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Qualifying scientific
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ZUO YONG

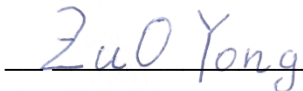
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THESIS
Stability of textured water-repellent surfaces

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The dissertation contains the results of personal research. The use of ideas, results, and texts from other authors are accompanied by references to the respective sources.

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ABSTRACT

Zuo Yong. Stability of textured water-repellent surfaces. - Qualified scientific work on the rights of the manuscript.

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The environmental durability of superhydrophobic surfaces remains a critical barrier to their practical application, particularly for the corrosion protection of aluminum alloys in demanding marine, aerospace, and industrial environments. Despite decades of research inspired by natural superhydrophobic systems such as the lotus leaf, the translation of laboratory-scale superhydrophobic coatings into real-world applications has been severely limited by rapid performance degradation under environmental stress. This dissertation confronts this challenge not through empirical trial-and-error, but through a mechanism-driven approach that integrates multi-scale surface characterization, accelerated degradation testing, rational composite design, and computational electrochemistry to establish a predictive engineering framework for durable superhydrophobic coatings.

The research began by moving beyond the limitations of static contact angle measurements, which provide only superficial insight into wetting behavior. A comprehensive characterization methodology was established that combines Owens-Wendt surface energy decomposition with dynamic contact angle analysis. This approach enabled quantitative assessment of both the dispersive and polar components of surface energy, revealing that stabilizing the Cassie-Baxter wetting state - where air pockets are trapped beneath water droplets - hinges on reducing the polar surface energy component to below 1 mJ/m^2 through silane functionalization. This quantitative threshold, inaccessible through static contact angle measurements alone, provides a clear design target for surface chemical modification. The multi-scale investigation spanned textures from 100 nm laser-induced periodic surface structures to $750 \text{ }\mu\text{m}$

milled grooves, systematically delineating the operational limits of classical wetting models. Notably, the Wenzel model, which assumes complete liquid penetration into surface roughness, was found to fail for large-scale microstructures due to contact line pinning at texture edges, a phenomenon that classical theory does not account for.

Having established a robust characterization framework, the research turned to identifying the primary failure pathway under environmental stress. Accelerated weathering protocols combining UV irradiation (340 nm, 0.89 W/m²) with elevated temperature (60°C) and humidity (50% RH) were employed to simulate months of outdoor exposure in compressed timescales. Through in-situ chemical analysis using Fourier-transform infrared spectroscopy, polymer photo-oxidation was unambiguously identified as the dominant degradation mechanism, evidenced by a 60-80% decrease in aliphatic C-H stretching vibrations (2850-2950 cm⁻¹) and a fivefold increase in carbonyl C=O absorption (1731 cm⁻¹). This mechanistic insight was critical: it demonstrated that particle erosion and mechanical delamination, often assumed to be primary failure modes, were in fact secondary to chemical degradation of the polymer binder. The implication was clear: durability could be enhanced not by strengthening adhesion or increasing coating thickness, but by minimizing the polymer binder content while maximizing the density of a hierarchical inorganic particle network that is inherently resistant to photo-oxidation.

This mechanism-driven approach culminated in an optimized composite coating formulation comprising 5 wt.% acrylic copolymer binder, 90 wt.% silane-functionalized calcium carbonate microparticles ($d_{50} \approx 5 \mu\text{m}$), and 5 wt.% fumed silica nanoparticles ($d_{50} \approx 12 \text{ nm}$). This hierarchical architecture combines the mechanical integrity provided by the polymer with the chemical stability of the inorganic particles, while the bifractional particle size distribution creates a dense, tortuous network that impedes electrolyte penetration. The coating demonstrated exceptional performance in 3.0 wt.% NaCl electrolyte under continuous immersion. Potentiodynamic polarization measurements revealed a +797 mV noble shift in corrosion potential, from -660 mV for bare AA6061 aluminum to +137 mV vs. saturated calomel electrode (SCE) for the coated substrate. Electrochemical impedance spectroscopy at 0.01 Hz showed

impedance magnitudes exceeding $688 \Omega \cdot \text{cm}^2$, representing a 2.3-fold improvement over unoptimized formulations. Critically, superhydrophobicity, with apparent contact angles exceeding 130° , was maintained after 72 hours of continuous immersion, a performance benchmark rarely reported in the literature for polymer-based coatings.

To move beyond purely empirical optimization, a multi-physics computational model was developed and experimentally validated. The model coupled Butler-Volmer electrode kinetics with porous media transport, accounting for both the tortuous diffusion path through the particle network and the electrochemical reactions at the aluminum-electrolyte interface. The model reproduced experimental polarization curves within 10% accuracy across the entire potential range, providing confidence in its predictive capability. More importantly, the model enabled mechanistic decomposition of the protection mechanisms, revealing a synergistic effect: a 3.2-fold increase in solution resistance from the tortuous particle network combined with a 5.8-fold increase in charge transfer resistance from surface passivation by the hydrophobic silane layer. This quantitative insight, inaccessible through experiment alone, demonstrates that durability arises not from a single dominant mechanism but from the synergistic interaction of multiple protective barriers.

The scientific novelty of this dissertation lies in the development of a comprehensive framework for understanding the formation, stability, and protective performance of superhydrophobic composite coatings through combined experimental and computational approaches. For the first time, it has been demonstrated that the Owens–Wendt surface energy decomposition method, when coupled with dynamic contact angle analysis, provides substantially greater predictive capability than conventional static measurements, revealing that stabilization of the Cassie–Baxter wetting regime is primarily governed by a drastic reduction in the polar component of surface energy from approximately 20 mJ/m^2 to below 1 mJ/m^2 after silane functionalization, which enables apparent contact angles exceeding 150° . The work also advances the understanding of the applicability limits of classical wetting models through a systematic investigation of textured surfaces spanning nearly three orders of magnitude in characteristic size, from laser-induced periodic surface structures of

about 100 nm to micromilled features approaching 750 μm , demonstrating that the Wenzel model becomes invalid for textures with periodicities above roughly 200 μm due to contact line pinning at structural edges, a mechanism not captured by equilibrium thermodynamic descriptions of wetting. Furthermore, the dominant degradation mechanism of superhydrophobic composite coatings under environmental exposure has been identified for the first time by combining ultraviolet aging with chemical analysis, showing that coating failure is primarily driven by photo-oxidative transformation of the polymer matrix rather than by particle erosion or delamination. Infrared spectroscopy revealed a pronounced decrease in aliphatic C–H stretching vibrations in the range of 2850–2950 cm^{-1} accompanied by a significant increase in carbonyl absorption near 1731 cm^{-1} , confirming the conversion of hydrophobic groups into oxygen-containing polar functionalities. Based on these findings, a mechanistic design principle for durable superhydrophobic coatings has been established, demonstrating that optimal performance is achieved by minimizing the polymer fraction while maintaining a dense inorganic particle network that defines the hierarchical surface morphology. An optimized composite formulation containing 5 wt.% acrylic copolymer, 90 wt.% silane-functionalized calcium carbonate microparticles, and 5 wt.% fumed silica nanoparticles was developed and experimentally validated, providing a substantial positive shift of corrosion potential, increased impedance magnitude at low frequencies, and preservation of high hydrophobicity after prolonged immersion in a sodium chloride electrolyte. In addition, a multi-physics computational model has been developed and validated that quantitatively reproduces electrochemical polarization behavior and allows mechanistic separation of the protective contributions of the coating structure. The modeling results demonstrate that the enhanced corrosion resistance arises from synergistic effects including increased solution resistance associated with tortuous ionic diffusion pathways through the particle network and elevated charge transfer resistance resulting from surface passivation induced by silane treatment. Overall, the obtained results reveal that a dense inorganic particle framework simultaneously generates the hierarchical roughness required for superhydrophobic wetting and acts

as a diffusion barrier that suppresses ionic transport, while the reduced polymer content limits water uptake and hydrolytic swelling. This integrated understanding establishes a mechanism-oriented approach to the design of durable superhydrophobic protective coatings.

The practical significance of the obtained results is substantial and multifaceted. First, this work delivers a viable, environmentally benign alternative to hexavalent chromium-based conversion coatings, which remain the industry standard for aluminum corrosion protection despite their well-documented carcinogenicity and environmental toxicity. The optimized superhydrophobic coating matches or exceeds the corrosion protection performance of chromate coatings while eliminating hazardous waste generation and worker exposure risks. Second, the mechanism-driven design methodology developed here is transferable to other composite material systems, providing a template for rational materials engineering in applications ranging from self-cleaning surfaces to anti-icing and anti-fouling coatings. Third, the validated computational model enables predictive design and optimization without exhaustive experimental testing, significantly reducing development time and cost. Fourth, the quantitative surface energy thresholds and formulation guidelines established in this work provide actionable design rules for industrial coating formulation, accelerating the translation of superhydrophobic technology from laboratory curiosities to commercial products.

In summary, this dissertation represents a critical step in advancing materials science from empirical discovery to predictive engineering. By integrating surface science, polymer chemistry, electrochemistry, and computational modeling, it establishes a comprehensive framework for designing durable superhydrophobic coatings that perform reliably in complex operational environments. The work demonstrates that durability is not an intrinsic material property to be discovered, but an engineered system-level behavior that emerges from the rational integration of hierarchical structure, interfacial chemistry, and protective mechanisms.

Keywords: superhydrophobic, polymer, composite, surface, modification, nanoparticles, silica, morphology, corrosion, contact angle, UV resistance, degradation, wetting

The list of applicants publication as follows:

Scientific papers:

1. Myronyuk, O., Baklan, D., Vanagas, E., Rodin, A. M., **ZUO. Y.** (2023). Owens–Wendt characterization of Femtosecond-Laser-Textured hydrophobic aluminum surfaces. *Coatings*, 13 (6), 1104. <https://doi.org/10.3390/coatings13061104> Scopus indexed journal (ISSN 2079-6412), Q2. *Authors contribution:* 1) O. Myronyuk – *Conceptualization, formal analysis, validation, investigation, resources, original draft preparation, writing - review and editing, supervision, project administration, funding acquisition;* 2) D. Baklan – *methodology, validation, investigation, data curation, writing - original draft preparation, visualization;* 3) E. Vanagas - *resources,* 4) A. Rodin - *methodology, resources, project administration, funding acquisition;* 5) **Z. Yong - data curation, investigation.**
2. Myronyuk, O., Baklan, D., **ZUO.Y.**, Rodin, A. M. (2022). Complex destruction of textured water-repellent coatings under the influence of UV and water flow. *Materials Today Communications*, 33, 104509. <https://doi.org/10.1016/j.mtcomm.2022.104509>. Scopus indexed journal (ISSN 2352-4928) , Q2. *Authors contribution:* 1) O. Myronyuk: *Conceptualization, Methodology, Validation, Formal analysis, Writing – original draft, Writing – review & editing, Supervision, Project administration;* 2) A. Rodin: *Conceptualization, Methodology, Writing – review & editing, Supervision, Project administration.* Denys Baklan: *Methodology, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization.* 3) **Z. Yong: Formal analysis, Investigation, Data curation, Writing – original draft.**
3. **Ц. Юн**, Д. Баклан., (2025) A review of fabrication techniques for superhydrophobic coatings. *Вісник Східноукраїнського національного*

університету імені Володимира Даля, (2025) 109-120.

<https://doi.org/10.33216/1998-7927-2025-291-5-109-120>. Authors contribution: 1) **Z. Yong - Formal analysis, Investigation, Data curation, Writing – original draft**; 2) D.Baklan - Conceptualization, Methodology, Validation, Formal analysis, Writing – original draft, Writing – review & editing, Supervision, Project administration.

4. **ZUO,Y.**, Baklan, D. V., Myronyuk, O. V. (2024). Corrosion resistance of polymer-silica-calcite textured surfaces. (2024). *Technologies and Engineering*, (1), 107–114. <https://doi.org/10.30857/2786-5371.2024.1.11>. Authors contribution: 1) **Z. Yong - Investigation, Data curation, Writing – original draft**; 2) D.Baklan - Validation, Formal analysis, Writing – original draft, Writing – review & editing; 3) O. Myronyuk - Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Supervision.

Conference proceedings:

5. Myronyuk, O., Baklan, D., Rodin, A., Pitak, Y., Balytska, N., & Zuo, Y. (2025). Determination of 60-500 μm textures on polydimethylsiloxane surfaces wetting properties. 2025 *IEEE 6th KhPI Week on Advanced Technology, KhPIWeek 2025*, 1–6. <https://doi.org/10.1109/KhPIWeek61436.2025.11288681> Authors contribution: 1) O.Myronyuk – conceptualization; 2) D.Baklan – validation, writing; 3)A.Rodin – funding acquisition 4) Y. Pitak – supervision; 5) N. Balytska – discussion, text editing; 5) **Z. Yong – experimental, writing, revision.**

6. Денис Баклан, Цзо Юн, Олексій Миронюк, Пуйкі Ленг., (2025). Супергідрофобні покриття на основі вуглецевих нанотрубок. *Композиційні матеріали 2025: Матеріали XIV Міжнародної науково-практичної WEB-конференції*. 2025, 11–19. <https://doi.org/10.20535/iwccmm2025326606> Authors contribution: 1) D.Baklan – validation, investigation, writing 2) **Z. Yong - experiment, validation, revision**; 3) O.Myronyuk – conceptualization, methodology supervision; 4) P.Leung – funding acquisition, discussion.

7. Денис Баклан, Цзо Юн, Олексій Миронюк, (2024). Корозійна стійкість біфракційних текстурованих покриттів. *Композиційні матеріали 2024:*

*Матеріали XIII Міжнародної науково-практичної WEB-конференції, 2024, 119-122. <https://doi.org/10.20535/iwccmm2024302146>. Authors contribution: 1) D.Baklan – original draft writing, validation, revision; 2) **Z. Yong** – **experimental investigation, revision**; 3) O.Myronyuk – conceptualization, supervision, methodology*

8. Myronyuk, O., Baklan, D., Rodin, A. M., **Yong Z.**, (2023). The combined effects of UV radiation and water flow on the deterioration of water-repellent coatings with textures. *Composite materials-Liha-Pres: monograph based on the materials of the XII International Scientific and Practical WEB Conference, 2023, 52-54. <https://ela.kpi.ua/handle/123456789/62006>. Authors contribution: 1) O.Myronyuk – conceptualization, supervision, methodology 2) D.Baklan – original draft writing, validation, revision; 3) A.Rodin – funding acquisition, discussion; 4) **Z. Yong** – **experimental investigation, revision**.*

9. Xi, L., Tang, L., Leung, P., **ZUO,Y**, Myronyuk, O., Liao, Q. (2023). Empowering organic redox flow batteries with organic acid electrolytes for enhanced energy densities. *Міжнародна конференція з хімії, хімічної технології та екології, присвяченій 125-річчю КПІ ім. Ігоря Сікорського Збірка тез доповідей, 2023, 143-145. https://drive.google.com/file/d/1wjXq3bFfMVJOqnKJ2kPlZBAEm00Qufpj/view?usp=drive_link Authors contribution: 1) Xi, L – supervision, methodology; 2) Tang, L. – writing, data analysis; 3) Leung, P. – funding, conceptualization; 4) **Z. Yong** – **writing, experimental, revision**; 5) O.Myronyuk – discussion; 6) Liao, Q. – investigation, validation.*

АНОТАЦІЯ

Цзо Юн. Стабільність текстурованих водовідштовхувальних поверхонь – Кваліфікаційна наукова праця на правах рукопису.

Дисертація на здобуття наукового ступеня доктора філософії за спеціальністю 161 – Хімічні технології та інженерія, галузь знань 16 – Хімічна та біоінженерія – Національний технічний університет України «Київський політехнічний інститут імені Ігоря Сікорського», Київ, 2026.

Стійкість до впливу навколишнього середовища залишається критичним бар'єром для практичного застосування супергідрофобних поверхонь, особливо для антикорозійного захисту алюмінієвих сплавів у складних морських, аерокосмічних та промислових умовах. Незважаючи на десятиліття досліджень, натхненних природними супергідрофобними системами, такими як лист лотоса, впровадження лабораторних супергідрофобних покриттів у реальні умови було суттєво обмежене через швидку деградацію їхніх властивостей під впливом навколишнього середовища. Ця дисертація вирішує цю критичну проблему не шляхом емпіричних спроб і помилок, а за допомогою механістично-орієнтованого підходу, що інтегрує багатомасштабну характеристику поверхні, прискорені випробування на деградацію, раціональне проектування композитів та обчислювальну електрохімію для створення прогностичної інженерної основи для довговічних супергідрофобних покриттів.

Дослідження розпочалося з виходу за межі обмежень статичних вимірювань кута змочування, які дають лише поверхневе уявлення про поведінку змочування. Була створена комплексна методологія характеристики, що поєднує розкладання поверхневої енергії за методом Оуенса-Вендта з динамічним аналізом кута змочування. Цей підхід дозволив кількісно оцінити як дисперсійну, так і полярну складові поверхневої енергії, виявивши, що стабілізація стану змочування Кассі-Бакстера, коли повітряні кишені утримуються під краплями води, залежить від зниження полярної складової поверхневої енергії до рівня нижче 1 мДж/м² за допомогою силанової

функціоналізації. Цей кількісний поріг, недосяжний за допомогою лише статичних вимірювань кута змочування, є чіткою проектною ціллю для хімічної модифікації поверхні. Багатомасштабне дослідження охоплювало текстури від 100 нм лазерно-індукованих періодичних поверхневих структур до 750 мкм фрезерованих канавок, систематично визначаючи експлуатаційні межі класичних моделей змочування. Зокрема, було встановлено, що модель Венцеля, яка передбачає повне проникнення рідини в шорсткість поверхні, не працює для великомасштабних мікроструктур через закріплення лінії контакту на краях текстури, явище, яке класична теорія не враховує.

