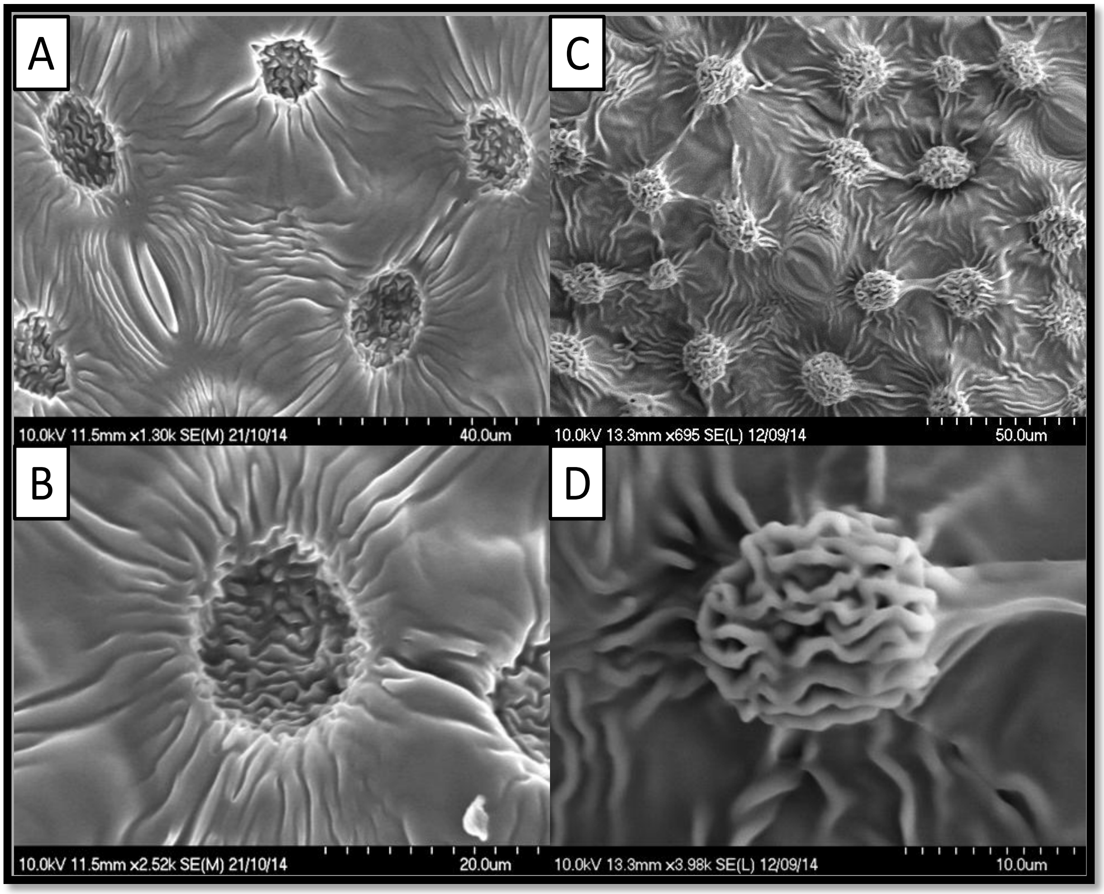

Figure 9: *SEM micrographs of (A) a range of pits present on the negative PDMS-replica (scale bar = 40μm), (B) channel like structures present on the pit boundary and its surrounding area (scale bar = 20 μm), (C) a range of flower-like protuberances present on the positive PDMS-replica (scale bar = 50μm), and (D) fiber-like network present on each protuberance and its surrounding area (scale bar = 10 μm).*

3.3. Silica modified PDMS-replica

Prior to the silica deposition, the PDMS-replica had undergone a mild wet oxidation treatment. As illustrated in **Figure 10**, the positive PDMS-replica obtained was treated with an oxidizing mixture of hydrochloric acid, hydrogen peroxide and water for 10 minutes to get the hydroxyl modified PDMS-replica (PDMS-replica^{OH}). The optimized time for the wet oxidation treatment was obtained after treating the sample with the oxidizing mixture for different times. **Figure 11** shows the SEM images recorded to understand the changes occurred on the surface patterns of the replica upon oxidation for varied duration.

