



Rapid and Solvent Free Synthesis of Bulk Superhydrophobic Coating

Athar mohi-ud-din Rather¹ DR. Sudeshna Ray²

1 M. Phil Research Scholar Rabindranath Tagore University (M.P. Bhopal)

2 Centre director of advanced material research centre and associate professor faculty of science, Rabindranath Tagore University (M.P. Bhopal)

Abstract: A single polymer is rapidly and covalently transformed into a chemically reactive and functional bulk polymeric coating through a catalyst-free mutual chemical reaction between acrylate and amine groups at ambient conditions in the absence of any external reaction solvent, which is unprecedented in the literature. This facile and external solvent free chemical approach provided a basis for developing biomimicked water wettability. The essential chemistry that conferred bio-inspired water wettability was optimized in the hierarchically featured polymeric material by post covalent functionalization of chemically reactive polymeric material with primary amine containing small molecules. The inherently sticky and “chemically reactive” polymeric gel having appropriate hierarchical topography is highly capable of providing substrate independent (irrespective of chemical compositions and mechanical strength of the substrates) stable coatings with robust bio-inspired extreme water repellency. The coating on different substrates doesn't demand any additional surface functionalities and the physical integrity as well as the anti-wetting property of the coatings remains intact under various physical and chemical insults.

Keywords: Superhydrophobic, biomimicked and coating

Introduction

The “chemically reactive” interfaces that provided a facile and robust avenue for tailoring various relevant chemical functionalities are fundamentally interesting and important for synthesizing smart and functional materials that have a wide range of potential applications including immobilization of desired bioactive molecules, synthesis of cell on a chip, controlled release of small molecules, multibiofunctionalization, smart sensing of various relevant chemical toxins and developing patterned interfaces etc. Most often, such chemically reactive functional interfaces are ultrathin (in the scale of nanometers), featureless and were prepared commonly through multistep deposition processes such as layer by layer (LbL) deposition of reactive polymer and chemical vapor deposition (CVD) followed by an uncontrolled polymerization process.

In the recent past, Lynn and co-workers extended this concept of chemically reactive coating, and they strategically synthesized a hierarchically featured and chemically “reactive” interface for developing durable super-water-repellant coating for several prospective applications including open microfluidics, high-throughput screening of drug, controlled drug delivery, oil/water separation etc. In general, the conventional and thin artificial superhydrophobic coatings are developed through appropriate co-optimization of

(1) essential chemistry and (2) topography only over a few nanometers across the thickness of the artificial biomimicked interface. Thus, a slight perturbation in either chemistry or controllable change in the topography in the conventional designing is expected to cause severe and permanent damage to the embedded special biomimicked wettability. In comparison to the conventional approach, the hierarchically featured and chemically “reactive” thick coatings inherently yielded highly durable biomimicked interfaces. Such chemically reactive approaches are inherently capable of providing a facile basis for tailoring essential chemistry three dimensionally and allowed to trap metastable air across the thickness of the material and eventually provided bulk superhydrophobicity. The synthesized bulk

superhydrophobic materials are inherently capable of sustaining severe physical damages including physical erosion of the synthesized material. However, the examples of such chemically “reactive” and hierarchically featured coatings are very rare in the literature, and few functional polymers are mostly associated following tedious multistep/complex synthetic procedures in the reported approaches in the recent literature. Moreover, single polymer based rapid synthesis of chemically reactive and hierarchically featured interfaces without using any catalyst and external reaction solvent at ambient conditions is unprecedented in the literature. In this chapter, branched poly (ethylenimine) (BPEI, Figure 5.1A) is spontaneously converted into a “chemically reactive” and functional polymeric material through solvent-free and catalyst-free mutual addition reaction with other liquid reactants dipentaerythritol penta-acrylate (5-Acl). On mixing the polymer (BPEI) and small molecule (5-Acl) in the absence of any external organic/aqueous solvents, a chemically reactive polymeric gel was spontaneously (within 30 seconds) formed through facile 1, 4-conjugate addition reaction (Figure 5.1B) between amine and acrylate groups at ambient conditions as shown in Figure 5.1C. This “reactive” and inherently sticky polymeric material was further exploited in developing substrate independent polymeric coatings that embedded with lotus leaf inspired artificial and durable bulk superhydrophobicity after covalent post chemical modification of the synthesized polymeric coating with octadecylamine (ODA) molecule.

Materials and Methods

Materials

Plastic and card board was obtained from local shop in Guwahati city (Assam India). Whatman filter paper was purchased from GE Healthcare Services (Bangalore India). Aluminum foil was obtained from Parekh Aluminex Limited (PAL) Maharashtra India. Wood pieces were collected from a local construction site in IIT Guwahati campus and was rinsed thoroughly prior to use. Preparation of Solvent Free ‘Reactive’ Polymeric Gel and Post-Chemical Modifications

Branched poly (ethylenimine) (BPEI) and dipentaerythritol penta-acrylate (5-Acl) were mixed in a single container with appropriately selected molar ratios. The mixture instantly turns into semisolid gel within 30 seconds, then the gel material was taken out and was subsequently rinsed with THF for removing the unreacted reactants. Afterwards the polymeric gel was transferred in the octadecylamine (ODA) solution (5 mg/mL of THF) for overnight. Other water wettabilities were obtained by post modifying the polymeric gel with different amine containing small molecules including propylamine (30 mg/mL), pentylamine (30 mg/mL), hexylamine (30 mg/mL), octylamine (30 mg/mL), decylamine (30 mg/mL) respectively. Next, the materials were rinsed with THF for one hour to remove the unreacted and loosely bound amine containing small molecules and were dried at ambient conditions. Afterwards the change in wettability was examined with digital images and contact angle measurements.