Після створення надійної методології характеристики, дослідження перейшло до визначення основного шляху руйнування під впливом навколишнього середовища. Були застосовані протоколи прискореного старіння, що поєднували УФ-опромінення (340 нм, 0,89 Вт/м²) з підвищеною температурою (60°C) та вологістю (50% RH) для імітації місяців експлуатації на відкритому повітрі в стислі терміни. За допомогою хімічного аналізу in-situ з використанням Фур'є-спектроскопії інфрачервоного випромінювання, фотоокислення полімеру було однозначно ідентифіковано як домінуючий механізм деградації, що підтверджується зменшенням на 60-80% аліфатичних C-H коливань (2850-2950 см⁻¹) та п'ятикратним збільшенням поглинання карбонільної групи C=O (1731 см⁻¹). Це механістичне розуміння було критично важливим: воно продемонструвало, що ерозія частинок та механічне відшарування, які часто вважаються основними режимами руйнування, насправді є вторинними по відношенню до хімічної деградації полімерного сполучного. Висновок був очевидним, довговічність можна підвищити не шляхом посилення адгезії чи збільшення товщини покриття, а шляхом мінімізації вмісту полімерного сполучного при одночасному максимальному збільшенні щільності ієрархічної неорганічної мережі частинок, яка є за своєю природою стійкою до фотоокислення.

Цей механістично-орієнтований підхід завершився створенням оптимізованої композиції покриття, що складається з 5 мас.% акрилового

кополімерного сполучного, 90 мас.% силанізованих мікрочастинок карбонату кальцію ($d_{50} \approx 5$ мкм) та 5 мас.% пірогенного діоксиду кремнію ($d_{50} \approx 12$ нм). Ця ієрархічна архітектура поєднує механічну цілісність, що забезпечується полімером, з хімічною стабільністю неорганічних частинок, тоді як біфракційний розподіл розмірів частинок створює щільну, звивисту мережу, що перешкоджає проникненню електроліту. Покриття продемонструвало виняткові характеристики в 3,0 мас.% розчині NaCl при безперервному зануренні. Потенціодинамічні поляризаційні вимірювання показали зміщення корозійного потенціалу в благородну сторону на +797 мВ, з -660 мВ для чистого алюмінію АА6061 до +137 мВ відносно насиченого каломельного електроду (НКЕ) для покритої підкладки. Електрохімічна імпедансна спектроскопія на частоті 0,01 Гц показала величини імпедансу, що перевищують $688 \text{ Ом} \cdot \text{см}^2$, що є 2,3-кратним покращенням порівняно з неоптимізованими складами. Критично важливо, що супергідрофобність, з видимими кутами змочування понад 130° , зберігалася після 72 годин безперервного занурення, що є показником ефективності, рідко згадуваним у літературі для полімерних покриттів.

Для виходу за межі суто емпіричної оптимізації була розроблена та експериментально підтверджена багатofізична обчислювальна модель. Модель поєднувала кінетику електродів Батлера-Фольмера з переносом у пористому середовищі, враховуючи як звивистий дифузійний шлях через мережу частинок, так і електрохімічні реакції на межі поділу алюміній-електроліт. Модель відтворювала експериментальні поляризаційні криві з точністю до 10% у всьому діапазоні потенціалів, що забезпечило впевненість у її прогностичній здатності. Що ще важливіше, модель дозволила провести механістичну декомпозицію захисних механізмів, виявивши синергетичний ефект: 3,2-кратне збільшення опору розчину завдяки звивистій мережі частинок у поєднанні з 5,8-кратним збільшенням опору переносу заряду завдяки пасивації поверхні гідрофобним силановим шаром. Це кількісне розуміння, недосяжне лише експериментальним шляхом, демонструє, що довговічність виникає не з одного домінуючого механізму, а із синергетичної взаємодії кількох захисних бар'єрів.

Наукова новизна дисертаційної роботи полягає у розробленні комплексної концепції формування, стабільності та захисних властивостей супергідрофобних композиційних покриттів на основі поєднання експериментальних досліджень і комп'ютерного моделювання. У роботі вперше показано, що застосування методу декомпозиції поверхневої енергії за Оуенсом–Вендтом у поєднанні з аналізом динамічного контактного кута забезпечує значно вищу прогностичну інформативність порівняно з традиційними статичними вимірюваннями, що дозволило встановити ключову роль зменшення полярної складової поверхневої енергії приблизно з 20 мДж/м² до значень менше 1 мДж/м² після силанування поверхні у стабілізації режиму змочування Кассі–Бакстера та досягненні уявних контактних кутів понад 150°. Подальший розвиток отримало розуміння меж застосовності класичних моделей змочування завдяки систематичному дослідженню текстурованих поверхонь, характерні розміри елементів яких охоплюють майже три порядки величини - від лазерно індукованих періодичних структур із масштабом близько 100 нм до мікрофрезерованих елементів розміром до 750 мкм. Показано, що модель Венцеля втрачає коректність для текстур із періодом понад приблизно 200 мкм унаслідок закріплення контактної лінії на краях структурних елементів, що не враховується у рівноважних термодинамічних описах змочування. Уперше встановлено домінуючий механізм деградації супергідрофобних композиційних покриттів під дією факторів навколишнього середовища на основі поєднання ультрафіолетового старіння та хімічного аналізу, що показало визначальну роль фотоокиснювального перетворення полімерної матриці, а не ерозії частинок або їх деламінації. Дані інфрачервоної спектроскопії засвідчили суттєве зменшення інтенсивності аліфатичних коливань розтягування C–H у діапазоні 2850–2950 см⁻¹ разом зі значним зростанням інтенсивності карбонільної смуги поблизу 1731 см⁻¹, що підтверджує перетворення гідрофобних груп у кисневмісні полярні функціональні групи. На основі отриманих результатів сформульовано механістичний принцип проєктування довговічних супергідрофобних покриттів, відповідно до якого оптимальні властивості досягаються за умови мінімізації

вмісту полімерної фази при формуванні щільної мережі неорганічних частинок, що визначає ієрархічну морфологію поверхні. Розроблено та експериментально підтверджено ефективність оптимізованої композиції, що містить 5 мас.% акрилового кополімеру, 90 мас.% силан-функціоналізованих мікрочастинок карбонату кальцію та 5 мас.% наночастинок пірогенного діоксиду кремнію, яка забезпечує суттєве позитивне зміщення корозійного потенціалу, зростання імпедансних характеристик на низьких частотах та збереження високої гідрофобності після тривалого контакту з електролітом хлориду натрію. Крім того, у роботі розроблено та експериментально верифіковано мультифізичну обчислювальну модель, що відтворює поведінку електрохімічної поляризації покриттів і дозволяє механістично розділити внесок окремих механізмів у формування їх захисних властивостей. Результати моделювання показали, що підвищена корозійна стійкість обумовлена синергічним поєднанням збільшеного опору розчину, пов'язаного з формуванням звивистих шляхів дифузії іонів у мережі частинок, та зростання опору перенесенню заряду внаслідок пасивації поверхні, спричиненої силановою модифікацією. У цілому встановлено, що щільна мережа неорганічних частинок одночасно формує ієрархічну шорсткість, необхідну для реалізації супергідрофобного стану поверхні, та створює дифузійний бар'єр для перенесення іонів, тоді як зменшений вміст полімеру обмежує водопоглинання і запобігає гідролітичному набуханню покриття, що формує механізмоорієнтований підхід до проектування довговічних супергідрофобних захисних покриттів.

Практичне значення отриманих результатів є значним і багатограним. По-перше, ця робота пропонує життєздатну, екологічно безпечну альтернативу конверсійним покриттям на основі шестивалентного хрому, які залишаються промисловим стандартом для захисту алюмінію від корозії, незважаючи на їх добре задокументовану канцерогенність та екологічну токсичність. Оптимізоване супергідрофобне покриття відповідає або перевищує антикорозійні характеристики хроматних покриттів, усуваючи при цьому утворення небезпечних відходів та ризики для здоров'я працівників. По-друге,

розроблена тут методологія проектування, орієнтована на механізми, може бути перенесена на інші композитні матеріальні системи, слугуючи шаблоном для раціонального матеріалознавства в таких сферах, як самоочисні поверхні, покриття проти обмерзання та обростання. По-третє, підтверджена обчислювальна модель дозволяє здійснювати прогностичне проектування та оптимізацію без вичерпних експериментальних випробувань, що значно скорочує час та вартість розробки. По-четверте, встановлені в цій роботі кількісні пороги поверхневої енергії та рекомендації щодо складу є дієвими правилами проектування для промислового виробництва покриттів, прискорюючи перехід супергідрофобних технологій від лабораторних диковинок до комерційних продуктів.

Таким чином, ця дисертація є критичним кроком у просуванні матеріалознавства від емпіричних відкриттів до прогностичного інжинірингу. Інтегруючи науку про поверхні, хімію полімерів, електрохімію та обчислювальне моделювання, вона створює комплексну основу для проектування довговічних супергідрофобних покриттів, які надійно працюють у складних експлуатаційних умовах. Робота демонструє, що довговічність - це не внутрішня властивість матеріалу, яку потрібно відкрити, а спроектована поведінка на системному рівні, що виникає в результаті раціональної інтеграції ієрархічної структури, міжфазної хімії та захисних механізмів.

Ключові слова: *супергідрофобний, полімер, композит, поверхня, модифікація, наночастинки, кремнезем, морфологія, корозія, кут змочування, УФ-стійкість, деградація, змочування*

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
ATR	Attenuated Total Reflectance
BSE	Backscattered Electrons
CA	Contact Angle
CAB	Cellulose Acetate Butyrate
CAH	Contact Angle Hysteresis
CB	Cassie-Baxter
CPC	Critical Polymer Concentration
CVD	Chemical Vapor Deposition
DI – Deionized Water	
EDS	Energy Dispersive X-ray Spectroscopy
EDX	Energy Dispersive X-ray Spectroscopy
EEC	Electrical Equivalent Circuit
EIS	Electrochemical Impedance Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
FOTS	Fluorooctyltriethoxysilane
FTIR	Fourier Transform Infrared Spectroscopy
GDP	Gross Domestic Product
LFS	Liquid Flame Spraying
LIPSS	Laser-Induced Periodic Surface Structures
OCP	Open Circuit Potential
OCTEO	Octyltriethoxysilane
ODA-RGO	Octadecylamine-modified Reduced Graphene Oxide
PDMS	Polydimethylsiloxane
PMMA	Polymethyl Methacrylate
POTS	1H,1H,2H,2H-Perfluorooctyltriethoxysilane
PTFE	Polytetrafluoroethylene

PVA	Polyvinyl Alcohol
PVD	Physical Vapor Deposition
SA	Sliding Angle
SCE	Saturated Calomel Electrode
SE	Secondary Electrons
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
THF	Tetrahydrofuran
UV	Ultraviolet
WCA	Water Contact Angle
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

INTRODUCTION

Relevance of the topic: Superhydrophobic surfaces have emerged as a critical area of materials science research due to their wide-ranging applications in self-cleaning surfaces, anti-fouling, anti-icing, drag reduction, and corrosion protection. These surfaces, inspired by natural examples such as the lotus leaf, achieve extreme water repellency through a synergistic combination of hierarchical surface roughness and low surface energy chemistry. However, a fundamental challenge limits their practical deployment: environmental durability. Most superhydrophobic coatings degrade rapidly under outdoor exposure due to UV-induced polymer photo-oxidation, mechanical abrasion, and electrochemical corrosion, with performance lifetimes often measured in weeks rather than years. This durability problem is particularly acute for aluminum and its alloys, which are extensively used in aerospace, automotive, and marine applications but suffer from corrosion-related failures. Traditional chromate-based conversion coatings, while effective, face worldwide regulatory phase-out due to carcinogenicity and environmental persistence. The development of durable, environmentally benign superhydrophobic coatings therefore represents both a scientific challenge and an industrial imperative. This work addresses this challenge through a mechanism-driven approach, integrating advanced surface characterization, accelerated degradation testing, rational composite design, and computational electrochemistry to establish design principles for superhydrophobic coatings with sustained performance under environmental stress.

The connection of the work with scientific programs, plans, and topics: The topic of the dissertation is included in the scientific work plan approved by the Department of Chemical Technology of Composite Materials at Igor Sikorsky Kyiv Polytechnic Institute, taking into account the law of Ukraine “About priority directions of science and technics development” No. 2623-III dated 11.07.2001 on the relevance of the thesis topic to the direction “novel substances and materials”.

The purpose of the research: The purpose of this study is to establish the mechanistic relationship between the structure, composition, and environmental durability of superhydrophobic composite coatings for metal corrosion protection, and to develop design principles for coatings with sustainable performance under combined UV, hydrodynamic, and electrochemical stresses.

Objectives of the research:

- To identify the gap of knowledge in the field of the statistical superhydrophobic coatings durability in aggressive environments.
- To establish a comprehensive characterization framework integrating surface energy thermodynamics with Owens-Wendt method and dynamic wetting analysis to quantify the role of hierarchical texture and chemical modification in stabilizing superhydrophobicity.
- To identify the dominant degradation mechanisms governing coating failure under accelerated environmental exposure including UV irradiation, hydrodynamic shear, electrochemical corrosion and to develop optimized composite coating formulations achieving sustained superhydrophobicity and corrosion resistance through rational control of polymer content, particle loading, and surface functionalization.
- To develop and experimentally validate a multi-physics computational model coupling electrochemical kinetics and porous media transport to enable quantitative prediction of coating performance and mechanistic decomposition of protection mechanisms.

Research Object: superhydrophobic composite coatings for aluminum corrosion protection, comprising hierarchically structured mineral particles dispersed in polymer matrices with controlled surface chemistry.

Research subject: the mechanistic relationships governing the formation, stability, and degradation of superhydrophobicity and corrosion resistance in composite coatings under environmental exposure.

Research Methodology: The research employed a multi-scale, multi-physics experimental and computational approach to establish structure-property-performance relationships in superhydrophobic coatings. Surface fabrication methods included femtosecond laser texturing of aluminum substrates to create hierarchical micro/nanostructures (100 nm to 750 μ m characteristic length scales) and spray deposition of composite coatings comprising acrylic copolymer binders, fumed silica nanoparticles ($d_{50} \approx 12$ nm), and calcium carbonate microparticles ($d_{50} \approx 5$ μ m) with silane functionalization. Surface morphology and chemical composition were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and Fourier-transform infrared spectroscopy (FTIR). Wetting behavior was quantified through static and dynamic contact angle goniometry, with surface energy components determined via the Owens-Wendt method using polar (water, glycerol) and non-polar (diiodomethane) probe liquids. Environmental durability was assessed through accelerated weathering protocols employing UV irradiation (equivalent to >1000 hours natural sunlight), hydrodynamic shear testing, and electrochemical evaluation in 3.0 wt.% NaCl electrolyte. Electrochemical characterization employed potentiodynamic polarization to determine corrosion potentials and current densities, and electrochemical impedance spectroscopy (EIS) over 0.01-100 kHz to quantify charge transfer and solution resistances. Computational modeling was performed using COMSOL Multiphysics finite element software, coupling Butler-Volmer electrode kinetics with asymmetric Tafel slopes, multicomponent species transport with Bruggeman effective medium corrections for porosity, and deformed geometry tracking via the level set method.

Scientific novelty:

- (1) For the first time, a comprehensive multi-scale characterization framework has been established demonstrating that the Owens-Wendt surface energy decomposition method, combined with dynamic contact angle analysis, provides substantially more predictive information than static contact angle measurements alone. It was shown that reduction of the polar surface energy component from approximately 20 mJ/m² to below 1 mJ/m² through silane functionalization is the critical factor stabilizing the Cassie-Baxter wetting regime and enabling apparent contact angles exceeding 150°.
- (2) This study advances the understanding of wetting model validity limits by systematically investigating textures spanning three orders of magnitude in characteristic length scale (100 nm laser-induced periodic surface structures to 750 µm micromilled features). It was demonstrated that the Wenzel model fails for textures with periodicities exceeding 200 µm due to contact line pinning at feature edges, a phenomenon not accounted for in equilibrium thermodynamic treatments.
- (3) For the first time, the dominant degradation mechanism of superhydrophobic composite coatings under environmental exposure has been unambiguously identified through combined UV aging and chemical analysis. FTIR spectroscopy revealed that polymer photo-oxidation, rather than particle erosion or delamination, constitutes the primary failure mode, with aliphatic C-H stretching vibrations (2850-2950 cm⁻¹) decreasing by 60-80% and carbonyl C=O absorption (1731 cm⁻¹) increasing fivefold, confirming conversion of hydrophobic groups to hydrophilic oxygen-containing functionalities.
- (4) This study establishes a mechanistic design principle for durable superhydrophobic coatings: minimizing polymer volume fraction while maximizing inorganic particle network density. An optimized formulation comprising 5 wt.% acrylic copolymer, 90 wt.% silane-functionalized calcium carbonate microparticles, and 5 wt.% fumed silica nanoparticles was developed

and validated, achieving a +797 mV noble shift in corrosion potential (from -660 mV to +137 mV vs. SCE), impedance magnitudes exceeding $688 \Omega \cdot \text{cm}^2$ at 0.01 Hz (2.3-fold improvement), and sustained superhydrophobicity (contact angles $>130^\circ$) after 72 hours of immersion in 3.0 wt.% NaCl electrolyte.

- (5) For the first time, a multi-physics computational model has been developed and experimentally validated that quantitatively reproduces electrochemical polarization behavior and enables mechanistic decomposition of protection mechanisms. The model revealed that superior performance arises from synergistic effects: a 3.2-fold increase in solution resistance due to tortuous ion diffusion pathways through the particle network, and a 5.8-fold increase in charge transfer resistance from surface passivation by silane treatment.
- (6) It has been demonstrated that the dense inorganic particle network in optimized coatings simultaneously provides the hierarchical roughness required for superhydrophobicity and a tortuous diffusion barrier that impedes ionic transport, while minimal polymer content prevents water uptake and hydrolytic swelling. This dual-function architecture represents a paradigm shift from component-centric to mechanism-centric coating design.

The Practical Significance of the Obtained Results.