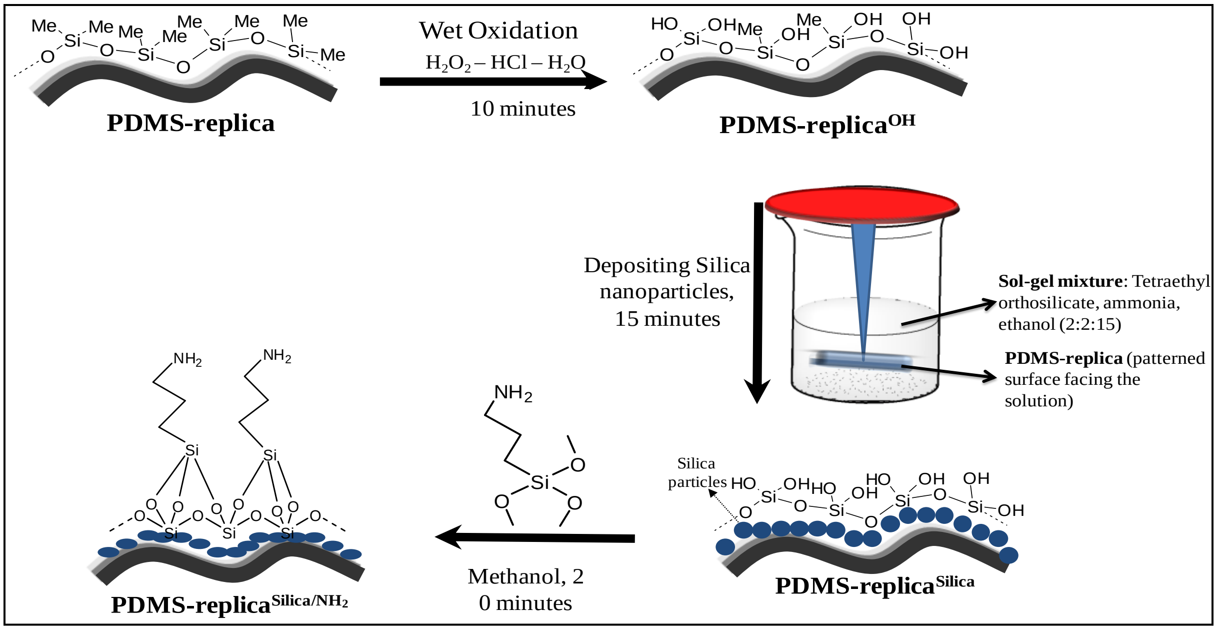

Figure 10: *Surface chemical modification of PDMS-replica to PDMS-replica*$^{silica/NH_2}$

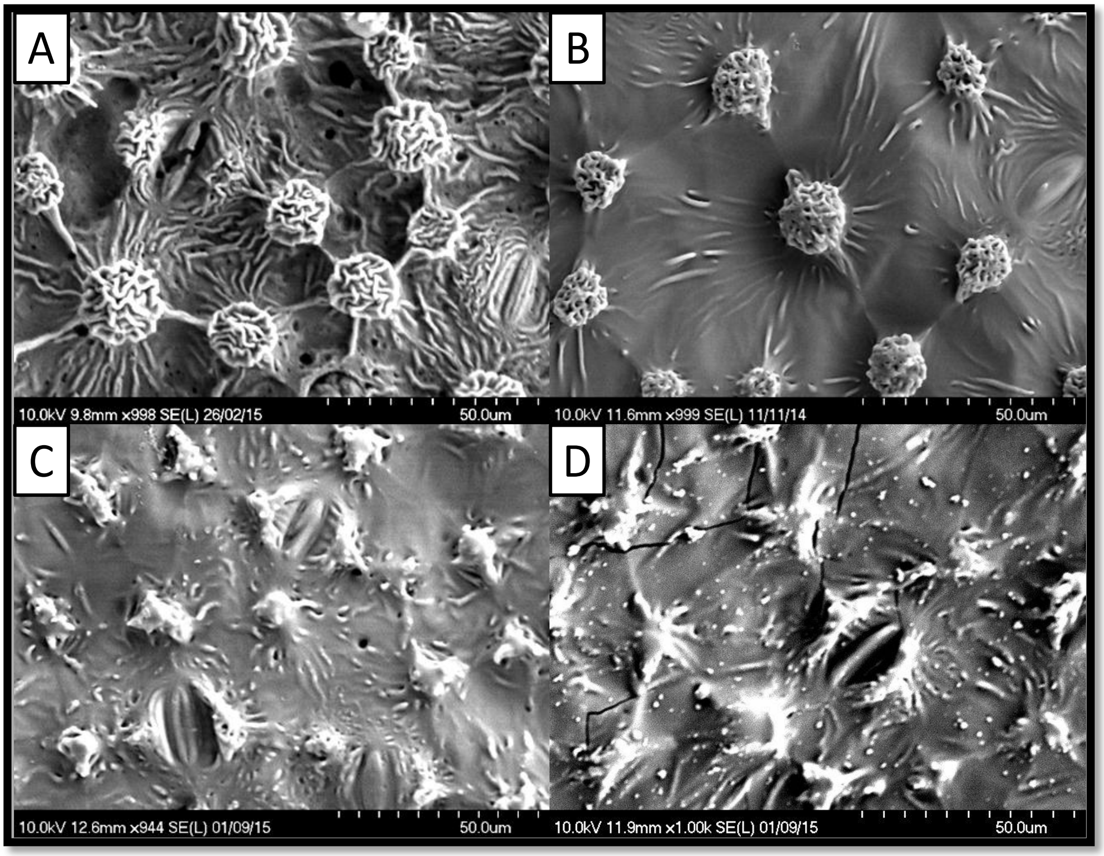

Figure 11: *SEM images of surface structures on the PDMS-replica subsequent to treatment with the oxidizing mixture for (A) 10, (B) 20, (C) 45 and (D) 60 minutes.*

Figure 11 A-D demonstrates the different surface morphologies attained after treatment of the PDMS-replica with the oxidizing mixture for 10, 20, 45, and 60 minutes respectively. It is observed that the micro-nano sized fine structures present on the surface of the PDMS-replicas were destroyed partly or fully upon sustained treatment with the oxidizing mixture. **Figure 11 D** shows the image of a completely damaged replica surface following 60 minutes of treatment with the oxidizing mixture. As evident from **Figure 11 A,** an optimized oxidation for just 10 minutes retained the surface patterns and turned the PDMS-replica sufficiently hydrophilic.