Coating on Various Substrates

The reactive polymeric composite films were fabricated by placing the highly sticky and chemically ‘reactive’ polymeric gel on the cleaned surface of various selected substrates including glass, wood, plastic, whatman filter paper, aluminum foil, card board. The polymeric gel was uniformly spread out using microscopic glass slide. Then the coated substrates were washed thoroughly for removing unreacted reactants. Thereafter, the substrates were post modified with ODA molecule for achieving the desired water wettability.

Results and Discussion

An unprecedented approach for rapid synthesis of covalently crosslinked, hierarchically featured and chemically reactive polymeric material was introduced without using any external reaction solvent and catalyst. The eco-friendly, solvent and catalyst-free synthesis approach provided a facile and rapid basis for adopting various important biomimicked interfaces that have enormous importance and prospective applications in practically relevant settings. In this current study (a) the strategic use of chemistry (b) the synthesis procedure and (c) the synthesized materials are completely different from previously discussed materials in the earlier chapters. Here in this current chapter, a series of controlled studies were performed, where the molar ratio (“mole to mole” ratio) of the liquid reactants (BPEI (the mole amount is calculated with respect to the repeating unit) and 5-Acl) was varied (from 1:3 to 1:5; BPEI:5-Acl) to achieve

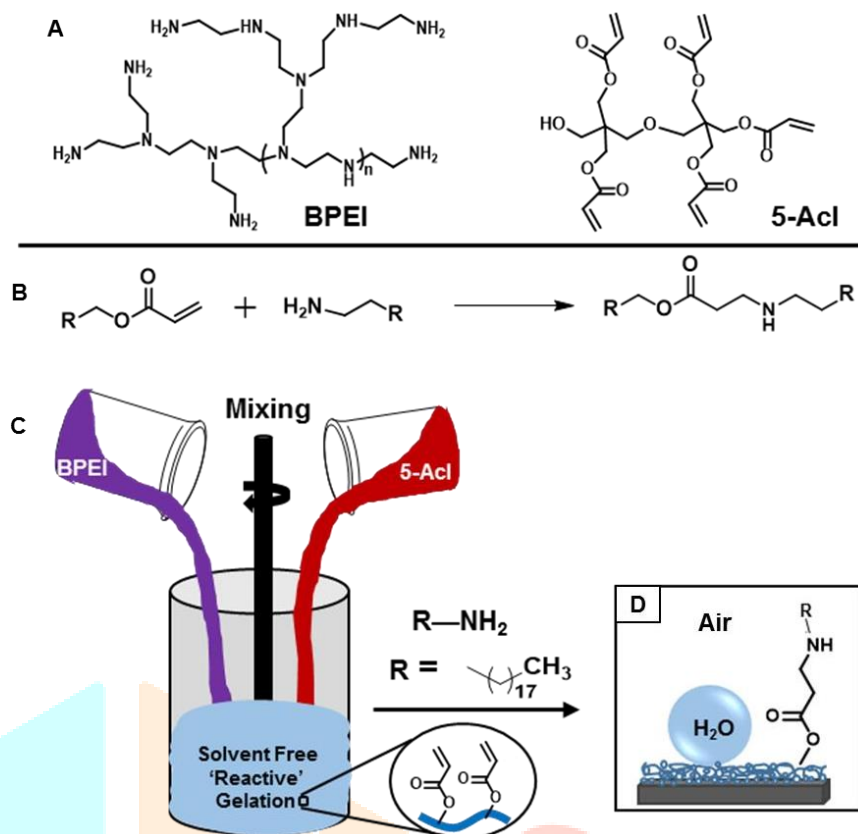


Figure 5.1. (A) Chemical structures of branched polyethylenimine (BPEI) and dipentaerythritol penta-acrylate (5-Acl). (B) Schematic illustration of 1, 4-conjugate addition reaction between primary amine and acrylate moieties. (C) Schematic illustrating the spontaneous synthesis of chemically “reactive” polymeric gel on continuous mixing of polymer (BPEI) and small molecules, without using any solvent and catalyst. (D) Further, appropriate post chemical modifications with octadecylamine through 1, 4- conjugate addition reactions yielded superhydrophobicity.

biomimicked wettability through controlled optimization of (i) essential topography and (ii) appropriate chemistry. The colorless mixture (Figure 5.2A) with molar ratio 1 (BPEI):3 (5-Acl) of liquid polymer (BPEI) and small molecules (5-Acl) was mixed rapidly to form an opaque gel (Figure 5.2E) within 30 seconds. The synthesized polymeric gel was inherently hydrophilic with water contact angle (WCA) of 73° and this WCA was increased from 73° to 85° after treatment with octadecylamine (ODA) molecules. This change in water wettability was further improved with varying the molar ratio of the selected reactants (BPEI and 5-Acl; 1:4) in the reaction mixture. On increasing the concentration of 5-Acl in the reaction mixture, the gel materials became more hydrophobic (with WCA of 120°) after ODA treatments (Figure 5.3A). The reaction mixture of BPEI/5-Acl with 1:5 molar ratio