- (1) The developed composite coating formulations based on environmentally benign materials - acrylic copolymers, silica, calcium carbonate, silane treatments - provide a viable alternative to hexavalent chromium-based conversion coatings, providing an environmentally benign alternative that addresses global corrosion challenges while eliminating carcinogenic and environmentally persistent compounds.
- (2) The validated multi-physics computational model enables predictive materials design and optimization without extensive experimental iteration, dramatically reducing development time and costs. The model can be extended to predict coating service life under specific environmental exposure spectra, enabling in-silico performance estimation before physical fabrication.

- (3) The mechanistic design principles established in this work-polymer minimization, high inorganic loading, siloxane-based surface treatments, hierarchical particle size distributions-are transferable to other metal substrate materials and application domains: solid-state batteries, heterogeneous catalysis, biomedical implants, where interfacial degradation limits operational longevity.
- (4) The systematic progression from mechanistic identification through rational design to computational validation demonstrated in this work represents a generalizable methodology for addressing complex materials challenges characterized by coupled multi-scale and multi-physics phenomena, contributing to the evolution of materials science from empirical discovery to predictive engineering.

Contributions of the author: All scientific results, conclusions, and statements presented for defense were obtained by the applicant personally. In the co-authored scientific works, the applicant participated in task formulation, conducting the experimental research, discussing and summarizing results, and writing and formatting the articles. In the co-authored publications, the author's contribution is primary. The research results have been presented by the applicant personally at scientific conferences. The co-authors of the scientific works are the scientific supervisor and researchers with whom the joint studies were conducted.

Approbation of the results of the dissertation: The results of the study were presented and discussed at 5 international conferences: “Composite Materials” (2023, 2024, 2025, Kyiv, Ukraine), IEEE 6th KhPI Week on Advanced Technology (2025, Kharkiv, Ukraine), conference on chemistry chemical technology and ecology on 125-years anniversary of Igor Sikorsky KPI.

Publications. The study results were published in 4 scientific publications, that are 4 scientific papers published in profile journals: 2 in category B of profile journals of Ukraine and 2 - indexed in Scopus international citations database.

Structure and scope of work

The paper consists of an introduction, six chapters, a list of 123 references. The total number of pages in the paper is 154 with 122 pages for the main part. It includes 42 figures, 17 equations, and 14 tables.

CHAPTER 1. Literature review

Superhydrophobic surfaces have become a subject of significant interest in material science due to their wide range of applications, including self-cleaning surfaces, anti-fouling, anti-icing, drag reduction, and oil/water separation. These surfaces are inspired by numerous examples in nature, such as the water spider (*Gerris remigis*) that can walk on water surfaces and the *Salvinia molesta* leaves that resist wetting even after weeks of submersion. The most famous example is the lotus leaf, which demonstrates exceptional water-repellent properties and gave rise to the well-known "Lotus effect." The mechanism of the lotus effect was first investigated and described by Barthlott and Neinhuis in 1997 [1, 2]. The development of corrosion-resistant superhydrophobic coatings has gained particular importance in recent years due to the economic and safety concerns associated with metal corrosion. In industrialized countries, corrosion-related costs typically amount to 1-4% of their GDP. Until recently, chromium-containing coatings were efficiently used for corrosion protection, but these have been restricted due to their harmful effects on humans and the environment. This has led to increased research in environmentally friendly alternatives, including polymeric coatings.

1.1. Superhydrophobicity: definition and requirements

Superhydrophobic surfaces are characterized by their extreme water repellence, which is achieved through a combination of two key factors: the inherent hydrophobicity of the surface material (low surface energy) and surface roughness. Materials with low surface energy naturally repel water because forming a new solid-liquid interface with water is energetically unfavorable [3, 4].

However, the maximum water contact angle [5] (WCA) that can be achieved by a flat, low surface-energy material is approximately 120° . To achieve superhydrophobicity, surface roughness must be introduced, which can increase the contact angle to above 150° using the same chemical composition. Furthermore,

building a structure with hierarchical roughness (combining dual-scale texture) has been reported to improve both hydrophobicity and surface durability. This approach is observed in nature, such as in the *Salvinia* leaves and water spider legs, and is replicated in synthetic coatings through micro/nanoscale surface structuring.

1.2. Fundamentals of surface wetting

The Lotus effect describes the self-cleaning mechanism observed on the lotus plant leaf surface (*Nelumbo nucifera*) [6]. The leaf surface as shown in the Figure 1.1. While water droplets slide along a tilted hydrophobic surface, on a superhydrophobic surface, the near-spherical droplets roll across the surface instead. This rolling action enhances the removal of surface contaminants like dirt particles and bacteria. Examining the structure of lotus leaves reveals a waxy surface coating that repels water, combined with complex 3D microstructure textures and an additional layer of smaller-scale hair-like features covering both the surface protrusions and flat regions. These microstructures trap air underneath the water upon wetting the surface, enabling the rolling motion of water droplets. Similar structures are found in the water spider's legs, which feature micron-sized filaments with nano-grooved textures, resulting in dual-scale roughness that contributes to their water-repellent properties. These natural examples highlight the importance of hierarchical structuring in achieving superhydrophobicity, with surfaces often displaying both micro and nano-scale roughness features.

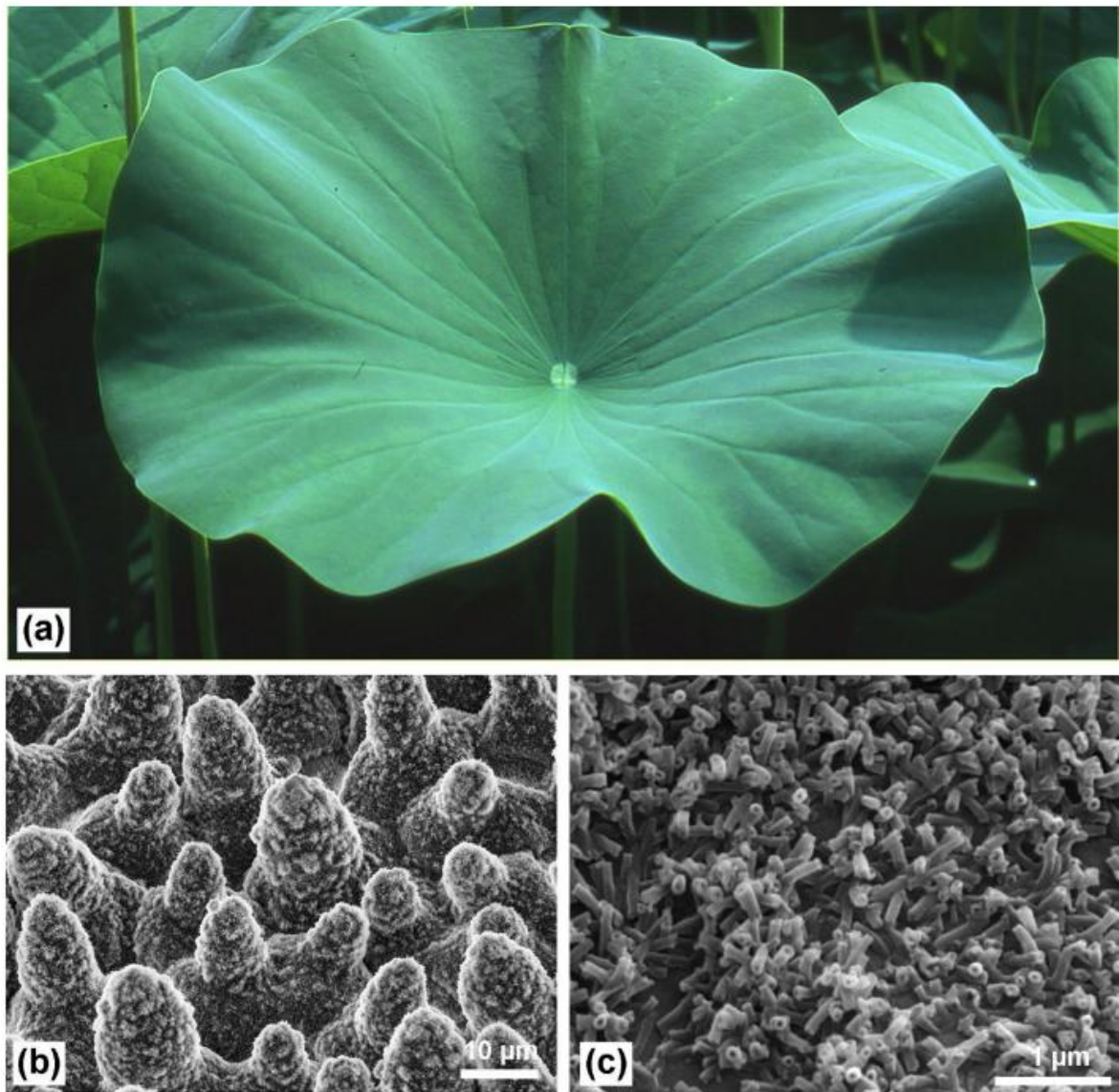


Figure 1.1. Natural water repellent surfaces: (a) Lotus leaves, which exhibit extraordinary water repellency on their upper side. (b) Scanning electron microscopy (SEM) image of the upper leaf side prepared by ‘glycerol substitution’ shows the hierarchical surface structure consisting of papillae, wax clusters and wax tubules. (c) Wax tubules on the upper leaf side. [6]

Surface wettability is typically evaluated using water contact angle (WCA) measurements, defined as the angle between the surface–water contact plane and the tangent of the water–air interface. Surfaces are classified by WCA: superhydrophilic ($\theta < 10^\circ$), hydrophilic ($10^\circ < \theta < 90^\circ$), hydrophobic ($\theta > 90^\circ$), and superhydrophobic ($\theta > 150^\circ$) (Figure 1.2.). A larger contact angle corresponds to more spherical droplets, while smaller angles indicate complete wetting.

Although WCA is widely used, it can be affected by variations in surface chemistry and topography. Moreover, superhydrophobic surfaces may exhibit either slippery behavior - where droplets roll off easily - or pinned behavior - where droplets adhere to the surface. To distinguish these, advancing and receding angles are often measured by gradually tilting the substrate until the droplet begins to move.

Droplet-Volume Method: In this approach, a droplet is placed on the surface with a needle gently contacting its apex. Water is gradually injected until the droplet expands without changing its contact angle (advancing angle) or withdrawn until it contracts while maintaining a constant angle (receding angle) (Figure 1.3). The difference between these two angles defines the contact angle hysteresis (CAH). On highly superhydrophobic surfaces with minimal pinning, CAH values are typically below 10° .

Alternative methods include measuring the tilting angle (the angle at which a droplet begins to move off the surface, usually $<10^\circ$ for highly hydrophobic surfaces) and water bouncing (where the number of bounces correlates with the degree of hydrophobicity).

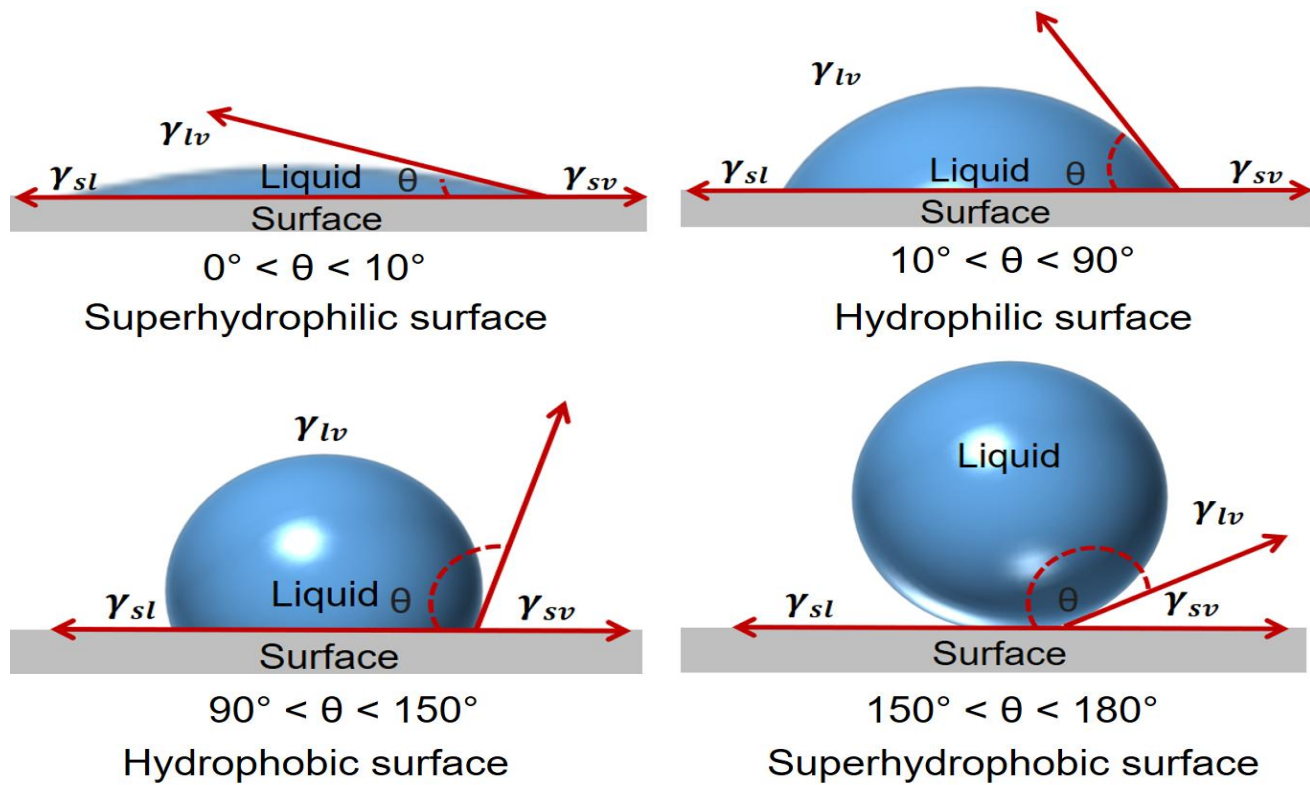


Figure 1.2. Wetting states [7]

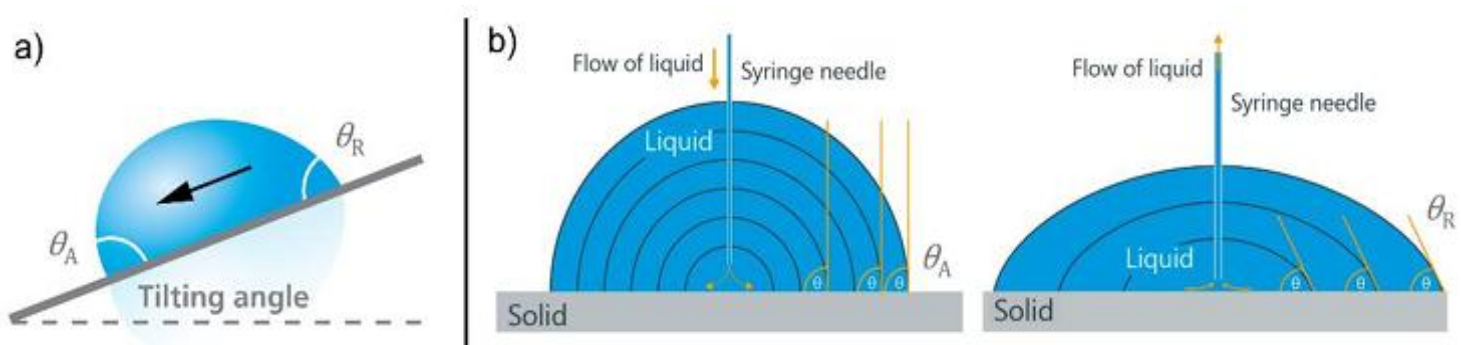


Figure 1.3. Measuring the advancing and receding angles by Jeevahan et al.[8]

From an energetic standpoint, the wetting behavior of liquids on solid surfaces can be interpreted using thermodynamic principles. When a liquid droplet comes into contact with a solid substrate, its contact angle reflects an equilibrium condition governed by the balance of interfacial tensions at the solid–liquid, liquid–vapor, and solid–vapor interfaces. This configuration minimizes the system’s Gibbs free energy,

placing the droplet in either a stable or metastable equilibrium state. For an ideal surface that is chemically uniform and topographically smooth, the contact angle (θ) at the three-phase line is defined by Young's equation (1805)[2, 7].

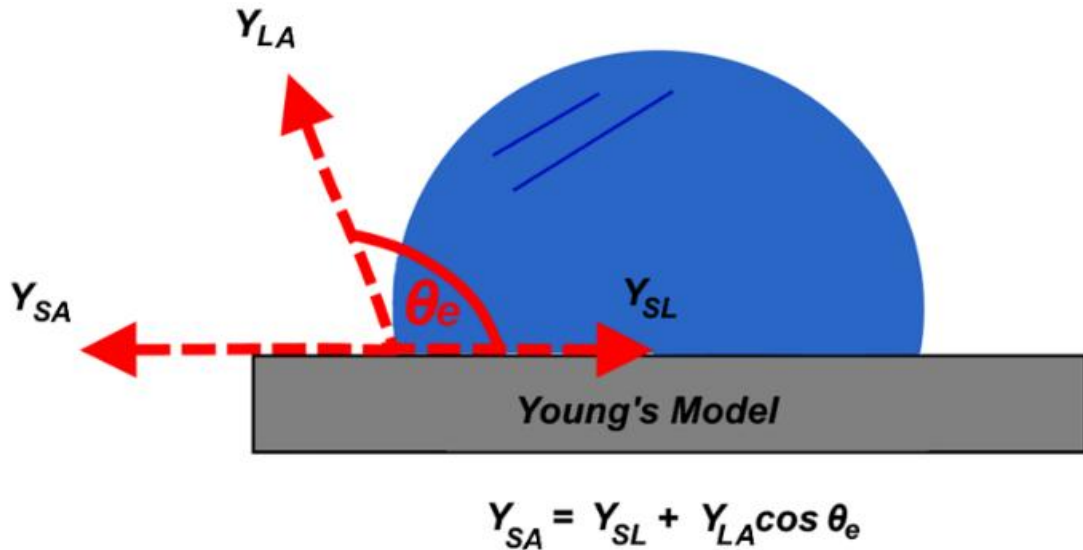


Figure 1.4. Schematic illustrating Young's Model, highlighting the equilibrium contact angle (θ_e) and interfacial surface tensions of a static water droplet on a flat surface.[7]

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta_e \quad (1.1)$$

Where:

θ_e = Contact angle of a water droplet on a flat surface;

γ_{SV} = Interfacial tension of solid vapor phase;

γ_{SL} = Interfacial tension of solid liquid phase;

γ_{LV} = Interfacial tension of liquid vapor phase.