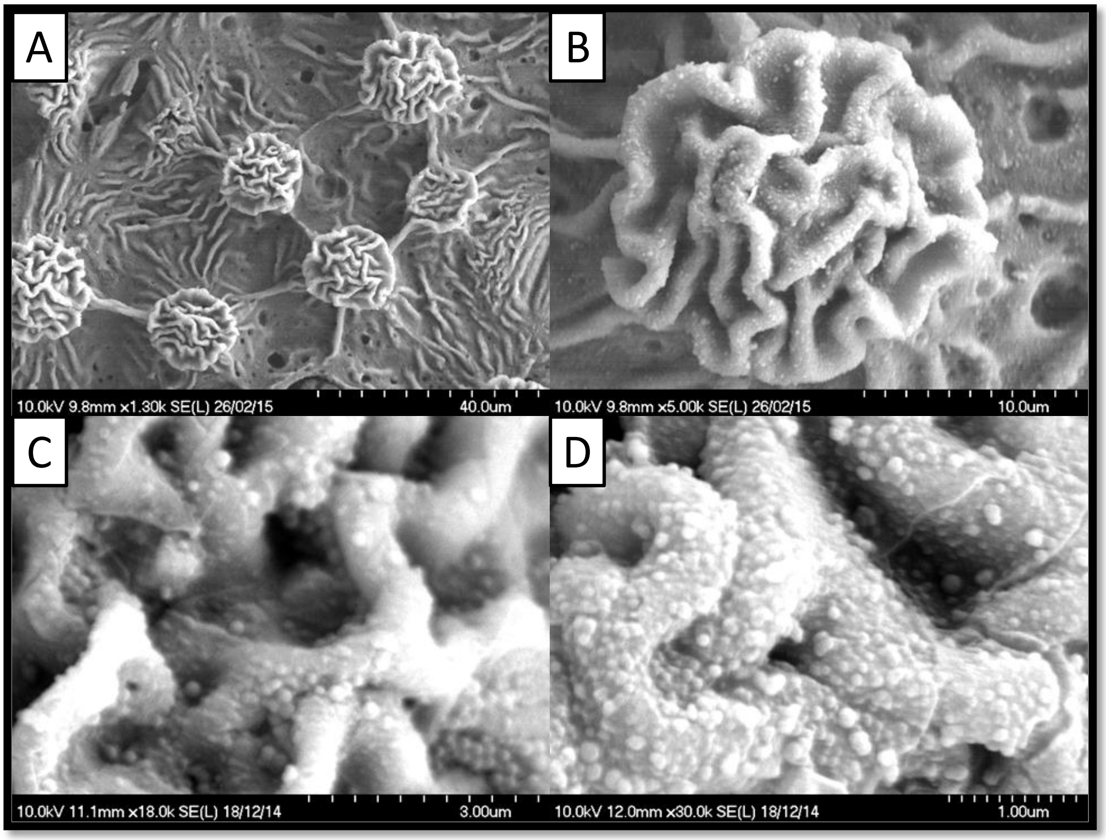

Figure 12: *SEM images of PDMS-replica^{silica} showing (A) a range of flower-shaped silica-modified protuberances (scale bar = 40 µm), (B) silica-modified protuberance (scale bar = 10 µm), (C) a silica-modified fiberlike mesh structure present on each protuberance (scale bar = 3 µm), (D)more magnified image of uniform silica deposition on the fiberlike mesh(scale bar = 1 µm)*

Immediately following the wet oxidation, the oxidized PDMS-replica (PDMS-replica^{OH}) was treated with a sol-gel mixture [38, 39] of tetraethyl orthosilicate, ammonia, and ethanol with volume ratios of 2:2:15, respectively, for 15 minutes to deposit nanosized silica particles (PDMS-replica^{silica}), as shown in **Figure 10**. The uniform distribution of silica nanoparticles on the fine structures present on the protuberances is shown in **Figure 12.**

3.4. Polyglycol functionalized PDMS-replica

The silica-modified positive replica functionalized with amino-silane (PDMS-replica $^{silica/NH_2}$) is used for the covalent attachment of epoxy terminated polyglycol to get the final hydrophilic polyglycol fabricated PDMS-replica (PDMS-replica$^{silica/NH_2/OH}$), as shown in **Figure 13**.