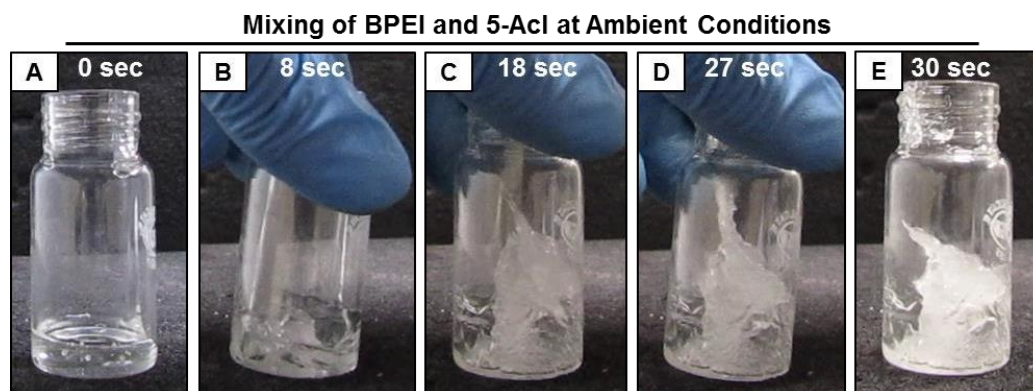


Figure 5.2 (A-D) Digital images illustrating the process of gelation on continuous mixing of BPEI and 5-Acl, where optically transparent mixture (A) of liquid reactants are transformed into opaque gel within 30 seconds (E).

yielded another hydrophilic material (Figure 5.3C, D); however, the synthesized chemically reactive material became superhydrophobic after ODA treatment, and the water droplet (red color aids visual inspection) beaded on the same gel material with an advancing water contact angle above 150° and contact angle hysteresis below 10° as shown in Figure 5.3E, F. This change in water wettability is mainly attributed to the inherent primary amine “reactivity” of the synthesized polymeric gel. The synthesized polymeric gel was loaded with residual acrylate groups as confirmed with standard FTIR spectral study. The IR peaks (Figure 5.3B, Black Spectrum) at 1735 cm^{-1} and 1410 cm^{-1} which correspond to the carbonyl stretching and symmetric deformation of the C–H bond for the β carbon of the vinyl groups unambiguously revealed the existence of acrylate groups in the synthesized polymeric gel. The depletion of the IR peak at 1410 cm^{-1} with respect to 1735 cm^{-1} (the internal standard, where carbonyl groups remained unperturbed in Michael addition reaction) after the postmodification with ODA molecules (Figure 5.3B, Red Spectrum) independently confirmed the presence of amine “reactive” functionality (i.e., residual acrylate groups) in the material and the covalent modification with desired chemistry in the material through robust 1, 4-conjugate addition reaction. The optimized chemistry in the polymeric gel conferred the biomimicked superhydrophobicity. Moreover, the microscopic morphology of the polymeric gel was investigated with FESEM study, where the top interface of the polymeric gel was noticed to have random porous structures as is shown in

Figure 5.3G, H. This porosity appeared likely due to the removal of unreacted reactants