As illustrated in Figure 1.4.[7], Young's equation arises from the mechanical equilibrium of interfacial forces acting at the contact line. At equilibrium, the horizontal components of the solid–liquid, solid–vapor, and liquid–vapor tensions balance, yielding the Young relationship. This equation quantitatively defines

wettability - the extent to which a liquid spreads or adheres to a solid surface. Surfaces with contact angles below 90° are classified as hydrophilic, while those above 90° are hydrophobic. Although straightforward in form, Young's equation encapsulates complex interfacial interactions and remains the foundation for studying real surfaces, which often involve roughness, chemical heterogeneity, and dynamic wetting behavior.

Young's equation is derived by considering an ideally smooth surface, however, almost every surface has some inhomogeneity practically. The imperfections or defects contribute to the surface roughness and can greatly influence its wetting properties. Therefore, Wenzel proposed a modification to account for surface roughness in relation to contact angle[9]:

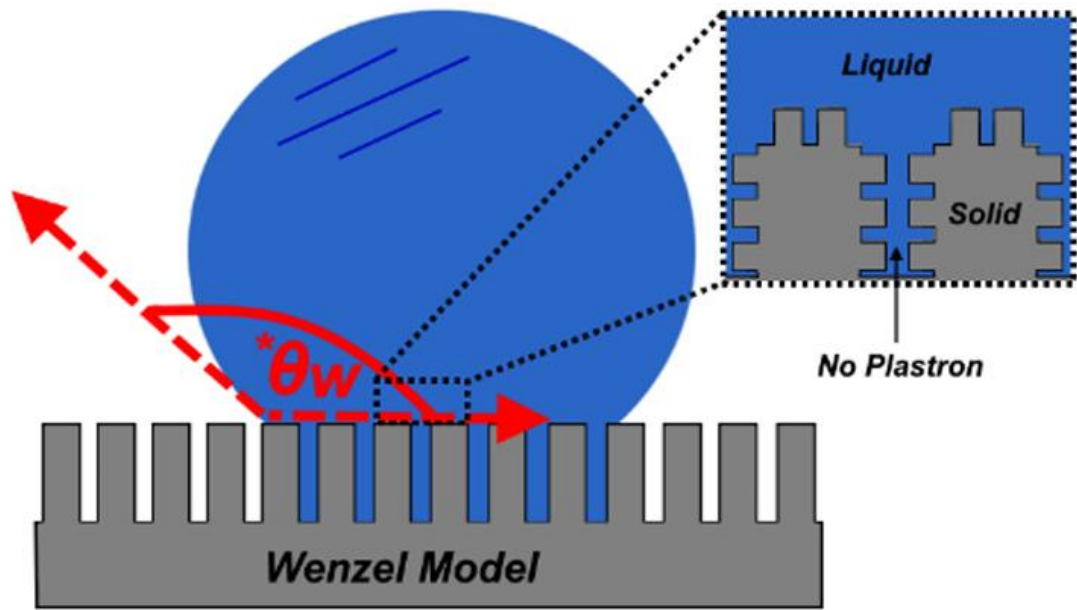


Figure 1.5. Schematic illustrating the wetting of a roughened surface according to the Wenzel model.[7]

$$\cos\theta_w = r \left(\frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \right) \quad (1.2)$$

Which by substitution into equation (1) becomes:

$$\cos\theta_w = r \cos\theta \quad (1.3)$$

And where:

θ_w is Contact angle of the rough surface (Wenzel contact angle);

θ is Contact angle on a perfectly flat surface (Young's contact angle).

r is Surface roughness

The Wenzel equation[9] effectively describes how surface roughness influences wettability. For hydrophilic materials, increased roughness enhances wetting, while for hydrophobic materials, it amplifies water repellency. This model applies to both rough and smooth surfaces. When the roughness factor r - the ratio of the actual to the projected surface area - equals 1 (representing an ideally smooth surface), the contact angle reduces to that predicted by Young's equation.

The Cassie-Baxter model[10] proposes a heterogeneous structure for superhydrophobic surfaces. The water droplet rests on the asperities of a rough surface rather than entirely penetrating into the features, thus making a solid-liquid-air interface, and the following relationship applies:

$$\cos\theta = f_1\cos\theta_1 + f_2\cos\theta_2 \quad (1.4)$$

Where:

θ is Contact angle of a water droplet (Cassie-Baxter)

f_1 is Fraction of material 1 in contact with surface

θ_1 is Contact angle of a water droplet with surface

f_2 is Fraction of material 2 in contact with air

θ_2 is Contact angle of a water droplet with air

If the surface features have been made by one solid, then f_1 represents the fraction of the solid which interacts with water and $f_2 (1 - f_1)$ is the area fraction of air pockets in contact with the water droplet. Water contact angle with air is 180° , therefore the equation can be simplified to the following form:

$$\cos\theta = f_s(1 + \cos\theta_s) - 1 \quad (1.5)$$

Where f_s denotes the fractional area of solid with contact angle θ_s in contact with water droplet.

Therefore, increasing surface roughness amplifies either hydrophilic or hydrophobic behavior, depending on the surface chemistry. For hydrophobic materials, the contact angle - and hence water repellency - significantly increases when surface features can trap air pockets. Consequently, hierarchically structured surfaces combine roughness, entrapped air, and low surface energy to produce superhydrophobic characteristics.[11].

The Cassie-Baxter model describes the wetting behavior of a liquid droplet on a rough or composite surface, where the droplet rests partially on a solid and partially on air trapped within the surface's texture. This composite interface is what distinguishes the model and drives its unique properties. In this model, the solid/air interface in a dry surface is replaced with solid/liquid and liquid/air interfaces when wetted. The areas of these interfaces and the energy associated with them are used to describe the surface wetting behaviour.

The Cassie-Baxter model describes the wetting behavior of a liquid on a rough surface where air pockets are trapped within the surface porosity, leading to a heterogeneous wetting state. This results in water bridging across the tops of surface microstructures, avoiding penetration into the grooves, which contrasts with the Wenzel model's assumption of full surface contact. Surfaces following this regime exhibit low water adhesion, often described as "slippery," with very low contact angle hysteresis (typically below 10°), which is the difference between advancing and receding contact angles. The model accounts for the interfacial areas and energies, including solid-liquid and liquid-vapor interfaces. The net free energy change (ΔD) for wetting a hydrophobic surface is energetically unfavorable, leading to a small wetted area and large contact angles, expressed as:

$$\Delta D = f_1\gamma_{sv} - f_1\gamma_{sl} + f_2\gamma_{lv} \quad (1.6)$$

where f_1 is the solid-liquid interfacial area, f_2 is the liquid-vapor interfacial area, and γ_{SL} , γ_{LV} are the respective interfacial energies. The apparent contact angle θ_{CB} is derived as:

$$\cos \theta_{CB} = \frac{-\Delta D}{\gamma_{LV}} = f_1 \cos \theta_e - f_2 \quad (1.7)$$

Where θ_{CB} is the apparent contact angle and θ_e is the equilibrium contact angle.

In the original model derived by Cassie and Baxter (eq (1.7)), the solid surface roughness is accounted for in the solid– liquid interfacial area term, f_1 , as it includes the roughness factor, γ . Therefore, if the liquid–vapour interfacial area is equal to zero, i.e. the surface no longer has any interfacial air, the Cassie–Baxter equation is now said to equal to the Wenzel equation, directly relating both wetting models.

On hydrophobic rough surfaces, the transition from the Wenzel to the Cassie-Baxter state signifies a fundamental change in the liquid's wetting behavior[12]. In the Wenzel state, the liquid completely penetrates the surface texture, maximizing solid-liquid contact. The Cassie-Baxter state, conversely, features the liquid suspended on top of the surface asperities, with air trapped underneath, creating a composite solid-liquid-air interface. Thermodynamically, this transition is favored when the reduction in solid-liquid contact area (and thus, lower surface energy) in the Cassie-Baxter state outweighs the energy cost of creating a larger liquid-air interface. Kinetically, an energy barrier must be overcome for the liquid to detach from the grooves of the Wenzel state. This activation energy can be supplied by external factors such as vibration, pressure fluctuations, or even changes in temperature, ultimately leading to a more stable or metastable Cassie-Baxter state. The precise conditions for the transition depend on the interplay of surface roughness (geometry and scale), the liquid's surface tension, and the inherent hydrophobicity of the material.[13-16]

1.3. Fabrication of superhydrophobic surfaces

Fabrication methodologies for superhydrophobic surfaces are categorically divided into two principal approaches: top-down and bottom-up methods[17-19]. The top-down methodology entails the structural modification of bulk material surfaces to generate roughness. This is accomplished through various surface topography alteration techniques, including lithography, etching, and laser treatment processes. Conversely, bottom-up methodologies facilitate surface roughness through the addition of small-scale materials. Implementation occurs via deposition techniques such as chemical vapor deposition, electroplating, and sol-gel processing. It should be noted that certain deposition procedures do not inherently yield rough surfaces; consequently, supplementary treatment of precursor materials or the deposited surface may be requisite to achieve the desired roughness characteristics. The determination of appropriate fabrication approaches and specific techniques is contingent upon the selected base materials, desired surface properties, and intended application parameters. Advanced superhydrophobic surface development frequently incorporates multiple fabrication phases, integrating both top-down and bottom-up elements to attain optimal surface characteristics.

Laser processing, particularly using ultrafast lasers like femtosecond lasers[20-24], is a precise method for creating micro- and nanostructures on surfaces. This technique allows for the fabrication of superhydrophobic surfaces without the need for additional coatings or surface treatments. Laser ablation can induce chemical and structural changes to the surface of materials, enhancing their water repellency[25, 26].

Long et al.[23] utilized femtosecond laser irradiation to fabricate superhydrophobic copper surfaces with tunable water adhesion properties, inspired by the contrasting wetting behaviors of lotus leaves and rose petals. By varying the laser scanning speed (10 – 200 mm/s), the researchers precisely controlled surface topographies, ranging from deep microstructures to shallower formations. Post-treatment chemical modification enhanced hydrophobicity, enabling surfaces to

transition between Cassie and Wenzel wetting states based on microstructural depth. Low-speed laser treatments resulted in surfaces with minimal water adhesion, exhibiting self-cleaning properties akin to lotus leaves, while high-speed treatments created surfaces with significant water adhesion, resembling rose petals. These surfaces demonstrated adjustable water contact angles (up to 159°) and sliding angles (from $<10^\circ$ to 90°), alongside varied adhesion forces ($10\ \mu\text{N}$ to $110\ \mu\text{N}$). Applications of this technique include liquid manipulation and self-cleaning technologies, highlighting its cost-effectiveness and precision in creating functional superhydrophobic surfaces. The changes in surface morphology during laser irradiation and the final microstructures of the laser irradiated copper surfaces with different v as shown in Figure 1.6.

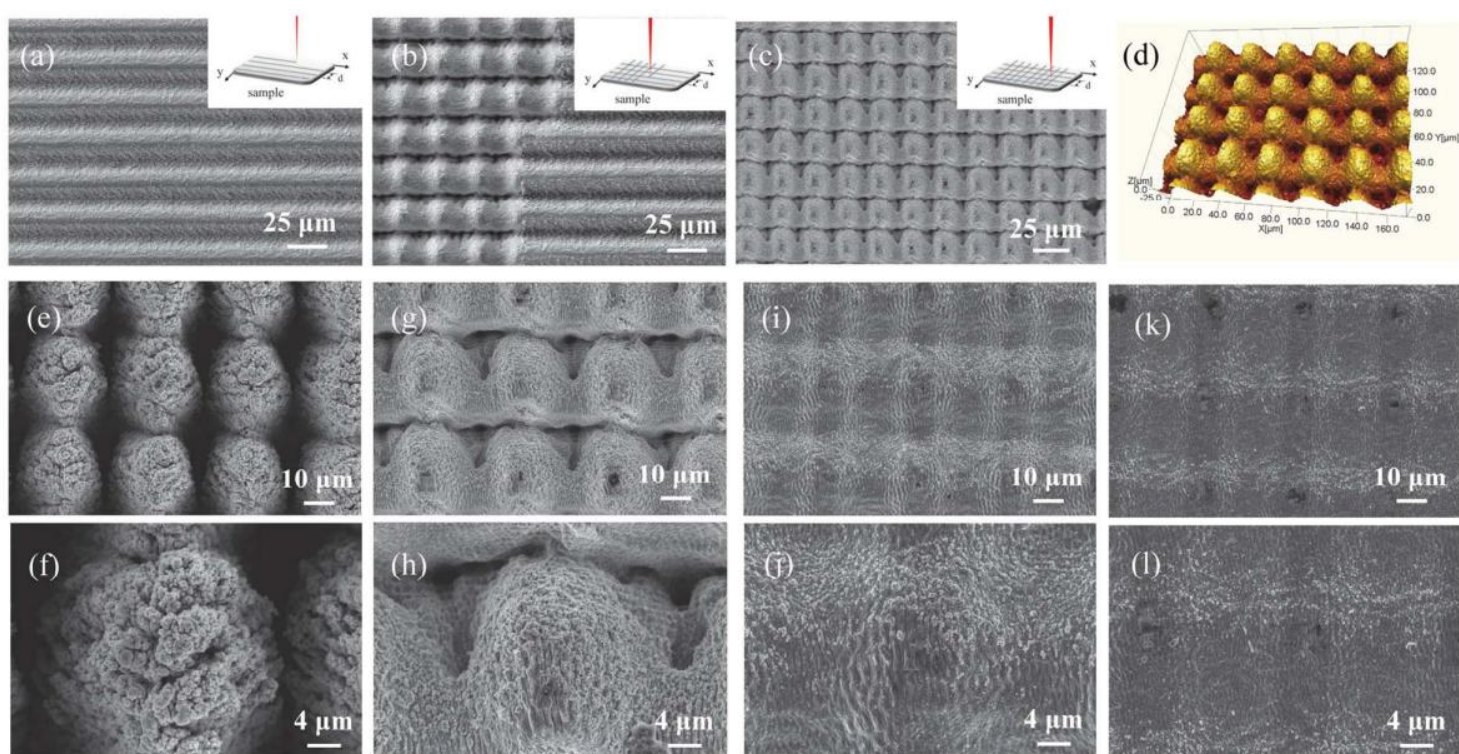


Figure 1.6. Fabrication of superhydrophobic surfaces [23] (a-c) The changes in surface morphology during laser irradiation process, insets on the top right show the schematics of the laser scanned paths. (d) Typical 3D images of the laser irradiated surface obtained by a 3D optical profilometer. (e-l) SEM images of the copper surface structured by an fs laser with different scanning speed, (e, f) $10\ \text{mm s}^{-1}$, (g, h) $50\ \text{mm s}^{-1}$, (i, j) $100\ \text{mm s}^{-1}$, (k, l) $200\ \text{mm s}^{-1}$

Etching[8, 27-30]. is a straightforward method for enhancing surface roughness, which is crucial for creating superhydrophobic surfaces. This process involves removing surface material in two primary ways: isotropically, where the removal is uniform in all directions, or anisotropically, where it occurs in specific directions. Various etching techniques exist, each with unique advantages, and they can be used alone or in combination with other fabrication methods to achieve complex, hierarchical textures. After etching, applying a low surface energy material is a common step to attain the desired superhydrophobic properties. Etching can be done through chemical routes, which are generally facile and not costly. These involve the removal of substrate material by exposure to harsh (acidic or basic) solutions.

Qian et al.[31] reported the synthesis of superhydrophobic surfaces on aluminum, copper, and zinc substrates by using dislocation-selective chemical etching. This process involves preferentially dissolving the dislocation sites in polycrystalline metals, creating hierarchical microstructures such as pits, grooves, and nanoparticles. After etching, the surfaces were treated with fluoroalkylsilane to enhance hydrophobicity, as shown in the Figure 1.7, resulting in water contact angles exceeding 150° and roll-off angles below 10° . The study demonstrates a simple yet effective method to fabricate superhydrophobic surfaces, with potential applications for other polycrystalline materials.