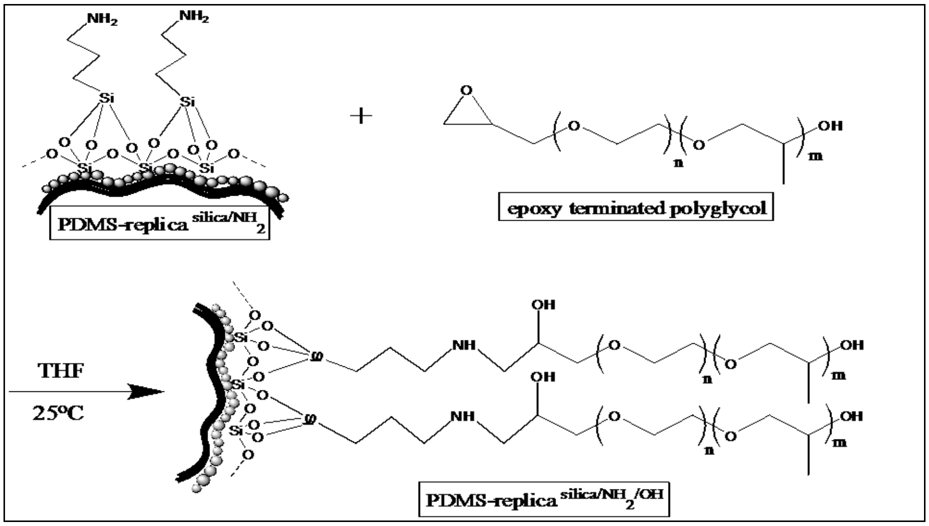

Figure 13: *Surface chemical modification of PDMS-replica*$^{silica/NH_2}$ *to PDMS-replica*$^{silica/NH_2/OH}$

3.5. Surface chemical composition and wettability of modified replica

The wetting behaviors of different PDMS surfaces were understood from the contact angle measurement data obtained at room temperature. **Figure 14** shows the goniometer images of water on different patterned surfaces and the **Table 2** shows the results of advancing and receding water contact angle measurements. Similar to natural colocasia leaf, the artificial leaf (PDMS-replica) also showed superhydrophobicity with advancing and receding water contact angles, θ_{water} of ~155° and ~148° respectively.

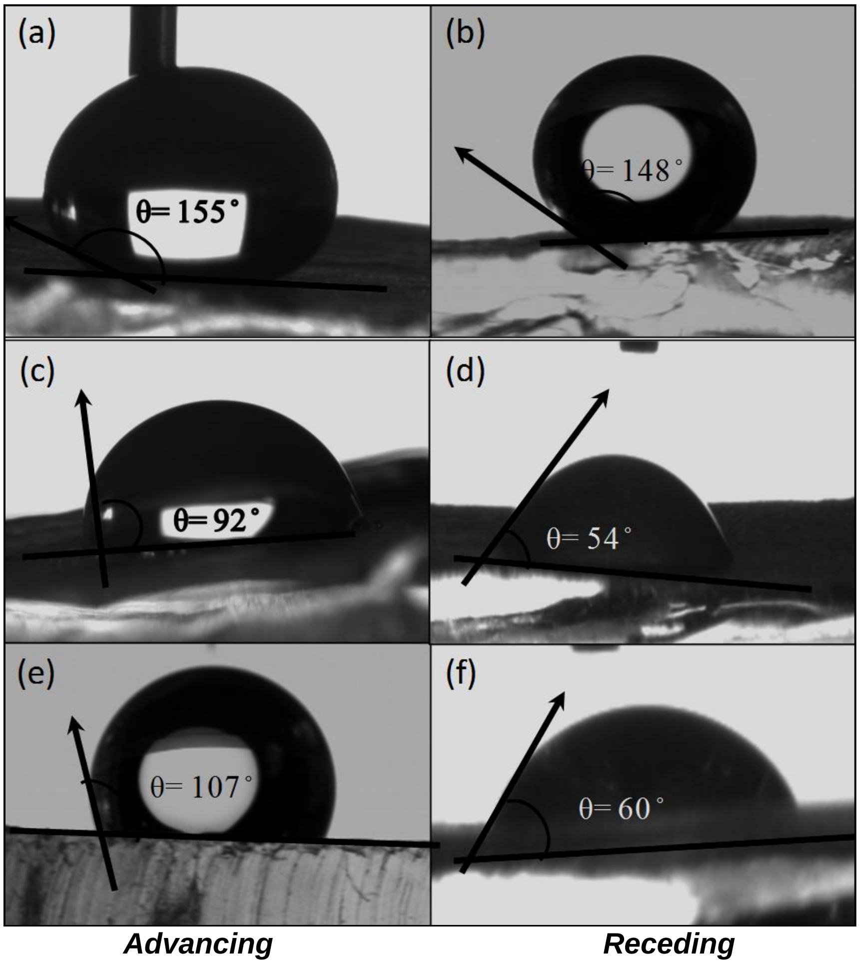

Figure 14: *Contact angle measurements: Images of advancing (as a) and receding (as b) water contact angles measured on bare PDMS-replica (a, b), PDMS-replica^{OH} (c, d) and PDMS-replica^{silica} (e, f) surfaces.*

Table 2: *Advancing and receding water contact angles measured on different surfaces*

Surfaces	Advancing contact angle (in deg.)	Receding contact angle (in deg.)
PDMS-replica	155	148
PDMS-replica^{OH}	92	54
PDMS-replica^{silica}	107	60