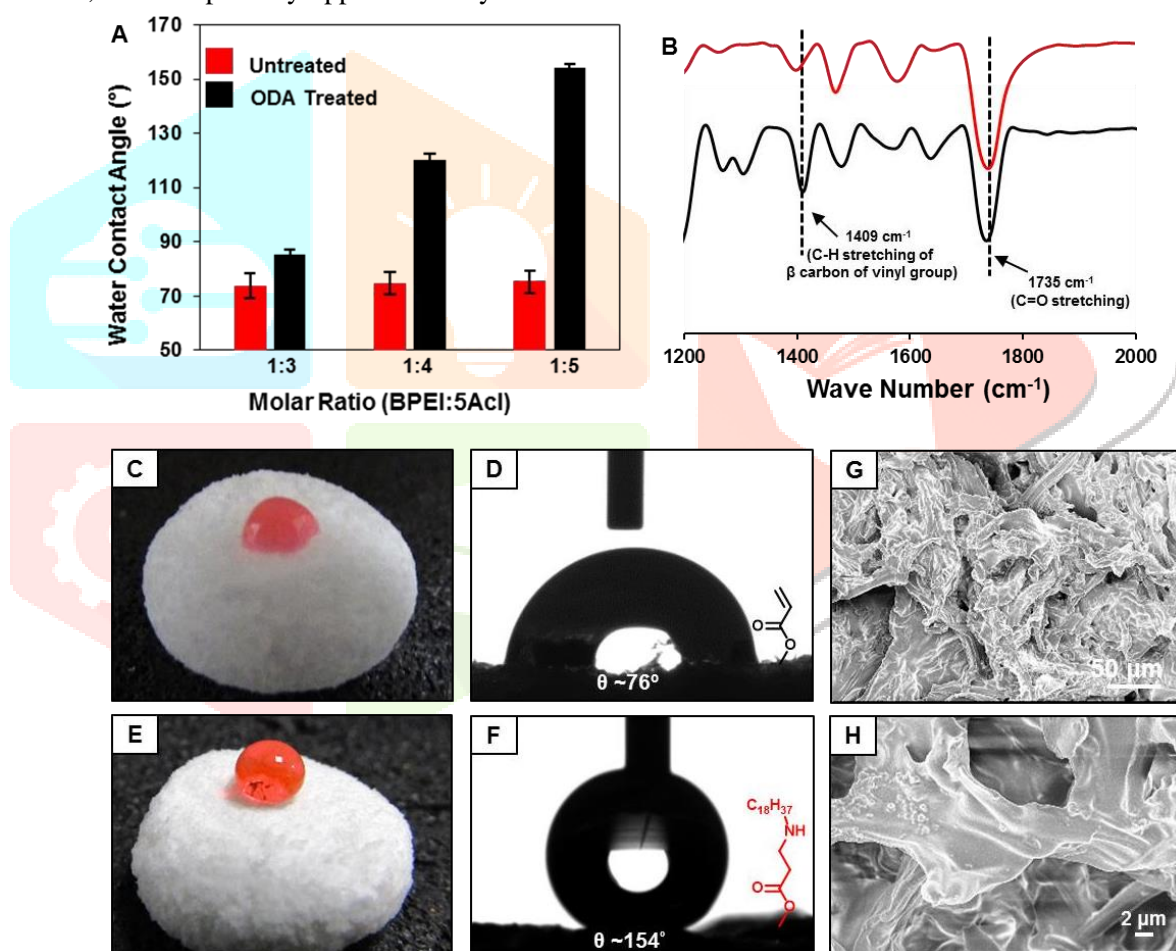


Figure 5.3. (A) The plot accounting for the change in contact angle of the chemically “reactive” polymeric gels that are prepared by mixing BPEI and 5-Acl with different molar ratio, before (red) and after (black) post treatment with ODA molecules. B) FTIR spectra of “reactive” polymeric gel before (black) and after (red) post functionalization with ODA molecules, where the IR peaks at 1735 cm^{-1} and 1410 cm^{-1} denoted the carbonyl stretching and symmetric deformation of the C–H bond for the β carbon of the vinyl group. C-F) Digital images (C, E) and contact angle images (D, F) of beaded water droplet on polymeric gel before (C, D) and after ODA treatment (E, F). G-H) FESEM images of solvent free polymeric gel with BPEI/5-Acl molar ratio of 1:5 in lower (G) and higher (H) magnifications.

during washing of the polymeric gel material. Thus, the “reactive” polymeric gel is embedded with appropriate hierarchical topography, which is an essential parameter for achieving anti-wetting property. Furthermore, this synthesized polymeric gel was capable of displaying inherently durable bulk superhydrophobicity, where the entire polymeric gel (molar ratio 1:5 BPEI/5-Acl) that was post modified with ODA molecules was arbitrarily

sliced into two parts to expose the interior of the material, and the interiors were observed

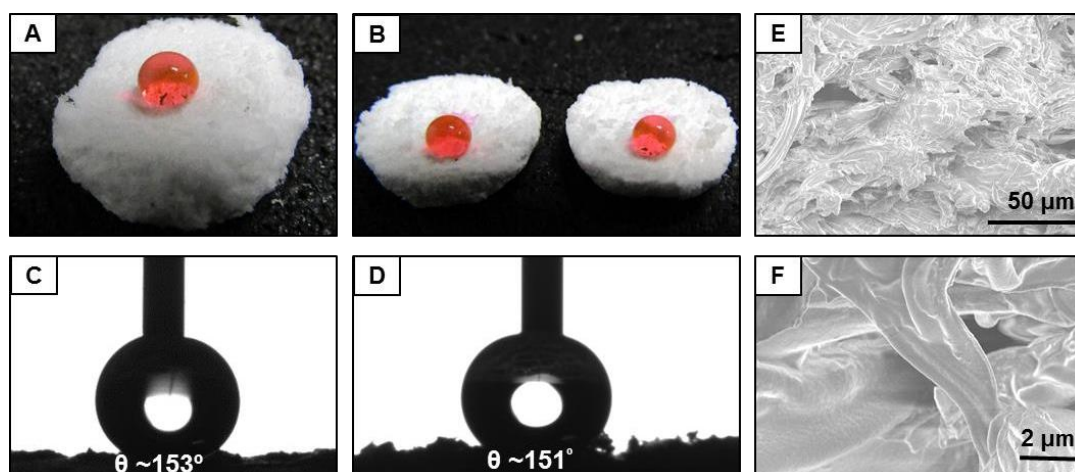
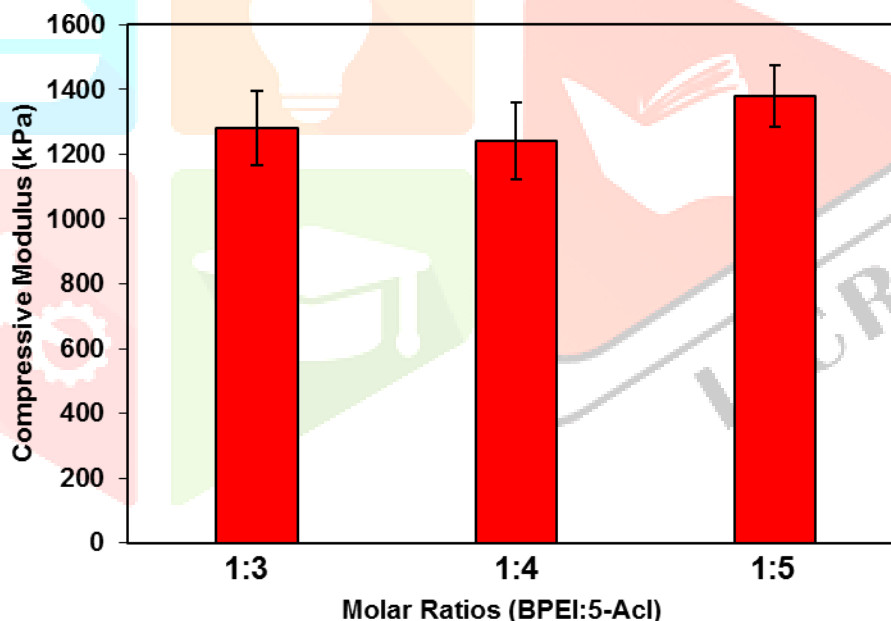