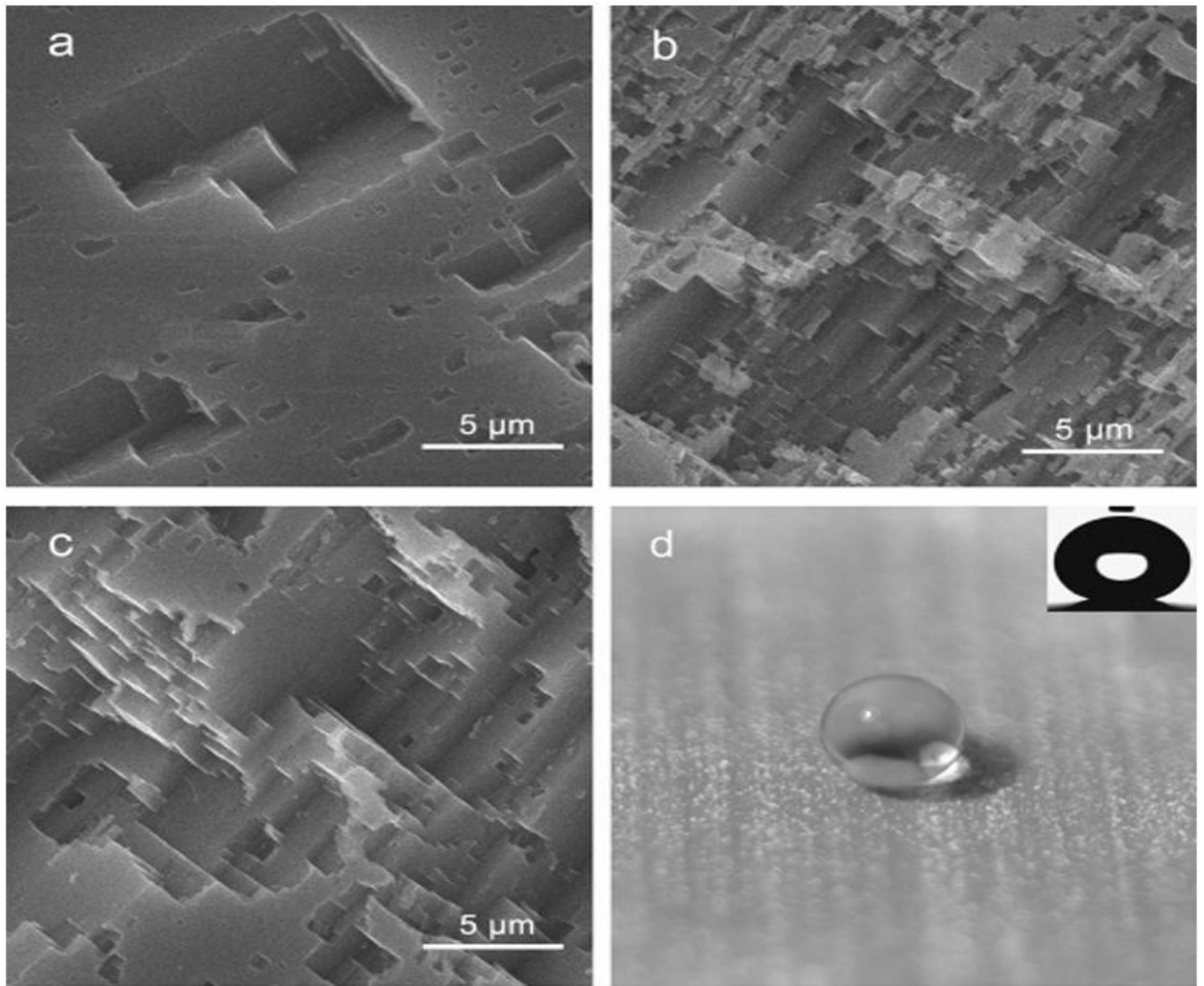


Figure 1.7. Surface morphologies [31] (a-c) SEM images of the aluminum surfaces etched with a Beck's dislocation etchant for 5s (a), 10s (b), or 15s (c) at room temperature. (d) The photograph of 8 μL water drops placed on the superhydrophobic surface prepared by treating the etched aluminum sheet (c) with fluoroalkylsilane. The insert showing that the water contact angle is about 156° .

Lithography[8, 30, 32, 33] is a technique commonly used in microelectronics to create patterns on surfaces. It involves coating a substrate with a light-sensitive material, exposing it to light through a patterned mask, and then developing the exposed areas. This method can be used to create microstructures that contribute to superhydrophobicity. Electron beam lithography is particularly precise and can be used to create complex patterns on a nanoscale.

Pozzato et al.[34] developed a cost-effective method for creating superhydrophobic silicon surfaces using nanoimprint lithography combined with wet chemical etching. Their process (Figure 1.8) begins with creating a patterned glass mold, which is then imprinted onto a photoresist layer on a silicon substrate. This pattern is subsequently transferred to a SiO₂ layer and finally to the silicon through etching techniques. The researchers employed two distinct etching approaches: 1) Isotropic etching with HNA to produce rounded channels; 2) Anisotropic etching with KOH to create rectangular channels. After etching, the surfaces were coated with octadecyltrichlorosilane (OTS) self-assembled monolayers to enhance hydrophobicity. Contact angle measurements revealed that the advancing contact angles closely aligned with Cassie model predictions, indicating the presence of trapped air beneath water droplets on these surfaces. A key advantage of this fabrication method is its tunability - the surface properties can be readily adjusted by modifying the etching method or mold parameters.

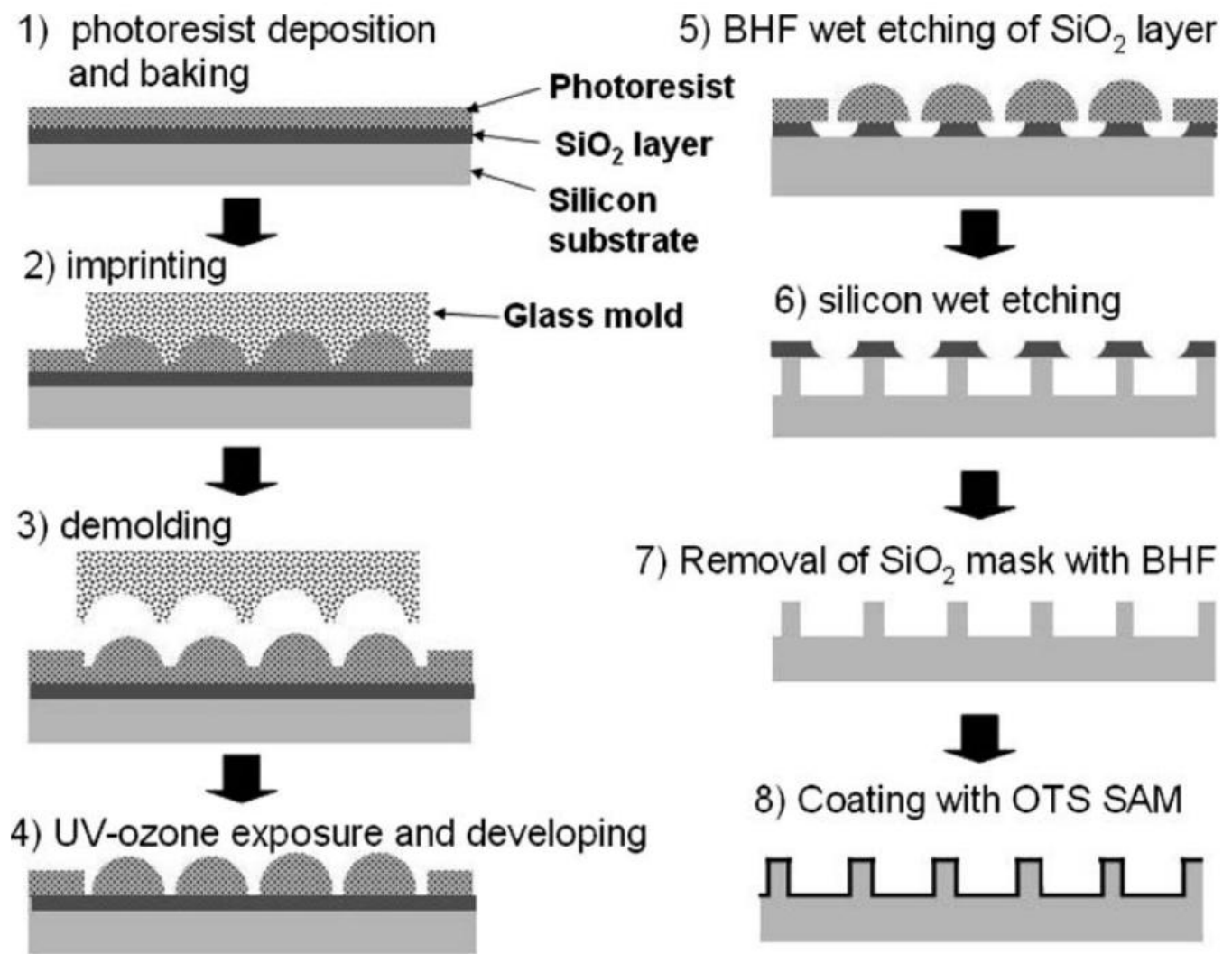


Figure. 1.8. [34].Schematic of fabrication process.

Template imprinting also termed ‘soft lithography’[35-39], and shares the main theory with photolithography in terms of creating a replica of a previously-prepared pattern[33]. Template imprinting is a versatile technique that shares the fundamental principle of photolithography in replicating patterns, unlike photolithography, which uses rigid photomasks, soft lithography employs flexible templates, typically made of polydimethylsiloxane (PDMS), to create micro- and nano-scale patterns. This method is cost-effective, environmentally friendly, and supports diverse applications, including biosensors and nanotechnology. Soft lithography offers advantages in scalability and material compatibility but faces challenges such as template deformation and defect control during the imprinting process.

3D printing technology represents an advanced deposition methodology for the fabrication of superhydrophobic surfaces[40-44]. This additive manufacturing approach shares fundamental principles with Layer-by-Layer (LbL) assembly techniques through its sequential construction of precisely controlled structural elements. However, 3D printing offers distinct advantages in the context of superhydrophobic surface engineering, including unprecedented geometric complexity, customizable hierarchical architectures, and reproducible surface topographies across multiple scales. The versatility of this manufacturing platform enables the precise implementation of biomimetic design principles while maintaining consistent quality parameters throughout the fabrication process.

It was reported[42] for the replication of the *Salvinia* leaf ‘eggbeater’ structure (Figure 1.9. a). the surfaces were fabricated by the Immersed surface accumulation three dimensional (3D) printing process. Multi-walled CNTs were added to the liquid photo-curable resin utilised to increase surface roughness. The number of arms of the eggbeater shape (N), as well as their spacing (d), was investigated for their effect on the superhydrophobic properties (Figure 9. b-g). It was found that the hydrophobicity is maximised when the spacing is kept at $d=0.5$. Moreover, applying $N=2$ resulted in a highly superhydrophobic surface ($WCA = 170^\circ$), although the reduced number of arms made the structures fragile. Applying $N=4$ was found to be a good compromise between both strength and superhydrophobicity ($WCA = 152^\circ$).

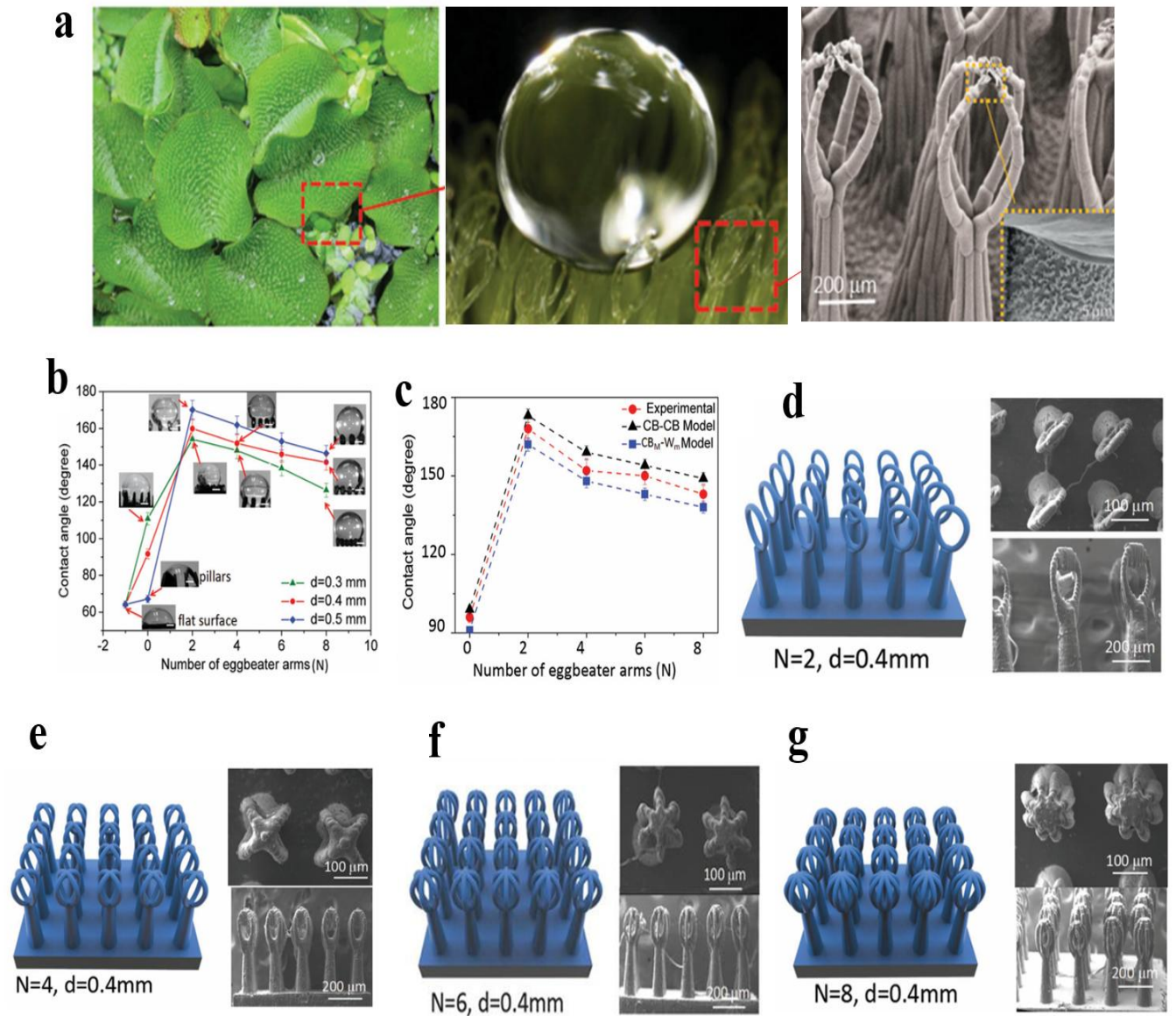


Figure 1.9.[42]. Biomimetic super-hydrophobic structure. a) Morphology of *S. Molesta* leaf, upper side of the leaf surface is densely covered with eggbeater hairs, a spherical water droplet on top and SEM image of the eggbeater hair structure; b) contact angle and test pictures for different numbers of N and gap distance d (scale bar 500 μm); c) a comparison of the experimental and simulated contact angles with CB–CB and W–CB models for different patterns.; (d–g) the models and SEM images of the 3D-printed eggbeater arrays with different number of arms (d , $N = 2$; e, $N = 4$; f, $N = 6$; g, $N = 8$)

Electrospinning is a fiber fabrication technique that employs a high-voltage electric field to draw a polymer solution or melt into continuous fibers with diameters from tens of nanometers to a few micrometers[45, 46]. It has become a key method for producing superhydrophobic coatings, as the resulting non-woven mats exhibit hierarchical roughness conducive to extreme water repellency. Recent research has optimized polymer systems (including recycled polymers such as PET) and developed multi-step processes that integrate electrospinning with methods like electrospraying and spin coating. These advances have yielded mechanically robust, self-cleaning surfaces with water contact angles $>150^\circ$, suitable for applications in protective, anticorrosion, and anti-icing coatings for aerospace, solar panels, and infrastructure. The relative simplicity, scalability, and potential for using sustainable feedstocks position electrospinning as a promising route for industrial-scale production of superhydrophobic materials[30, 47-49].

Álvarez et al.[50] presented a novel superhydrophobic and anticorrosive coating using a three-step process involving electrospinning, spin coating, and electrospraying, the schematic as illustrated in the Figure 1.10. They combined polytetrafluoroethylene (PTFE) with poly(acrylic acid) + β -cyclodextrin (PAA + β -CD) to create a composite coating on aluminum alloys. The electrospun PAA + β -CD layer provided adhesion and a porous network for PTFE particles, while the spin-coated PTFE layer ensured uniform distribution. The final electrosprayed layer enhanced particle bonding through heat treatments, achieving water contact angles (WCA) above 150° and excellent corrosion resistance.

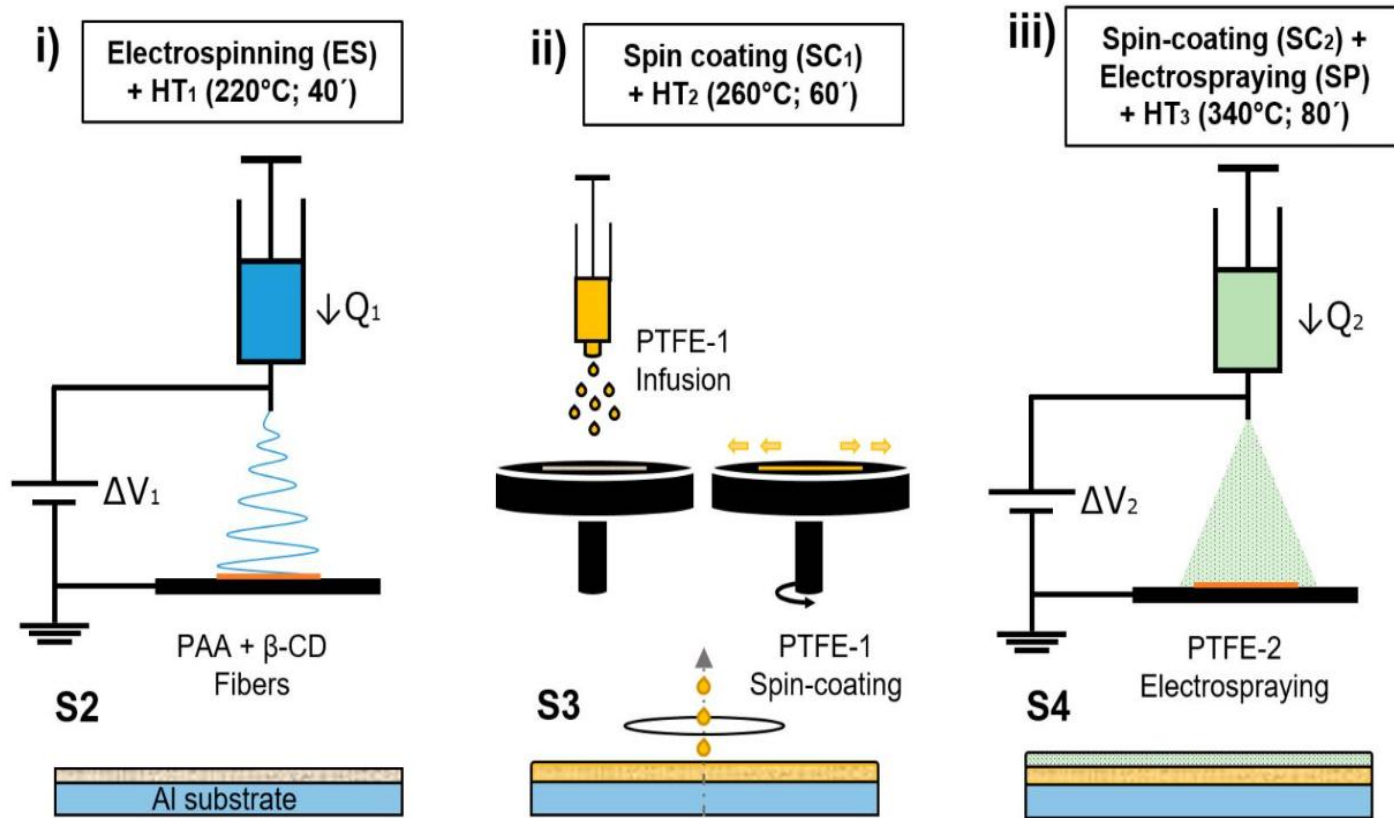


Figure 1.10.[50]. Schematic illustration of the fabrication methods to produce S2, S3, and S4 composite samples. (i) Electrospinning a PAA + β -CD fibrous coating and HT₁. (ii) S2 + spin-coating with PTFE-1 dispersion and HT₂. (iii) S3 + spin-coating with PTFE-1 dispersion, electro spraying with PTFE-2 dispersion and HT₃.