For both PDMS-flat and negative PDMS-replica, we observed low oil contact angle under water, $\theta_{oil} \sim 23°$, most probably due to the presence of -SiCH$_3$ terminal groups as earlier XPS studies [40] have shown that PDMS films possess surface -SiCH$_3$ groups which endows surface energy of ~22 mJ/m^2. **Figure 17** shows the oil contact angles obtained for various patterned and non-patterned substrates under water. Interestingly, a slightly higher underwater oil contact angle, θ_{oil}~40° was obtained for positive PDMS-replica compared to PDMS-flat and negative PDMS-replica. It could be due to the embedded dodecyltrichlorosilane groups on the surface of the positive PDMS-replica. XPS was used to resolve the surface chemical composition of PDMS-replica. **Figure 15 A** shows the likely surface and bulk chemical composition of positive PDMS-replica. The XPS survey spectrum showed peaks at 531.1, 283.5, 153.0, and 101.2 eV due to O 1s, C 1s, Si 2s, and Si 2p respectively for PDMS-replica, as shown in **Figure 15 B**.

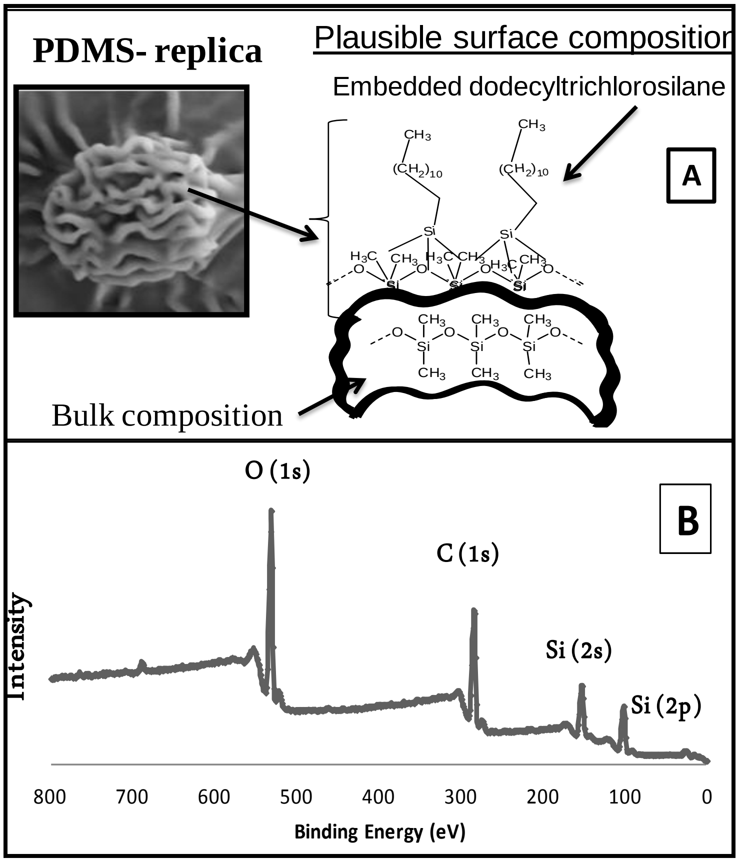

Figure 15: *(A) Plausible surface and bulk chemical composition of PDMS-replica (B) XPS survey spectrum obtained at 90^o takeoff angle for PDMS-replica.*