Figure 5.4. (A-D) Digital images (A, B) and water contact angle images (C, D) of beaded water droplet on solvent free polymeric gel (post modified with ODA) before (A, C) and after (B, D) slicing the material. E-F FESEM images of the interior (bulk) of the polymeric material in lower (E) and higher (F) magnifications.

to be superhydrophobic as the freshly exposed interiors repelled the beaded water droplets with water contact angle above 150° as shown in Figure 5.4A-D. The topography of the material was also investigated in the bulk and was found the porous network similar to that of top surface (Figure 5.4E, F),



which infers that the hierarchical topography and essential low surface energy coating is present all throughout the material. The compressive modulus of the gel materials prepared with different ratios of BPEI:5-Acl was calculated, and the gel materials that are prepared varying the molar ratio of BPEI:5-Acl are with similar compressive modulus as is shown in Figure 5.5. The facile chemical approach of synthesizing chemically “reactive” and porous polymeric gel allowed us to tailor various other wettabilities through appropriate post chemical modification in the polymeric gel material (molar composition of the BPEI and 5-Acl mixture was maintained to be 1:5). The post covalent modifications of the chemically reactive polymeric material with various small molecules (having primary amine groups and hydrophobic tails) were characterized with FTIR spectral studies, where the peak at 1410 cm^{-1} was significantly reduced after post chemical modification with selected small molecules, where all the IR peaks are normalized with respect to carbonyl stretching (1735 cm^{-1}) as is shown in Figure 5.6. The chemically reactive (inherently hydrophilic) polymeric gel became moderately hydrophobic (WCA $\sim 107^\circ$) and highly hydrophobic (120°) to superhydrophobic ($\theta > 150^\circ$)

Figure 5.5. Plot accounting the compressive modulus of polymeric gels that are synthesized by changing composition (molar ratio) of the reactants (BPEI/5-Acl) including 1:3, 1:4, and 1:5, in absence of the external solvent.

on increasing the carbon number (from C5 to C18) in the primary amine containing small molecules, which were covalently attached on the polymeric gel through 1, 4-conjugate addition reaction as shown in Figure 5.7. Eventually, the same polymeric material is capable of displaying both homogeneous and heterogeneous wettability. This chemically “reactive” and inherently sticky gel was further coated on glass substrate and after post chemical modification with octadecylamine, the polymeric coating displayed superhydrophobicity with contact angle greater than 150° as is shown in Figure 5.8A, B. The stream of water was observed to readily bounce away after hitting the biomimicked interface (Figure 5.8C), and these simple studies supported the existence of nonadhesive durable superhydrophobicity. Moreover, the morphology of the coating was also found to be similar to the self-standing polymeric monolith as is shown in Figure 5.8D. The coating was further extended to other substrates irrespective of their chemical composition and wettability including glass, plastic film, aluminum foil, filter paper, and wood surface. An amount of 2.8 g of amine reactive gel, which was prepared just by mixing BPEI and 5-Acl (with 1:5 molar ratio), was placed on the surface of selected and cleaned substrates and spread out with one end of the microscopic glass slide uniformly over 21.6 cm^2 area. Then,