Chemical vapor deposition (CVD) is an advanced gas-phase technique for fabricating superhydrophobic surfaces, offering precise control of micro- and nanoscale morphology. In CVD, volatile precursors are transported to a heated substrate, where they react or decompose to form solid films with tunable hierarchical roughness and low surface energy in single- or multistep processes. The method enables the growth of carbon nanotubes, fluorocarbon and silicon-based polymers, and metal oxides that achieve water contact angles $>150^\circ$ with minimal hysteresis. Compared with other fabrication routes, CVD yields highly conformal, strongly adherent, and mechanically robust coatings on complex geometries, making it particularly suitable for high-performance industrial applications despite its need for specialized equipment and stringent process control[47].

Lau et al. [51] were among the pioneers in fabricating superhydrophobic CNT forests by modifying vertically aligned CNTs (VACNTs) with a polytetrafluoroethylene (PTFE) coating using the chemical vapor deposition (CVD) method, as shown in Figure 1.11. The resultant surface exhibited outstanding water repellency, with advancing and receding contact angles (CAs) of 170° and 160° , respectively. This work demonstrated the effectiveness of surface functionalization in achieving high hydrophobicity by facilitating the Cassie-Baxter wetting regime, where air is trapped between the water droplet and the surface, minimizing liquid-solid contact.

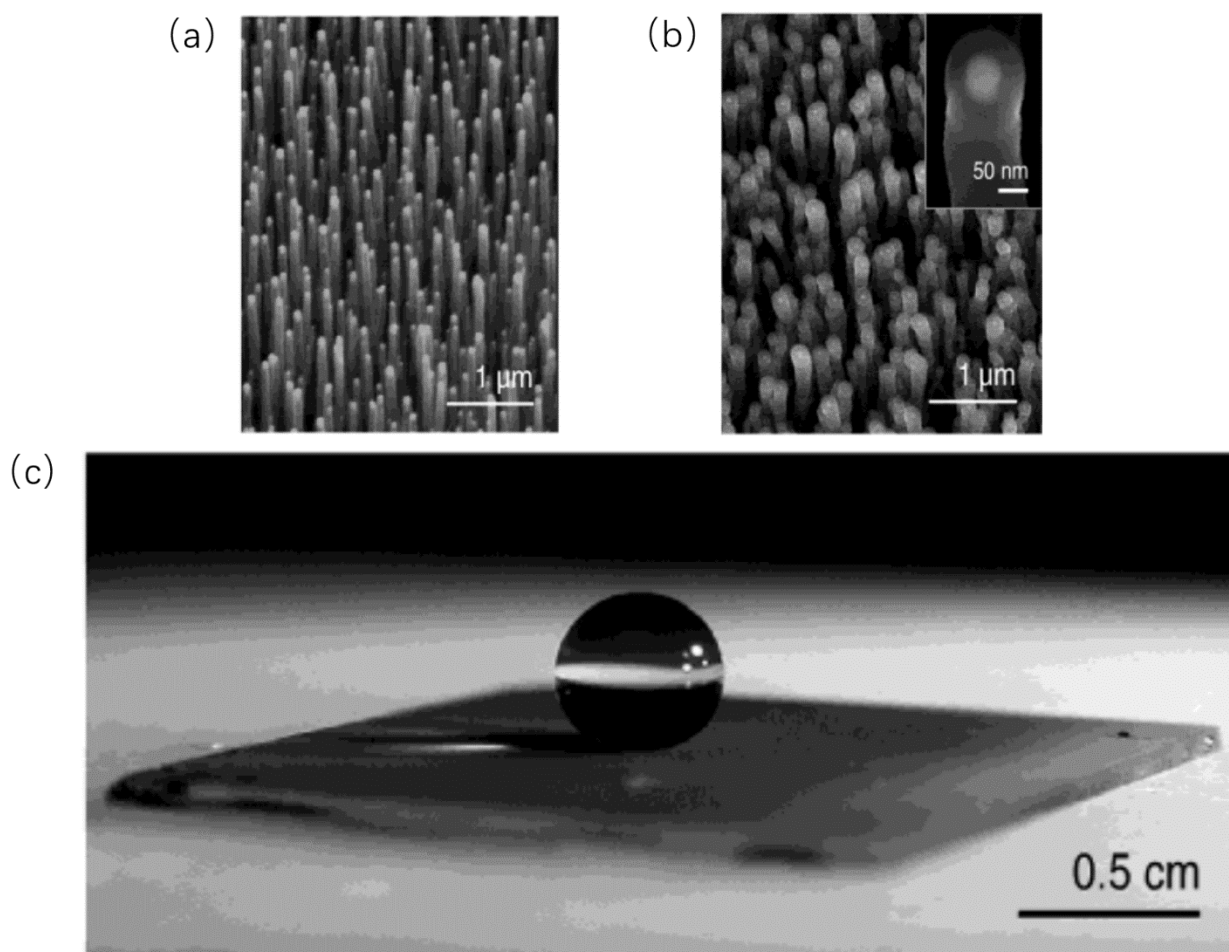


Figure 1.11.[51]. SEM images of carbon nanotube forests. (a) As-grown forest prepared by PECVD with nanotube diameter of 50 nm and a height of 2 μm, (b) PTFE-coated forest after HFCVD treatment, and (c) an essentially spherical water droplet suspended on the PTFE-coated forest.

The layer-by-layer (LbL) assembly technique is a highly adaptable and cost-effective method for fabricating coatings with precisely controlled chemical composition and nanostructure[52], Sutar et al.[53] the fabrication of robust self-cleaning superhydrophobic coatings by depositing polymer layers on candle soot surfaces. This approach combined the hierarchical structure of soot with a polymer layer to improve durability and self-cleaning properties, making it suitable for oil-water separation and industrial applications.

Covalent functionalization is a critical strategy in the development of durable superhydrophobic coatings, enabling chemical bonding between hydrophobic agents and substrate surfaces. This approach enhances the mechanical, chemical, and thermal stability of coatings while ensuring long-term functionality under harsh conditions[54].

Zhang et al.[55] prepared carbon nanotubes (CNTs) grafted with silica nanoparticles to create CNTs-SiO₂ hybrids, which were incorporated into an epoxy matrix using a one-step spraying method, the schematic as shown in the Figure 1.12. The resulting superhydrophobic coating achieved a water contact angle of 159.3° when the ratio of CNTs to SiO₂ was 1:3. The entwined CNTs-SiO₂ hybrids created a micro-nano hierarchical structure, enhancing water repellency and providing good mechanical durability and chemical stability. Additionally, the coating demonstrated significant photothermal conversion capabilities, delaying water freezing and efficiently melting ice under laser irradiation.

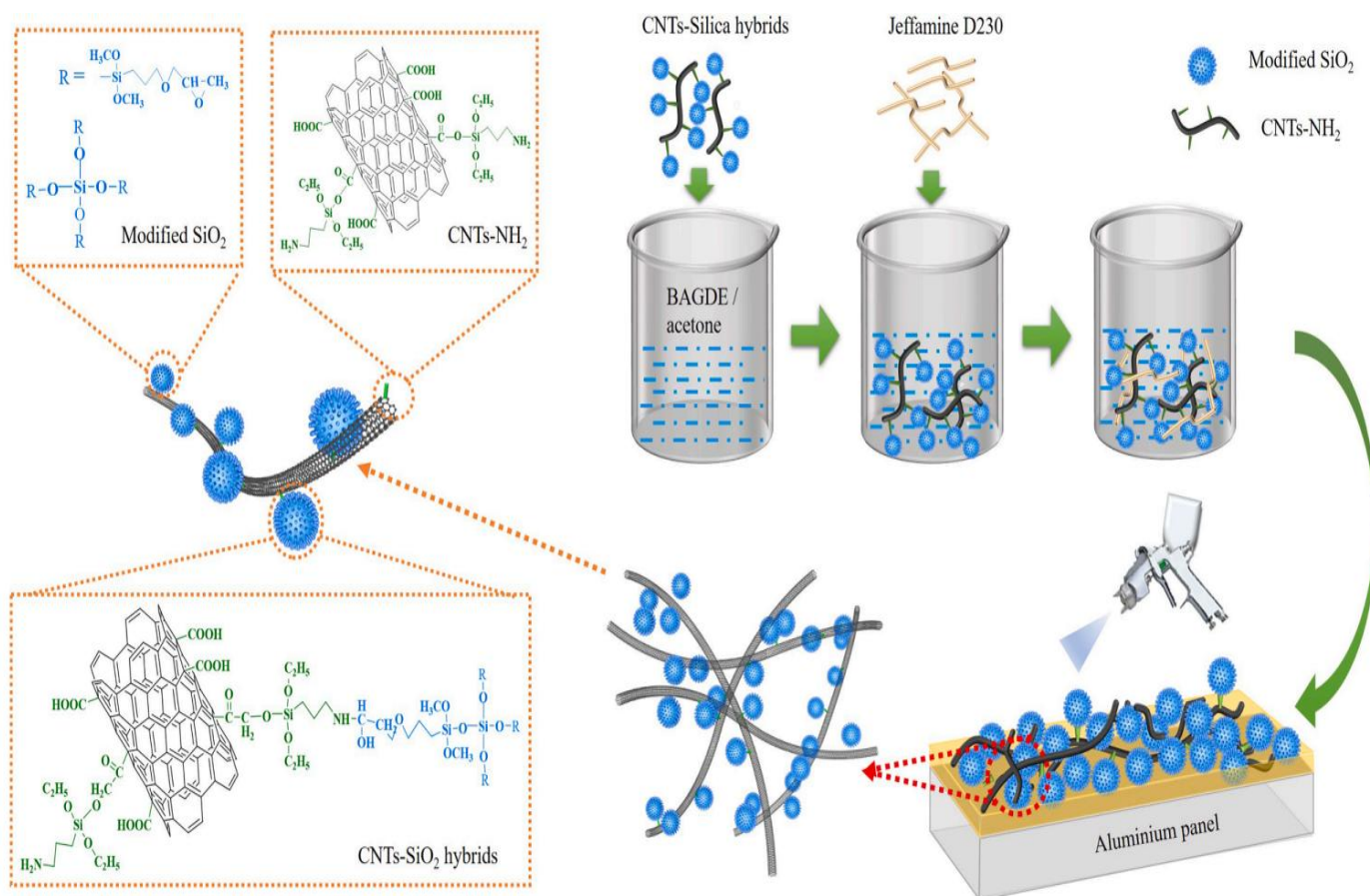


Fig. 1.12. [55]. The synthesis process of CNTs-SiO₂ hybrids and the superhydrophobic coating.

Problem of Research Statement

Despite decades of research inspired by natural systems, the widespread practical application of superhydrophobic coatings remains unrealized. The central problem is a critical lack of environmental durability. Most existing approaches to coating development have been largely empirical, relying on trial-and-error methodologies that yield coatings with impressive initial performance but rapid degradation under real-world conditions. This approach has failed to produce a fundamental, predictive understanding of the complex interplay between surface chemistry, hierarchical structure, and environmental degradation pathways (e.g., photo-oxidation, electrochemical attack). Consequently, a significant gap exists between laboratory demonstrations and industrially viable products. There is an urgent need for a shift

from empirical discovery to predictive, mechanism-driven engineering. This dissertation directly addresses this problem by seeking to establish a quantitative and mechanistic foundation for the design of durable superhydrophobic coatings, aiming to bridge the gap between scientific potential and practical application.

The purpose of the research: The purpose of this study is to establish the mechanistic relationship between the structure, composition, and environmental durability of superhydrophobic composite coatings for metal corrosion protection, and to develop design principles for coatings with sustainable performance under combined UV, hydrodynamic, and electrochemical stresses.

Objectives of the research:

- (1) To identify the gap of knowledge in the field of the statistical superhydrophobic coatings durability in aggressive environments.
- (2) To establish a comprehensive characterization framework integrating surface energy thermodynamics with Owens-Wendt method and dynamic wetting analysis to quantify the role of hierarchical texture and chemical modification in stabilizing superhydrophobicity.
- (3) To identify the dominant degradation mechanisms governing coating failure under accelerated environmental exposure including UV irradiation, hydrodynamic shear, electrochemical corrosion and to develop optimized composite coating formulations achieving sustained superhydrophobicity and corrosion resistance through rational control of polymer content, particle loading, and surface functionalization.
- (4) To develop and experimentally validate a multi-physics computational model coupling electrochemical kinetics and porous media transport to enable quantitative prediction of coating performance and mechanistic decomposition of protection mechanisms.

Research Object: superhydrophobic composite coatings for aluminum corrosion protection, comprising hierarchically structured mineral particles (silica, calcium carbonate) dispersed in polymer matrices with controlled surface chemistry.

Research subject: the mechanistic relationships governing the formation, stability, and degradation of superhydrophobicity and corrosion resistance in composite coatings under environmental exposure.

The results of the analysis of scientific literature conducted during the preparation of this section are presented in the following publications:

1. Ц. Юн, Д. Баклан., (2025) A review of fabrication techniques for superhydrophobic coatings. *Вісник Східноукраїнського національного університету імені Володимира Даля*, (2025) 109-120. <https://doi.org/10.33216/1998-7927-2025-291-5-109-120>.
2. Денис Баклан, Цзо Юн, Олексій Миронюк, Пуйкі Ленг., (2025). Супергідрофобні покриття на основі вуглецевих нанотрубок. *Композиційні матеріали 2025: Матеріали XIV Міжнародної науково-практичної WEB-конференції*. 2025, 11–19. <https://doi.org/10.20535/iwccmm2025326606>

CHAPTER 2. Materials and methods

Building upon the research problems and objectives outlined in Chapter 1, this chapter presents the comprehensive methodological framework developed to pursue a mechanism-driven strategy for designing durable superhydrophobic coatings. To address the key knowledge gaps in understanding environmental degradation mechanisms and to fulfill the research objectives, a dual-strategy approach was implemented. Specifically, an extractive fabrication method (femtosecond laser texturing) was employed for fundamental wetting investigations, while an additive method (pneumatic spray coating) was developed for scalable, corrosion-resistant coating applications. The following sections describe in detail the selected materials, the stepwise experimental procedures, and the comprehensive suite of analytical techniques used for morphological, chemical, and performance characterization.

2.1 Justification of the choice of manufacturing technology

Superhydrophobic surfaces can be fabricated through two fundamentally different approaches: extractive methods, which remove material from the substrate to create surface texture, and additive methods, which deposit texture-forming materials onto the substrate. The selection of fabrication technology depends on multiple factors including the desired surface morphology, scalability, cost-effectiveness, substrate compatibility, and intended application. This thesis investigates both approaches to provide a comprehensive understanding of superhydrophobic surface fabrication for corrosion protection applications.[56-58]

2.1.1 Extractive method for obtaining superhydrophobic surfaces (femtosecond laser)

Femtosecond laser ablation represents a highly precise extractive method for creating micro- and nanotextured surfaces through controlled material removal. This

technology offers several distinct advantages that justify its investigation in this thesis[59, 60].

First, femtosecond laser processing provides exceptional control over surface morphology at multiple length scales. By adjusting laser parameters such as pulse energy, spot size, scanning speed, and pulse overlap, both microscale features (periodic grooves, pillars, or pyramids with periods of 10-100 μm) and nanoscale features (laser-induced periodic surface structures with periods of 100-500 nm) can be created on the same surface[61]. This hierarchical structure is essential for achieving stable superhydrophobicity in the Cassie-Baxter wetting state. Second, the ultra-short pulse duration (femtosecond timescale) minimizes heat-affected zones and thermal damage to the substrate, resulting in well-defined features with minimal debris or recast layer formation. Third, femtosecond laser texturing is a non-contact, single-step process that does not require chemical reagents, making it environmentally friendly and suitable for complex geometries. Fourth, the process is highly repeatable and programmable, allowing precise control over texture geometry through computer-aided design. Fifth, femtosecond laser processing can induce spontaneous hydrophobization of metal surfaces through adsorption of atmospheric hydrocarbons onto the freshly created high-surface-area nanostructures, potentially eliminating the need for additional surface modification steps[62].

Despite these advantages, femtosecond laser texturing faces several limitations that restrict its widespread industrial application. The primary limitation is scalability: laser processing is inherently a serial technique where the laser beam must scan across the entire surface area, resulting in relatively slow processing speeds (typically 1-10 cm^2/min depending on texture density). For large-area applications such as architectural panels or automotive components, this processing speed is economically impractical. Second, femtosecond laser systems require significant capital investment, high maintenance costs, and specialized operator training. Third, the process is energy-intensive, with most of the laser energy being dissipated as heat rather than contributing to material removal. Fourth, laser-textured surfaces may exhibit limited mechanical

durability, as the surface features are integral to the substrate and cannot be easily repaired if damaged[63].