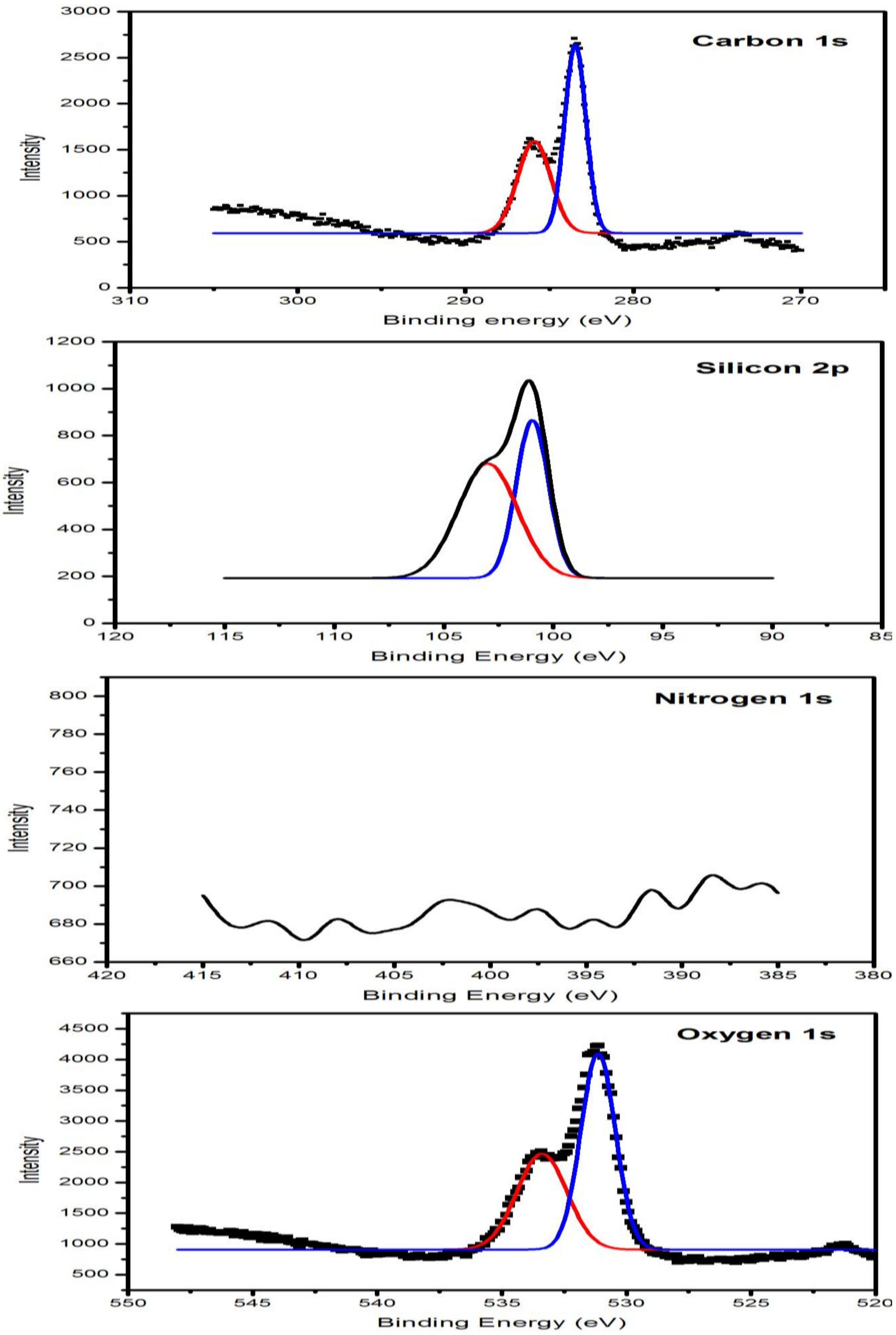

Figure 16: *High resolution XPS spectra of carbon 1s, silicon 2p, nitrogen 1s and oxygen 1s obtained at 90^{o} take off angle for PDMS-replica.*

Figure 16 shows the high resolution spectra of C 1s, Si 2p, N 1s and O 1s from the PDMS-replica. The peak corresponding to the C (1s) atom caused by the $–CH_3$ groups in the PDMS segment appeared at 283.5 eV. Also, a low intensity peak due to the C atom in the $CH_3(CH_2)_{11}Si$- appeared at 286.1 eV. The peaks originated from the Si (2p) and O (1s) atoms present in the Si-O backbone of the PDMS elastomer appeared at 101.2 and 531.1 eV respectively. A low intensity peak due to the Si (2p) atom from the embedded $CH_3(CH_2)_{11}Si$- group appeared at 103.6 eV. The peak corresponding to N (1s) was not present as expected. XPS data revealed presence of the modifying agent, dodecyltrichlorosilane on the PDMS-replica surface.

Underwater contact angle measurement studies were carried out using oil on different patterned and non-patterned surfaces. As expected, the silica modified –OH terminated PDMS-replica$^{silica/NH_2/OH}$ showed maximum underwater oil contact angle (θ_{oil}) of 142^o and good hydrophilicity with θ_{water} of ~ 17^o. The polyglycol modified PDMS-flat showed a θ_{oil} of 59^o. The oil based contact angle studies were carried out using light liquid paraffin oil having a surface tension of about 35 dyne/cm at 25^oC. [41] **Figure 17** shows a summary of the underwater oil contact angle studies.