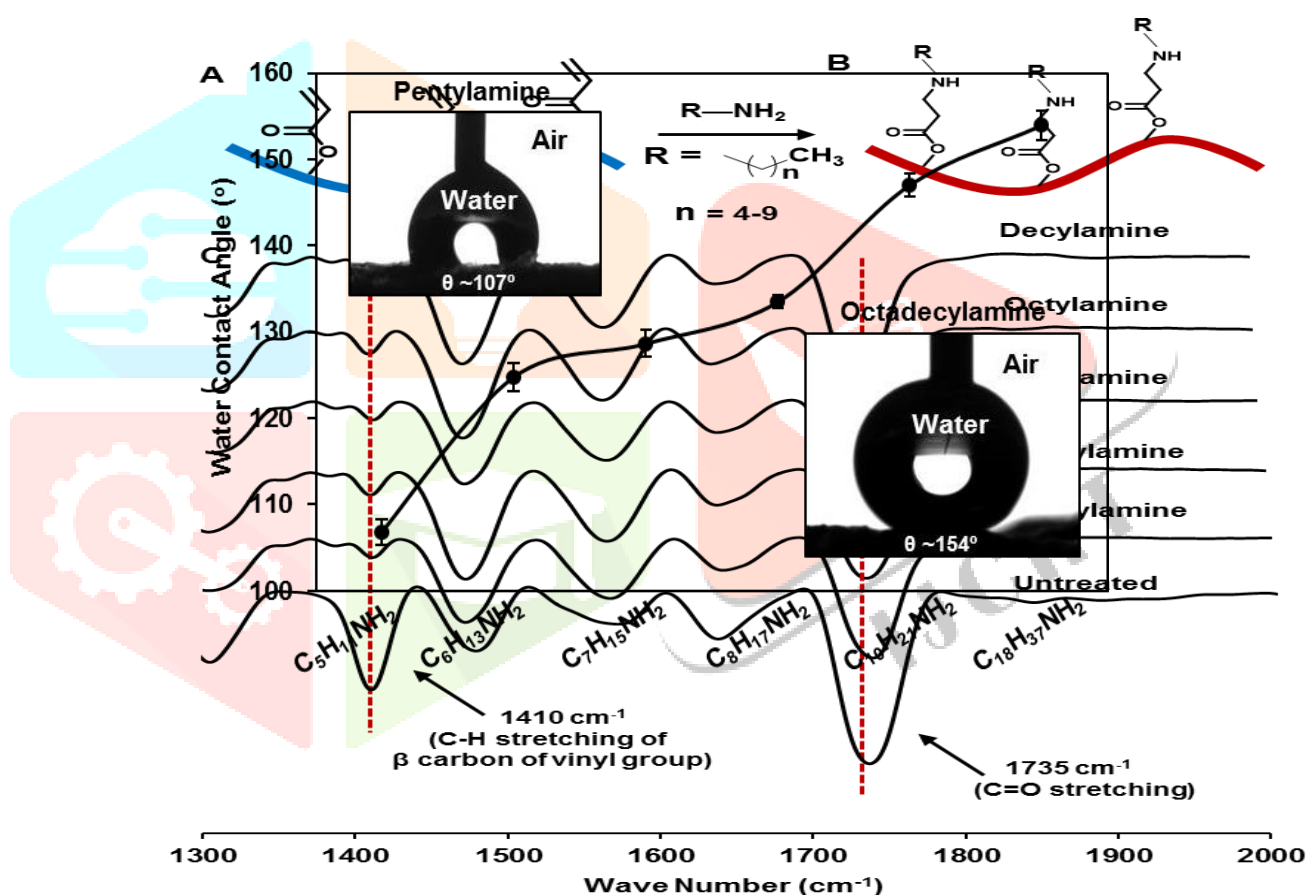
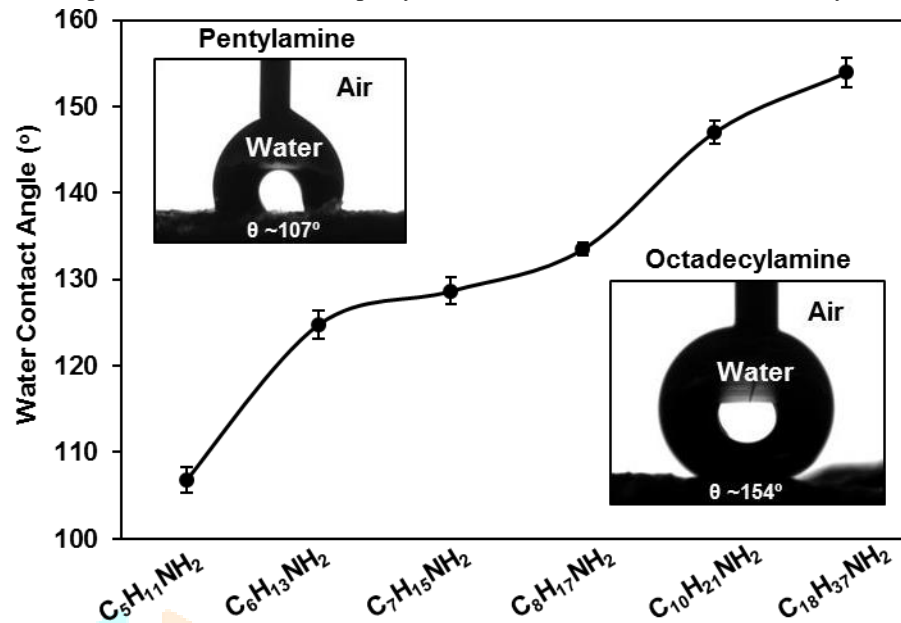


Figure 5.6. (A, B) Schematic illustration of polymeric gel having residual and reactive acrylate moieties and its post chemical modification with primary amine containing small molecules (having shorter or longer hydrocarbon tails (B)). (C) FTIR spectra of the solvent free and ‘reactive’ polymeric gel before and after post modification with various amine containing small molecules including propylamine, pentylamine, hexylamine, octylamine and decylamine respectively. The IR peaks at 1736 cm^{-1} and 1410 cm^{-1} denoted the carbonyl stretching and symmetric deformation of the C-H bond for the β carbon of the vinyl group respectively.

the extreme water wettability was adopted on covalently cross-linked “reactive” and polymeric coatings ($555 \mu\text{m} \pm 40 \mu\text{m}$) through the appropriate post chemical modification with octadecylamine (Figure 5.8E-L). This simple approach provided a facile and substrate independent bulk superhydrophobic coating and the water droplets are beaded with high

Figure 5.7. Plot showing the change in the water contact angle on the polymeric gel, after the post modification of the material with amine containing small molecules that have different hydrocarbon tail length; insets are the water contact angle (WCA) images of gel after post modification with pentylamine (WCA $\sim 107^\circ$) and octadecylamine (WCA $\sim 154^\circ$),