Despite these limitations, femtosecond laser texturing is investigated in this thesis (Chapter 3) for several important reasons. First, it provides a well-controlled platform for fundamental studies of wetting behavior and surface energy characterization using the Owens-Wendt method, as the texture geometry can be precisely defined and systematically varied. Second, it allows investigation of spontaneous hydrophobization phenomena and comparison of different surface modification strategies (fluorinated silanes, hydrocarbon silanes, fatty acids) on identical texture geometries. Third, the insights gained from laser-textured surfaces regarding optimal texture geometry, hierarchical structure design, and surface chemistry provide valuable guidance for designing additive coatings. Fourth, for high-value applications where superior performance justifies higher cost (aerospace components, medical implants, precision instruments), laser texturing remains a viable technology[21, 64].

2.1.2 Additive Method for Obtaining Superhydrophobic Surfaces

Additive coating methods, which involve depositing texture-forming particles dispersed in a polymer binder onto substrates, represent a complementary approach to extractive methods. Pneumatic spray coating of particle-polymer suspensions is investigated as the primary additive method in this thesis.[65]

Spray coating offers several critical advantages that make it attractive for large-scale industrial applications. First and foremost, it is inherently scalable: large areas can be coated rapidly using industrial spray equipment, with processing speeds of 10-100 m²/hour being readily achievable[65]. This represents a 100-1000× improvement in throughput compared to laser texturing. Second, spray coating requires minimal capital investment, as pneumatic spray equipment is widely available and inexpensive (typically \$100-\$1,000 for laboratory-scale systems, \$10,000-\$50,000 for industrial systems)[66]. Third, the process is compatible with complex three-dimensional geometries, internal surfaces, and substrates that cannot be easily accessed by laser beams[67, 68]. Fourth, coating composition can be easily adjusted by changing the formulation, allowing rapid optimization and customization for specific applications

without modifying equipment[69, 70]. Fifth, spray-coated surfaces can potentially be repaired by reapplication if damaged, unlike laser-textured surfaces where damage to the substrate is permanent. Sixth, the process is energy-efficient, requiring only compressed air and moderate heating for solvent evaporation[71].

However, spray coating also presents significant challenges that must be addressed through careful materials selection and formulation design. The primary challenge is achieving long-term environmental durability, as spray-coated surfaces consist of multiple components (particles, polymer binder, hydrophobic treatments) that may degrade at different rates under environmental stressors such as UV radiation, water immersion, mechanical abrasion, and corrosive media. Understanding the degradation mechanisms of each component and their interactions is essential for designing durable formulations[72]. Second, the coating must provide adequate adhesion to the substrate while maintaining superhydrophobicity, which requires balancing polymer content (higher polymer improves adhesion but increases surface energy and water absorption) against particle content (higher particle content improves hydrophobicity but may reduce adhesion)[73]. Third, the hierarchical structure must be carefully designed by selecting appropriate combinations of nanoscale and microscale particles to achieve stable Cassie-Baxter wetting. Fourth, the coating must provide effective corrosion protection through both barrier mechanisms (impeding ion and water transport) and inhibitive mechanisms (preventing electrochemical reactions at the substrate surface)[74].

Spray coating is the primary focus of this thesis (Chapters 4 and 5) because it represents the most promising path toward practical, large-scale implementation of superhydrophobic corrosion protection. Chapter 4 investigates the fundamental degradation mechanisms of spray-coated hierarchical surfaces under UV radiation and water flow (Stage 1) and applies the mechanistic insights to optimize coating composition for maximum corrosion resistance in chloride-containing environments (Stage 2). This two-stage approach allows identification of which coating components are most vulnerable to environmental attack, establishment of design principles for durable formulations, and validation of these principles through systematic

electrochemical evaluation. Chapter 5 extends this work by developing computational models of the electrochemical processes at superhydrophobic coating-electrolyte interfaces, providing insights into protection mechanisms that cannot be easily obtained experimentally and enabling predictive design of optimized coatings.

The investigation of both extractive (laser texturing) and additive (spray coating) methods in this thesis is not redundant but rather complementary. Laser texturing provides a controlled platform for fundamental wetting studies and surface energy characterization (Chapter 3), establishing baseline understanding of how texture geometry and surface chemistry influence wettability. Spray coating addresses the practical requirements of scalability, cost-effectiveness, and corrosion protection performance (Chapters 4 and 5). Together, these approaches provide a comprehensive understanding of superhydrophobic surface design, fabrication, characterization, and application.

2.2 Materials for obtaining superhydrophobic coating compositions

All chemicals were used as received from their respective suppliers without further purification. The selection of each material was guided by its specific function within the coating system and its relevance to the research objectives.

2.2.1 Substrates

The substrates chosen were anodized aluminum alloy 6063 for the spray coating studies, due to its prevalence in corrosion-prone applications, and aluminum alloy 7500 ($20 \times 20 \text{ mm}^2$ samples, polished to a mirror finish) for the laser texturing experiments[75]. For the dynamic wetting experiments on laser-textured surfaces, a flexible polymer substrate was produced from a two-component, platinum-cured polydimethylsiloxane (PDMS) formulation. The mixture contained 100 parts vinyl-terminated PDMS, 3 parts methylhydrosiloxane–dimethylsiloxane copolymer as the crosslinker, and 200 ppm of Karstedt's platinum catalyst (Gelest Inc.). After thorough mixing, the material was poured into metal molds and cured at room temperature for 48 hours.

2.2.2 Fillers for Hierarchical Structure Formation

Fumed silica (Aerosil R972, Evonik, Germany) with a primary particle size of 12 nm and specific surface area of approximately 110 m²/g was used as the nanoscale texture-forming component. This material was obtained pre-treated with dimethyldichlorosilane, providing inherent hydrophobicity through stable siloxane surface groups[76]. R972 was selected because silane-treated silica exhibits superior UV stability compared to organic hydrophobic treatments, as demonstrated in preliminary degradation studies.

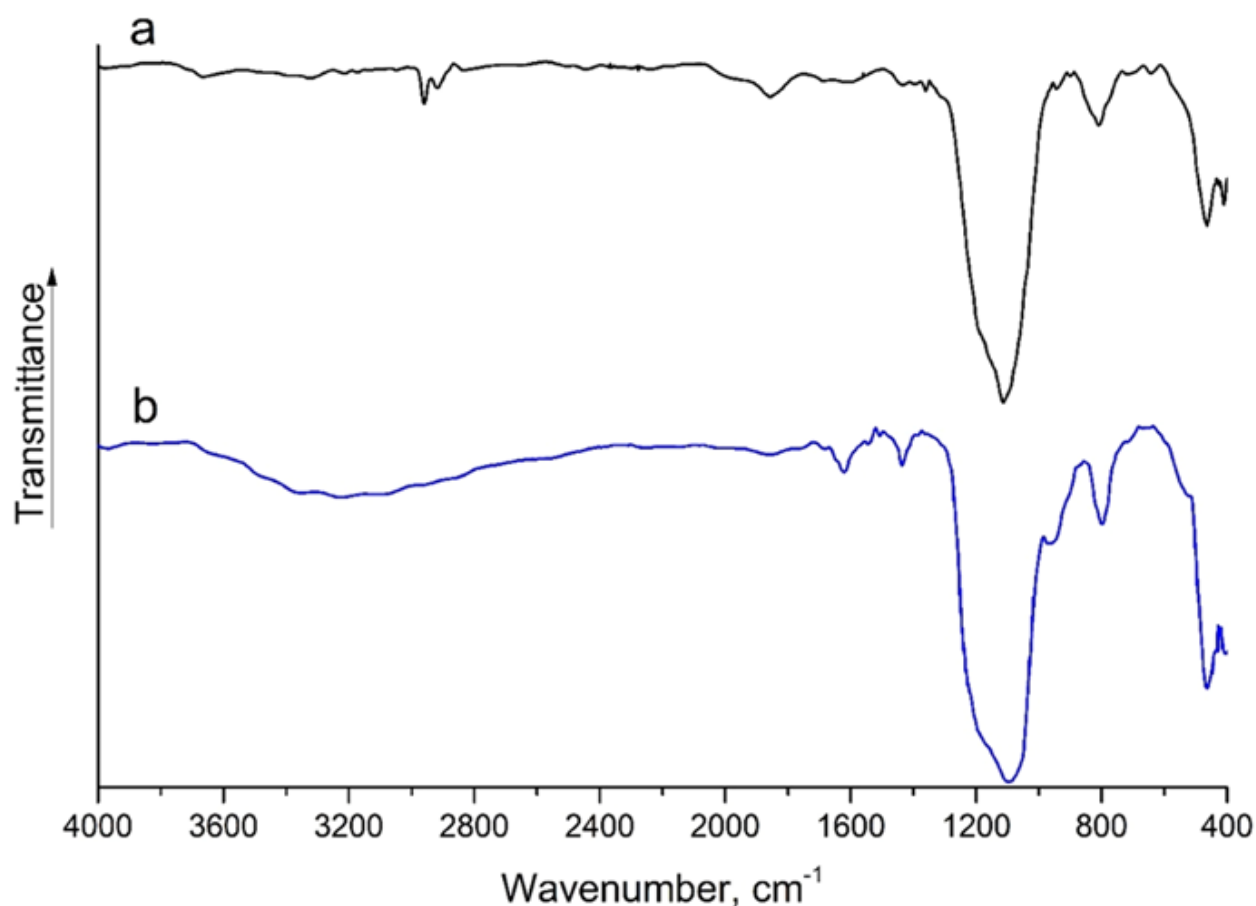


Figure.2.1. FTIR spectra: (a) dimethyldichlorosilane treated silica; (b) untreated silica. [77]

Figure.2.1. presents the FTIR spectra of (a) dimethyldichlorosilane-treated (hydrophobized) silica and (b) untreated silica. The spectrum of untreated silica (b) displays a broad O–H stretching band centered at approximately 3400 cm⁻¹, characteristic of surface silanol (Si–OH) groups and physisorbed water, alongside the

prominent Si–O–Si asymmetric stretching vibration at $\sim 1100\text{ cm}^{-1}$ and a weaker bending mode near 800 cm^{-1} . In marked contrast, the hydrophobized silica (a) exhibits new absorption bands at 2921 cm^{-1} and 2853 cm^{-1} , assigned to the asymmetric and symmetric C–H stretching vibrations of the methyl ($-\text{CH}_3$) groups from the grafted $-\text{Si}(\text{CH}_3)_2$ moieties. Notably, the broad O–H band at $\sim 3400\text{ cm}^{-1}$ is substantially diminished or absent, signifying the effective consumption of surface silanols through silane condensation. These spectral signatures - emergence of alkyl C–H features coupled with silanol suppression - collectively confirm the successful chemical grafting of dimethyldichlorosilane, yielding a hydrophobic organosilane layer on the silica surface.

Ground calcium carbonate (Normcal 2, Som Calcite, Turkey) with median particle size of $4.8\text{ }\mu\text{m}$ and specific surface area of $0.8\text{ m}^2/\text{g}$ was used as the microscale texture-forming component. Calcium carbonate was selected for its low cost, availability, non-toxicity, and ability to form dense physical barriers when present at high weight fractions[77, 78].

Calcium Carbonate Modification[79]: The initial stage involves drying the material at a temperature of $105\text{--}110\text{ }^\circ\text{C}$. Subsequently, a 3 wt.% stearic acid solution is prepared in isopropyl alcohol. To facilitate complete dissolution of the stearic acid, the mixture is gently heated. The dried calcium carbonate is then introduced into the stearate solution under continuous magnetic stirring (300 rpm) and maintained for 0.5–1 hour to ensure uniform coating and dispersion. Following the mixing stage, the suspension is allowed to stand for 24 hours to promote cooling and precipitation. The solvent is then removed by decantation, and the modified filler is separated via vacuum filtration using a Büchner funnel. To enhance the removal of residual stearate, the precipitate can be additionally washed with isopropyl alcohol. The obtained material is finally dried at $60\text{ }^\circ\text{C}$ to constant weight, the schematic as shown in the Figure 2.1.

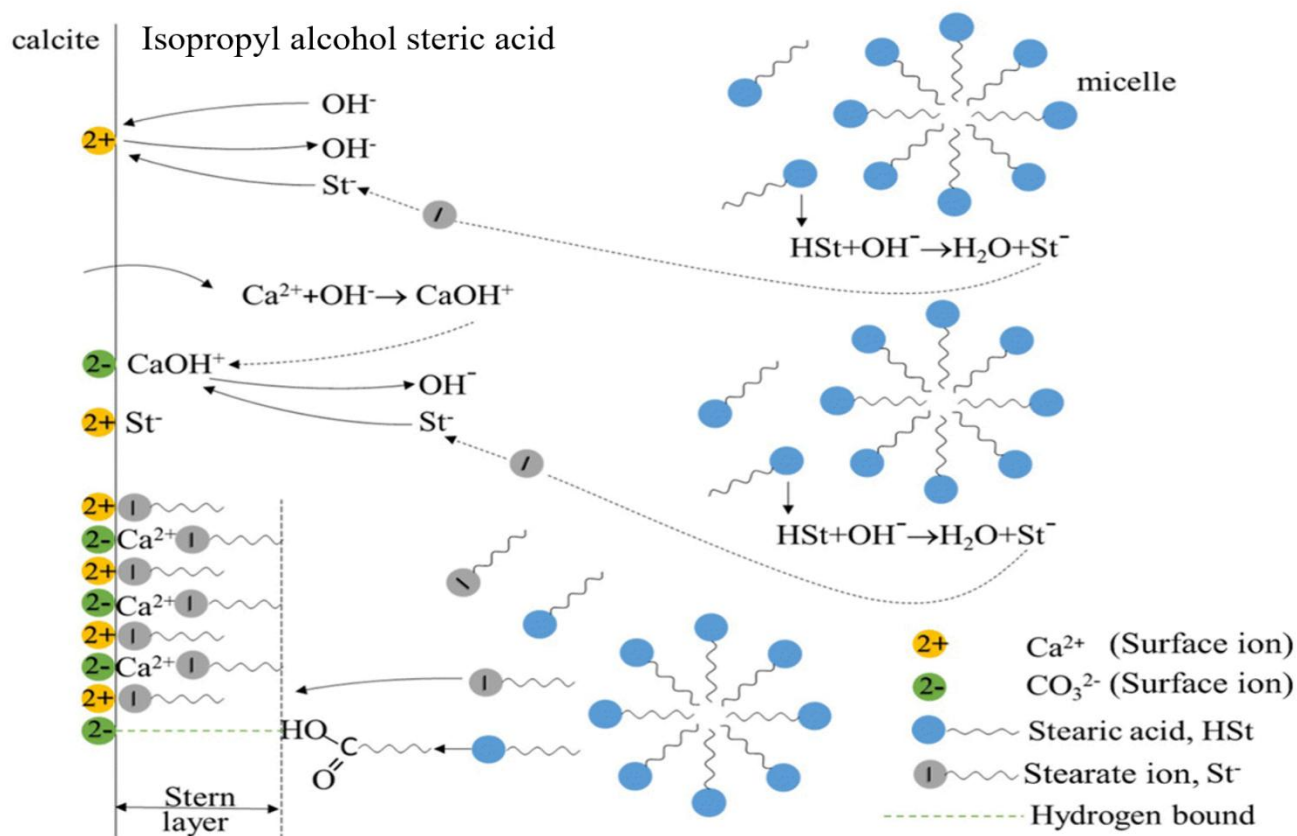


Figure.2.2. Schematic diagram illustrating the surface modification of calcite using stearic acid (SA) via the “wet process.”[79]

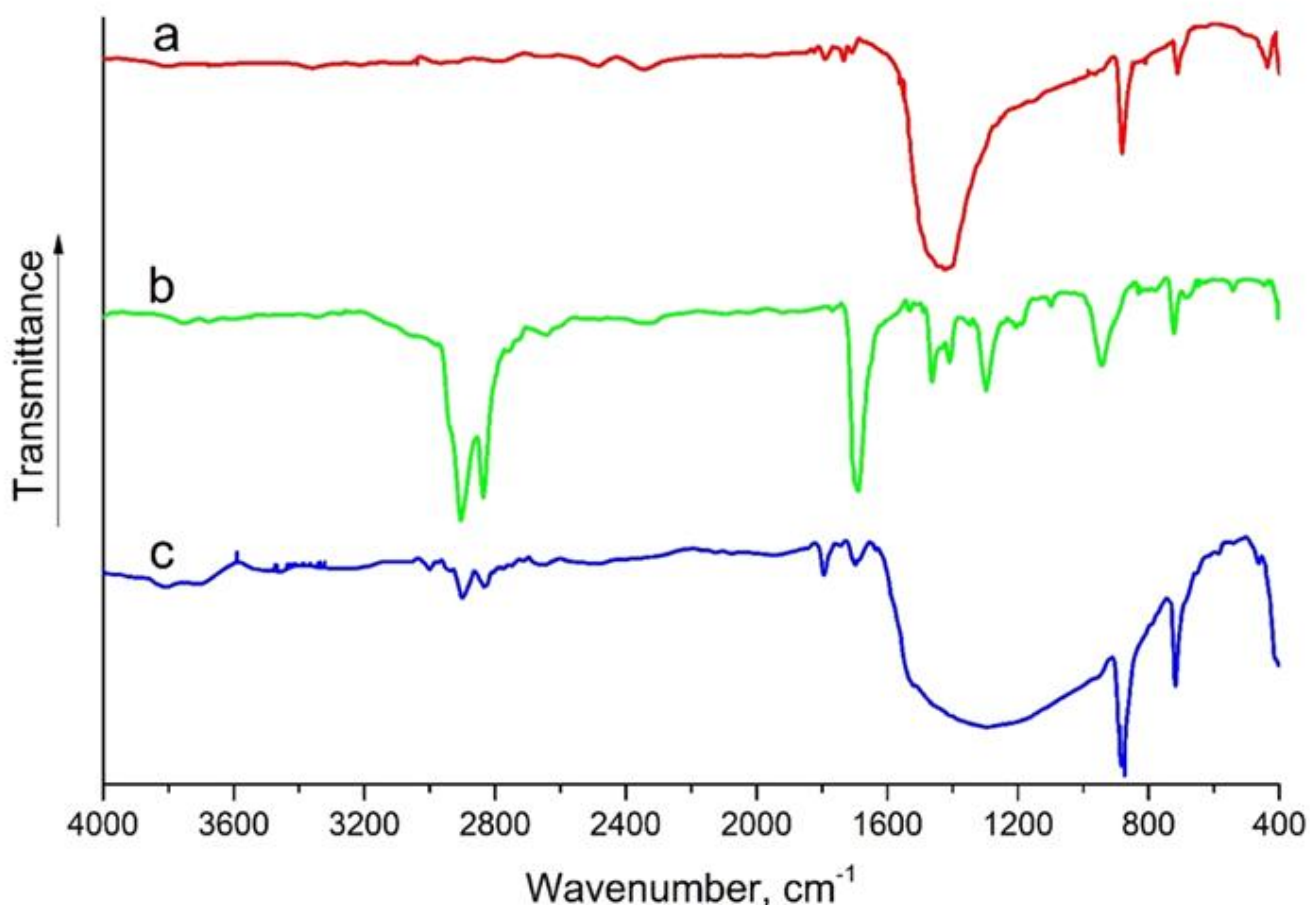


Figure.2.3. FTIR spectra: (a) CaCO_3 ; (b) stearic acid; (c) CaCO_3 treated with stearic acid ($\text{CaCO}_3 - \text{tSt}$). [77]