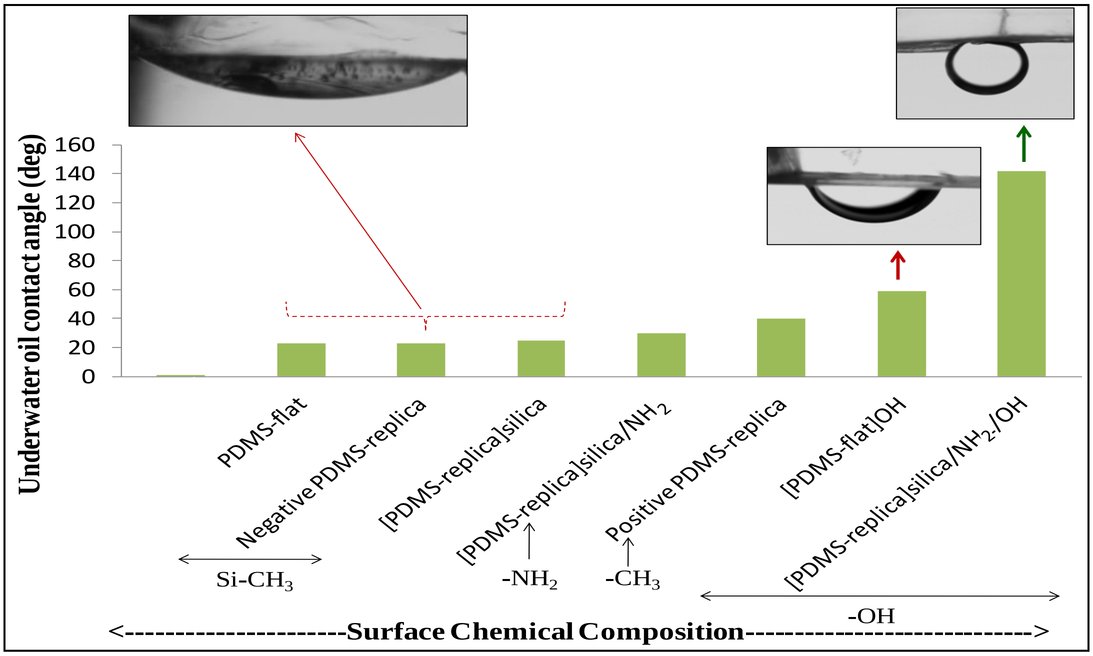

Figure 17: *Underwater oil contact angle obtained on various patterned and non-patterned PDMS surfaces along with the Goniometer images.*

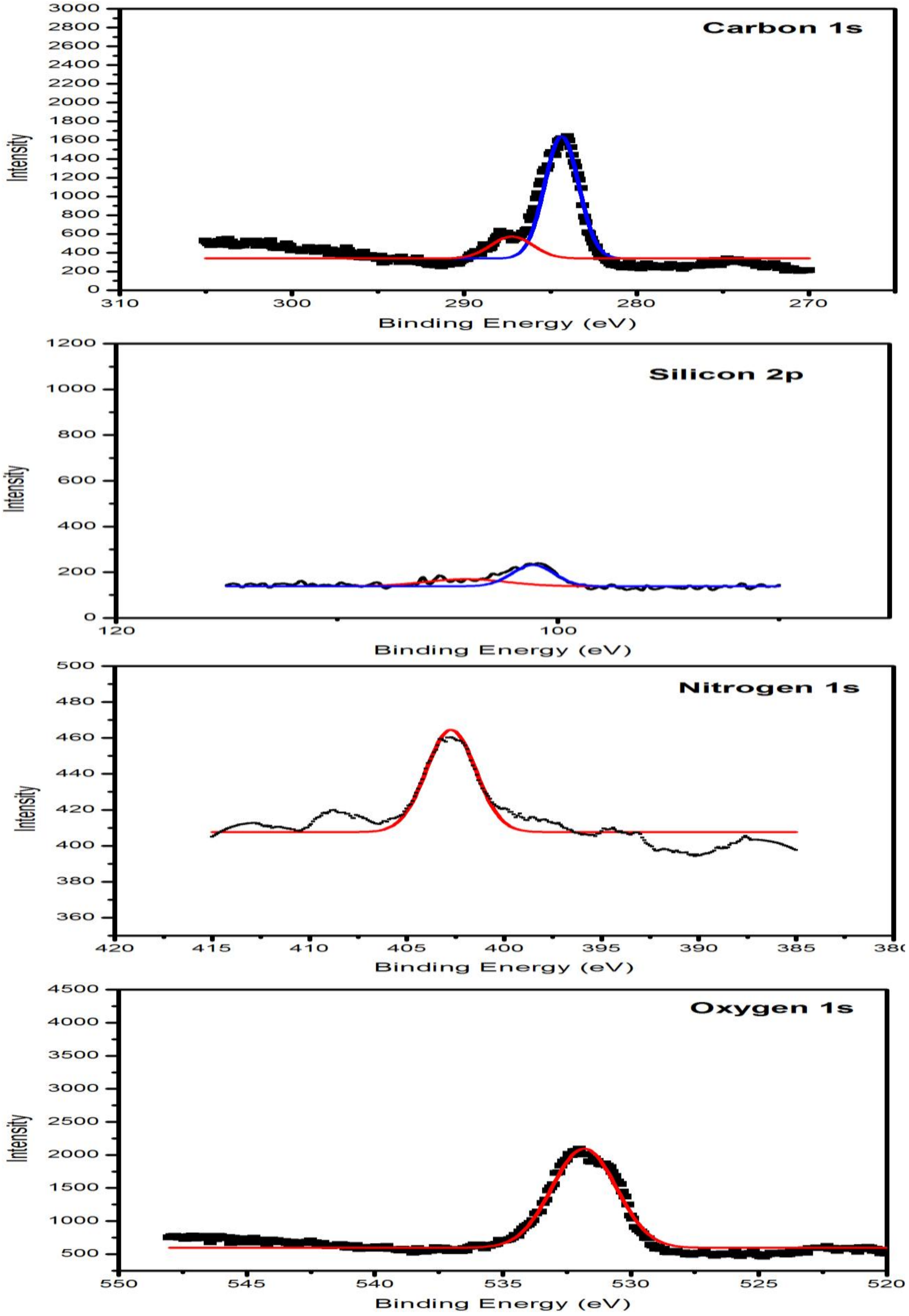

Figure 18: *High resolution XPS spectrum of carbon 1s, silicon 2p, nitrogen 1s and oxygen 1s obtained at* 90^o *take off angle for PDMS-replica*$^{silica/NH_2}$.