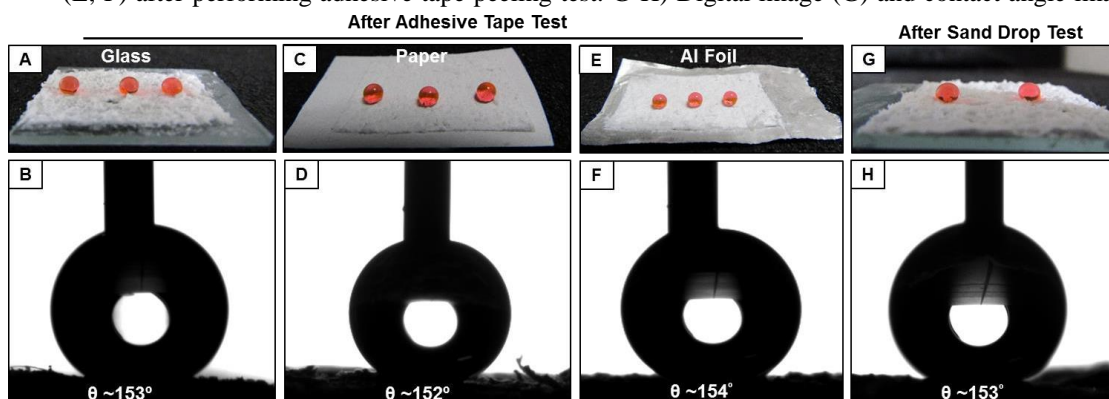
respectively.

contact angles (above 150°) and low contact angle hysteresis (below 10°) as shown in Figure 5.8E-L. This current approach did not demand any additional surface modification on the selected substrates. Additionally, the durability of these coatings was examined in details where the polymeric coatings on Al foil, glass, and filter paper were strategically exposed to adhesive tape with 100 g of applied load, and during the peeling of the adhesive tape, some top portion of the film was transferred to the adhesive tape. However, the superhydrophobicity remained intact with the remaining portion of the coating on the selected substrates even after this severe physical damage as shown in Figure 5.9A-F. Hence, this simple study revealed the existence of strong interfacial interaction between the substrate and deposited film likely through nonspecific hydrogen bonding and electrostatic interaction, similar to that of nonspecific interactions in Mussel-inspired coatings.³⁰ Furthermore, the deposited polymeric coating is embedded with inherently durable bulk superhydrophobicity. The biomimicked coatings were then exposed to 100 g of sand from 15 cm distance, and the embedded special wettability was found to be unaffected (Figure

Figure 5.8. (A-B) Digital images (A) and contact angle images (B) of beaded water droplets on the polymeric coatings (post modified with ODA) on glass. C) Digital image showing the stream of water is bouncing away from superhydrophobic surface. D) FESEM image of solvent free polymeric gel coating on glass substrate with BPEI/5-Acl molar ratio of 1:5. E-L) Digital images (E, G, I, K,) and contact angle images (F, H, J, L) of beaded water droplets on the polymeric coatings on the various substrates including plastic (E, F), filter paper (G, H), aluminum foil (I, J), wood (K, L) respectively.

5.9G, H). Next, the superhydrophobic coating was exposed to UV irradiations ($\lambda_{max} = 254$ and 365 nm) for 5 days, and extreme water repellency was observed to be unaltered with

Figure 5.9. (A-F) Digital images (A, C, E) and water contact angle images (B, D, F) of polymeric coating on various substrates (post modified with ODA) after adhesive tape test including glass (A, B), filter paper (C, D), aluminum foil (E, F) after performing adhesive tape peeling test. G-H) Digital image (G) and contact angle image (H) of polymeric



coating on glass substrate (post modified with ODA) after performing sand drop test.

advancing water contact angle above 150° after 5 days of exposure as is shown in Figure 5.10A-H. Further, these biomimicked interfaces were exposed to various complex aqueous phases including extremes of pH (1 and 12), artificial seawater and river (Brahmaputra River, Guwahati, India) water, however, the polymeric coating continued to repel these chemically complex phases with advancing contact angle above 150° and contact angle hysteresis below 10° (Figure 5.11). Thus, all these results signify the existence of both

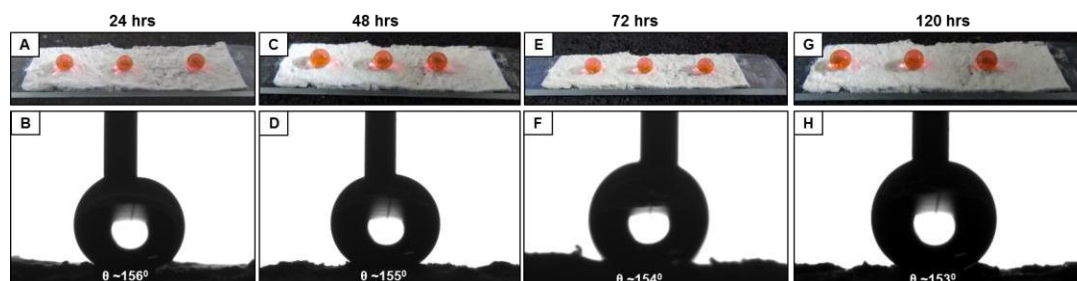


figure 5.10. (A-H) Digital images (A, C, E, G) and contact angle images (B, D, F, H) of beaded water droplet on the polymeric coating (post modified with ODA) on glass substrate after continuous exposure to UV radiations at short (254 nm) and long (365 nm) wavelengths for 24 hours (A, B), 48 hours (C, D), 72 hours (E, F) and 120 hours (G, H) respectively.

physical and chemical durable superhydrophobicity in the as synthesized polymeric coatings. Hence, this current simple and rapid chemical approach provided a single avenue for the synthesis of chemically reactive and covalently cross-linked polymeric coatings capable of displaying durable super-water repellency. This approach could be further exploited in developing other functional bio-interfaces and chemically patterned interfaces.¹⁵⁻¹⁷ Thus, this material could be useful in synthesis of antibiofouling coating, drug delivery, anticorrosive coatings, tissue engineering, developing functional patterned interfaces, etc.

Conclusion

In summary, a chemically “reactive” and covalently crosslinked functional polymeric interface is introduced through a solvent/catalyst-free facile and rapid 1, 4-conjugate addition reaction. Further, the presence of residual acrylate groups made this polymeric material inherently chemically reactive and were strategically used in covalent modification with primary amine containing hydrophobic small molecules for developing durable and bulk superhydrophobicity. Moreover, the inherently sticky and reactive gel was coated on various substrates irrespective of their nature and chemical composition. After the appropriate post chemical modification with essential low surface energy molecule, the polymeric coatings displayed superhydrophobicity with high physical and chemical durability. This simple and environmentally friendly single chemical approach could be useful in synthesizing other functional interfaces (i.e., various chemically patterned interfaces, patterned wettability, etc.) for various smart and prospective applications in practically relevant diverse settings

References

- (1) Lahann, J.; Balcells, M.; Rodon, T.; Lee, J.; Choi, I. S.; Jensen, K. F.; Langer, R. *Langmuir* **2002**, *18*, 3632–3638.
- (2) Lahann, J.; Balcells, M.; Lu, H.; Rodon, T.; Jensen, K. F.; Langer, R. *Anal. Chem.* **2003**, *75*, 2117–2122.
- (3) Liang, Z.; Wang, Q. *Langmuir* **2004**, *20*, 9600–9606.
- (4) Buck, M. E.; Zhang, J.; Lynn, D. M. *Adv. Mater.* **2007**, *19*, 3951–3955.
- (5) Chen, H.; Lahann, J. *Langmuir* **2011**, *27*, 34–48.
- (6) Deng, X.; Friedmann, C.; Lahann, J. *Angew. Chem.* **2011**, *123*, 6652–6656.
- (7) Manova, R.; Van-Beek, T. A.; Zuilhof, H. *Angew. Chem., Int. Ed.* **2011**, *50*, 5428–5430.
- (8) Spruell, J. M.; Wolffs, M.; Leibfarth, F. A.; Stahl, B. C.; Heo, J.; Connal, L. A.; Hu, J.; Hawker, C. J. *J. Am. Chem. Soc.* **2011**, *133*, 16698–16706.

(9) Broderick, A. H.; Azarin, S. M.; Buck, M. E.; Palecek, S. P.; Lynn, D. M.

Biomacromolecules **2011**, *12*, 1998–2007.

(10) Bechler, S. L.; Lynn, D. M. *Biomacromolecules* **2012**, *13*, 1523–1532.

(11) Bally, F.; Cheng, K.; Nandivada, H.; Deng, X.; Ross, A. M.; Panades, A.; Lahann, J.

ACS Appl. Mater. Interfaces **2013**, *5*, 9262–9268.

(12) Yoshii, T.; Onogi, S.; Shigemitsu, H.; Hamachi, I. *J. Am. Chem. Soc.* **2015**, *137*, 3360–3365.

(13) Carter, M. C. D.; Jennings, J.; Speetjens, F. W.; Lynn, D. M.; Mahanthappa, M. K.

Macromolecules **2016**, *49*, 6268–6276.

(14) Liu, P.; Zhang, H.; He, W.; Li, H.; Jiang, J.; Liu, M.; Sun, H.; He, M.; Cui, J.; Jiang, L.; Yao, X. *ACS Nano* **2017**, *11*, 2248–2256.

(15) Bog, U.; Los, A. D.; Pereira, S.; Mueller, S. L.; Havenridge, S.; Parrillo, V.; Bruns, M.; Holmes, A. E.; Emmenegger, C. R.; Fuchs, H.; Hirtz, M. *ACS Appl. Mater. Interfaces* **2017**, *9*, 12109–12117.

(16) Chen, H. Y.; Hirtz, M.; Deng, X.; Laue, T.; Fuchs, H.; Lahann, J. *J. Am. Chem. Soc.*

2010, *132*, 18023–18025.

(17) *Yaqoob suhail 2020 relationship of participation in physical activity with depression and mental health of muslim women:special reference to geriatric population DOI: 10.13140/RG.2.2.12596.68487.*

(18) Li, J.; Li, L.; Du, X.; Feng, W.; Welle, A.; Trapp, O.; Grunze, M.; Hirtz, M.; Levkin, P. A. *Nano Lett.* **2015**, *15*, 675–681.

(19) Buck, M. E.; Schwartz, S. C.; Lynn, D. M. *Chem. Mater.* **2010**, *22*, 6319–6327.