The presence of amino-silane on the PDMS-replica was determined using XPS. The high resolution spectra of the individual atoms present on the surface is shown in **Figure 18.** The peak corresponding to the C (1s) atom due to the $–CH_3$ groups in the PDMS segment appeared at 284.0 eV. Also, a low intensity peak due to the C atom in the $NH_2(CH_2)_3Si$- appeared at 287.7 eV. The peaks due to the Si (2p) and O (1s) atoms aroused from the Si-O backbone in the PDMS elastomer appeared at 101.0 and 532.1 eV respectively. A low intensity peak due to the Si (2p) atom from the $NH_2(CH_2)_3Si$-group appeared at 105.0 eV. The peak corresponding to N (1s) from the $NH_2(CH_2)_3Si$-group appeared at 403.0 eV. XPS data revealed the presence of amino-silane on the PDMS-replica surface. The decrease in the intensities of C (1s), Si (2p) and O (1s) peaks also confirms the presence amino-silane layer on the replica. **Figure 19** shows the plausible surface and bulk compositions of PDMS-replica$^{silica/NH_2}$.

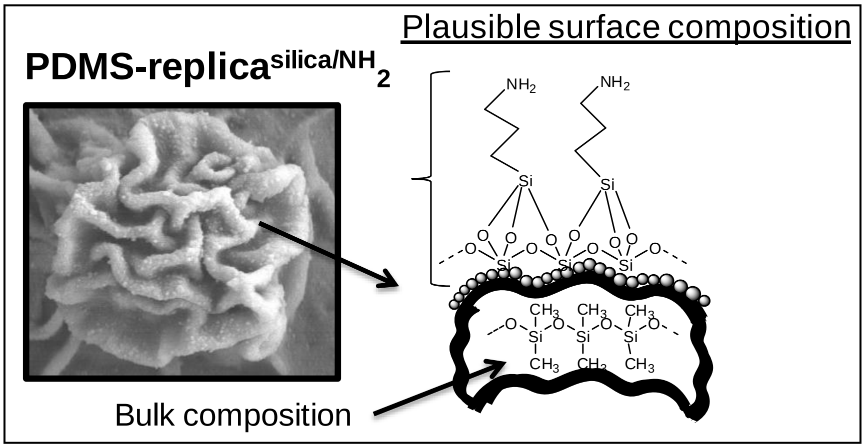

Figure 19: Plausible surface and bulk chemical composition of PDMS-replica$^{silica/NH_2}$

The tethering of polyglycol on the amine modified PDMS-replica was assumed from the sudden drop in θ_{water} of PDMS-replica$^{silica/NH_2}$ from 35° to 17° after treating with PG-Ep. The SEM image obtained for PDMS-replica$^{silica/NH_2/OH}$ looked intact as expected (**Figure 20**). XPS study of PDMS-replica$^{silica/NH_2/OH}$ is underway.

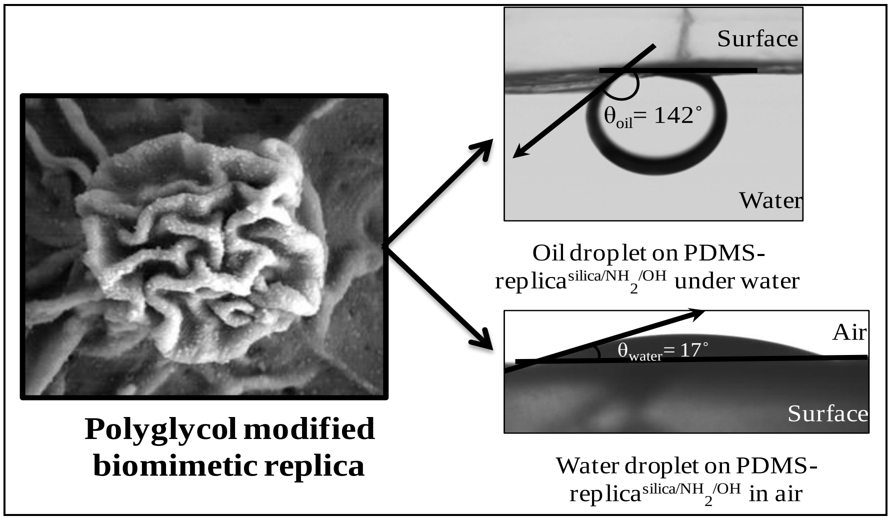

Figure 20: *SEM image showing the polyglycol modified PDMS-replica*$^{silica/NH_2/OH}$ *along with the contact angle measurement images on its surface*

4. Conclusions

Developing a superhydrophilic surface having high surface energy with an underlying hierarchical surface roughness is a challenge. We have successfully developed a superhydrophilic surface with under-water oil repellency by chemically modifying the surface composition of an intrinsically hydrophobic PDMS based biomimetic replica, following a facile and inexpensive method. The PDMS-replica surface was made hydrophilic by the covalent attachment of polyglycol (PDMS-replica$^{silica/NH_2/OH}$). The PDMS-replica$^{silica/NH_2/OH}$ showed oil repellency with an oil contact angle, θ_{oil} of ~142° under-water. SEM results revealed that the surface topography of the replica was successfully retained subsequent to all the chemical transformations. Based on the results obtained from XPS and contact angle measurements, we could conclude that the PDMS- replica surface was modified with polyglycols and is superoleophobic under-water.

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