As the Figure. 2.2. shows, the FTIR spectrum of pristine CaCO_3 exhibits the characteristic carbonate bands, namely a strong band at around 1420 cm^{-1} assigned to the asymmetric stretching vibration of the CO_3^{2-} group, together with the out-of-plane and in-plane bending modes located at approximately 875 and 712 cm^{-1} , respectively. In contrast, pure stearic acid shows intense absorption bands at 2918 and 2849 cm^{-1} , corresponding to the asymmetric and symmetric C–H stretching vibrations of the methylene and methyl groups in the long alkyl chain, as well as a sharp carbonyl band at about $1700\text{--}1710 \text{ cm}^{-1}$ arising from the C=O stretching of the carboxylic acid group. After treatment, the spectrum of $\text{CaCO}_3\text{-tSt}$ contains new bands at 2918 and 2849 cm^{-1} , indicating the presence of stearate alkyl chains on the CaCO_3 surface. Meanwhile, the disappearance of the carboxylic C=O band of stearic acid and the emergence of new absorption bands in the $1540\text{--}1580 \text{ cm}^{-1}$ ($\nu_{\text{as}}(\text{COO}^-)$) and $1400\text{--}1450 \text{ cm}^{-1}$ ($\nu_{\text{s}}(\text{COO}^-)$) regions demonstrate that the carboxylic groups have been converted into

carboxylate anions coordinated to Ca^{2+} . These spectral changes collectively confirm that stearic acid has chemically reacted with the CaCO_3 surface to form a calcium stearate layer rather than being merely physically adsorbed.

2.2.3 Polymer binders

Two styrene-butyl-methacrylate copolymers from different manufacturers were used in this thesis, collectively referred to as «AC» in the abbreviated form. NeoCryl B 880 (DSM, Netherlands), a styrene-butyl-methacrylate copolymer, was used in the UV degradation and water flow studies (Chapter 4, Stage 1)[77]. AC80 (OMNOVA Solutions, USA), also a styrene-butyl-methacrylate copolymer, was used in the corrosion protection optimization studies (Chapter 4, Stage 2). Both copolymers provide good adhesion to aluminum substrates, form continuous films upon solvent evaporation, and exhibit moderate hydrophobicity. These styrene-acrylic copolymers were selected because they represent a widely used class of coating polymers with good environmental resistance and commercial availability. The acrylate system employs a styrene-butyl methacrylate copolymer, as shown in the Figure 2.2.

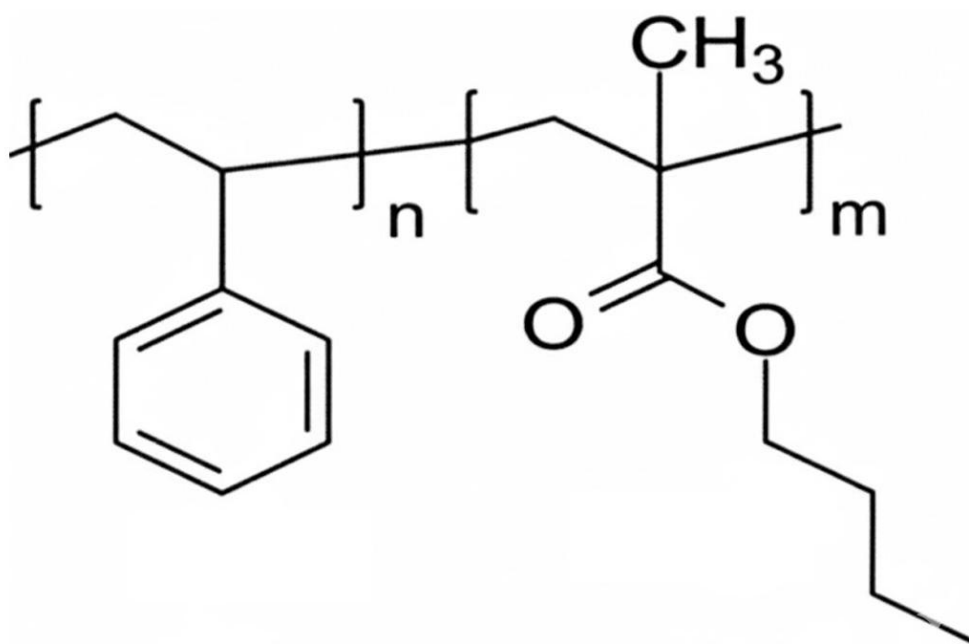


Fig. 2.4. Structural formula of a copolymer of styrene and isobutyl methacrylate.

Table 2.1. Properties of NeoCryl B 880.

Property	Value
Molar mass	90000 g/mol
Polymer content	$\geq 98\%$
Ash content	$< 0.04\%$
Average density	1.05 g/cm ³
Viscosity	350-550 mPa·s (Brookfield rotational viscometry, 25 °C, 38.5% solution, solvents 90% toluene + 10% white spirit).

Cellulose acetate butyrate (CAB-381-0.5, Eastman Chemical Company, USA) was used as an alternative polymer binder for comparative degradation studies. CAB exhibits different chemical structure and degradation behavior compared to AC, allowing investigation of polymer type effects on coating durability[80].

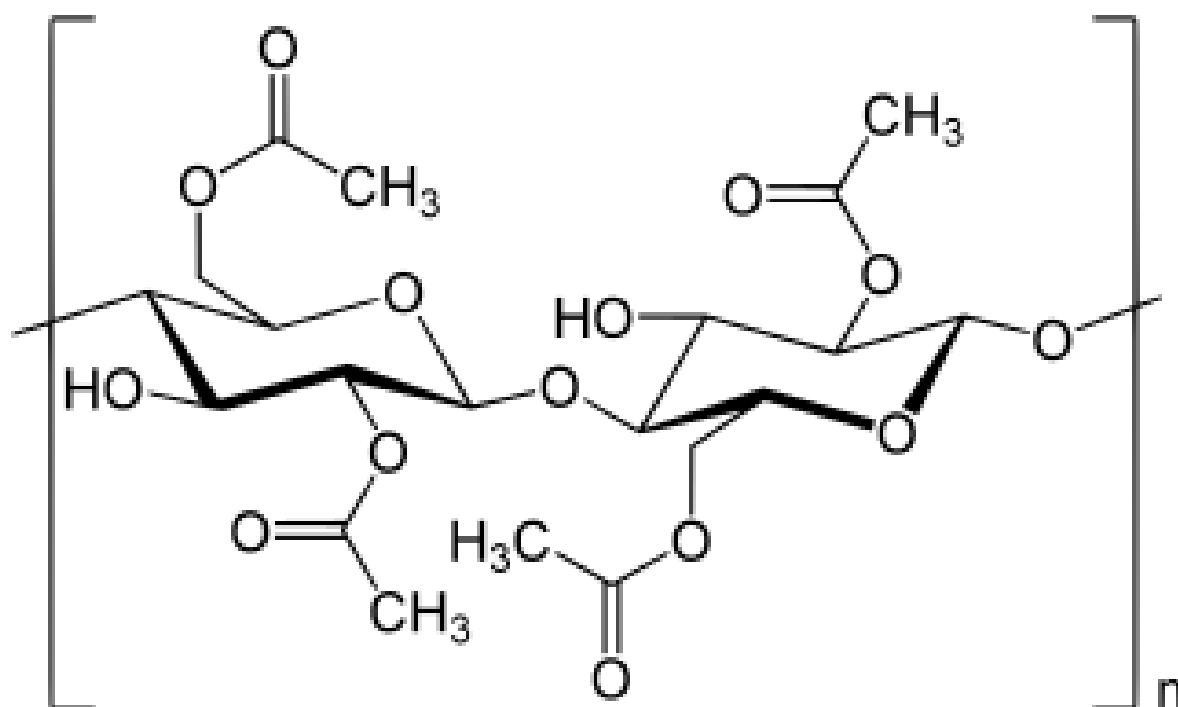


Fig.2.5. Structural formula of cellulose acetate butyrate

Table 2.2. Properties of CAB.

Property	Value
Molar mass	30,000 g/mol
Polymer content	$\geq 97\%$
Ash content	$<0.05\%$
Average density	1.2 g/cm ³
Butyryl Content	37 wt%
Appearance	White solid
Melting Point	155-165°C

2.2.4 Surface modifiers for laser-textured surfaces

Four different hydrophobic modifiers were used to reduce the surface energy of laser-textured aluminum surfaces, representing three chemical classes: fluorinated silanes, hydrocarbon silanes, and organic compounds.

1H,1H,2H,2H-Perfluorooctyltriethoxysilane (POTS) (CAS 51851-37-7, Alfa Aesar) is a fluorinated silane that provides the lowest surface energy and highest water repellency among common modifiers. POTS was selected as the benchmark high-performance modifier. Octyltrimethoxysilane (OCTEO) (CAS 3069-40-7, Alfa Aesar) is a hydrocarbon silane that provides a fluorine-free, more environmentally friendly alternative to POTS while maintaining good hydrophobicity. Stearic Acid (CAS 57-11-4, Alfa Aesar) is a saturated fatty acid (C18) that provides moderate hydrophobicity at low cost through physical adsorption and chemical bonding to metal oxide surfaces.

Squalane (CAS 111-01-3, Alfa Aesar) is a branched hydrocarbon ($C_{30}H_{62}$) that provides hydrophobicity through physical adsorption, representing the simplest modification approach.

2.2.5 Solvents

o-Xylene (99% purity) was used as the primary solvent for AC polymer due to its good solvation properties and appropriate evaporation rate. Isopropyl Alcohol (99.5% purity) was used as the solvent for CAB polymer, for surface modifier solutions, and for cleaning procedures. Ethanol (99.5% purity) was used for stearic acid treatment of calcium carbonate and for preparing water-ethanol probe liquid mixtures. Xylene (mixture of para- and ortho-isomers) was used for diluting spray coating suspensions.

2.3. Experimental procedures

2.3.1 Femtosecond laser texturing process

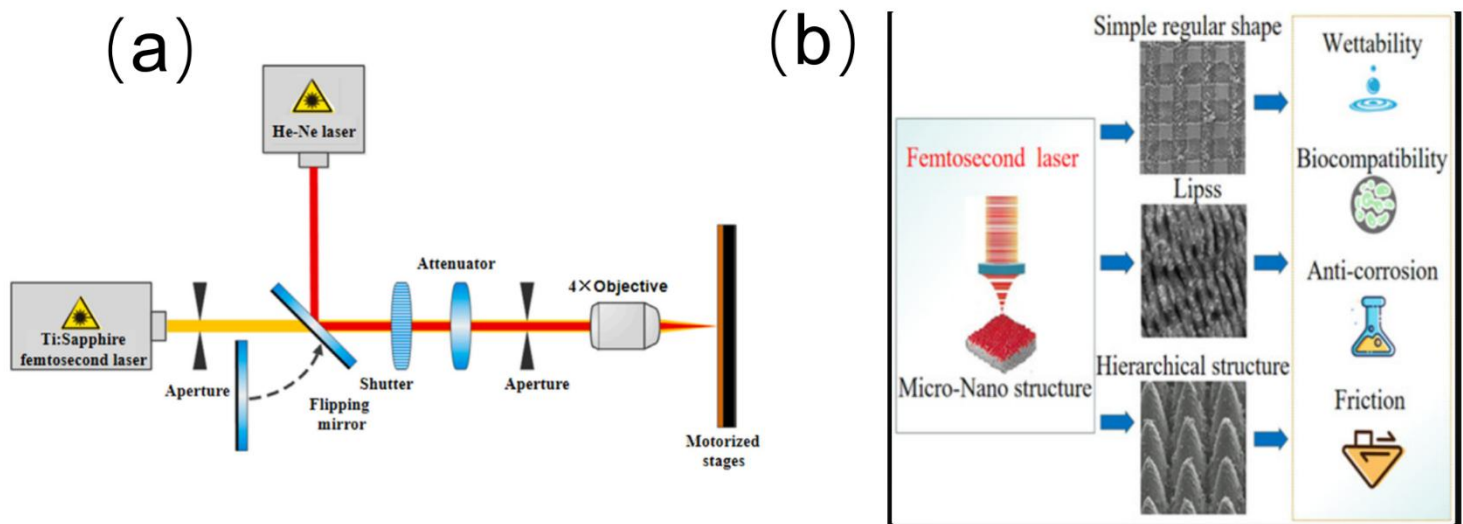


Figure.2.6 a) Femtosecond laser fabrication system schematic. b) Functional effects of femtosecond laser-induced micro-nanostructures. [81]

Micro- and nanotextured surfaces were fabricated on aluminum alloy 7500 substrates using a femtosecond laser system (Carbide, Light Conversion, Lithuania) operating at 1030 nm wavelength with 360 fs pulse width, 60 kHz repetition rate, and up to 6 W average power. Sample translation was controlled using X-Y linear stages (Aerotech, Inc.) at 60 mm/s scanning speed.

For nanotexture formation, the laser beam was focused to approximately 80 μm spot diameter with 46 μJ pulse energy (0.9 J/cm^2 energy density). Laser spots were overlapped by 60% with 30 μm step between passes, producing disordered nanocrystalline structures with 100-200 nm feature sizes.

For microtexture formation, the laser beam was sharply focused to approximately 5 μm spot diameter with 21-35 μJ pulse energy ($107\text{-}178 \text{ J/cm}^2$ energy density). Two microtexture types were created: periodic square pillars (45-60 μm period, 15-45 μm pillar width) and periodic grooves (45-60 μm period, 16-45 μm groove width).

After laser texturing, samples were cleaned by rinsing with isopropyl alcohol and drying at 80 °C for 15 minutes.

Metal templates (negatives) were fabricated using micromilling on a DMU monoblock 65 FDS–2nd Generation five-axis vertical machining center. GARANT Master Titan solid carbide micromills with diameters of 0.2 mm, 0.5 mm, and 1 mm were used to create textures on NiTi alloy plates. The resulting PDMS positives replicated these milled features.

Table 2.3. Geometry of Microtextures Fabricated on Aluminum and PDMS

Sample ID	Material	Fabrication Method	Period (μm)	Groove/Trench (μm)	Width
B	Aluminum	Laser Texturing	45	20	
C	Aluminum	Laser Texturing	57	20	
E	Aluminum	Laser Texturing	60	45	
1	PDMS	Laser Texturing	60	15	
2	PDMS	Micromilling	100	50	
3	PDMS	Micromilling	750	300	

2.3.2 Surface Modification of Laser-Textured Surfaces

Laser-textured samples were modified with hydrophobic agents using immersion treatment. For silane modifiers (POTS, OCTEO), samples were immersed in 1 wt. % isopropyl alcohol solution for 30 minutes at room temperature, then dried at 130 °C for 30 minutes to promote siloxane bond formation. For organic modifiers (stearic acid, squalane), samples were immersed in 0.5 wt. % solution (isopropyl alcohol for stearic acid, xylene for squalane) for 30 minutes at room temperature, then dried in a desiccator at 65 °C for 30 minutes.

2.3.3 Preparation of composite coating formulations

Aluminum 6063 substrates were ultrasonically cleaned in acetone for 10 minutes, rinsed with ethanol, and dried under nitrogen gas. Polymer solutions were prepared by dissolving 1 g of polymer in 9 g of solvent (o-xylene for AC, isopropyl alcohol for CAB), yielding a 1:9 polymer-to-solvent ratio by weight; after complete dissolution, hydrophobized fillers (R972 and/or CaCO_3) were added in the desired weight fractions and stirred for 30 minutes, and additional xylene was subsequently added to maintain a 4:1 xylene-to-solids ratio to achieve suitable viscosity for pneumatic spraying. The resulting suspensions were applied to the substrates using a pneumatic spray gun in a ventilated fume hood, with multiple passes performed to build the desired coating thickness, allowing brief drying intervals between passes. Coated substrates were then heated at 100 °C for 1 hour to remove residual solvent and promote polymer film formation, followed by cooling to room temperature. Multiple coating compositions with systematically varied filler types, filler weight fractions, and polymer types were prepared, with specific formulations detailed in the corresponding experimental chapters.

2.4. Instrumental methods of characterization

The scanning electron microscope (SEM) is a powerful instrument for studying the micro- and nanoscale morphology of materials. Its operation begins with an electron gun, typically a thermionic or field-emission source, which emits a high-energy beam of electrons. This beam is accelerated by a high voltage potential between the cathode and anode and directed down the electron column. A series of magnetic lenses (condenser and objective lenses) are used to focus the electron beam into a fine probe, which is then raster-scanned across the surface of the sample by a set of scanning coils. As the primary electron beam interacts with the sample, it generates a variety of signals from a small interaction volume. For morphological imaging, the most important of these are secondary electrons (SE) and backscattered electrons (BSE). Secondary electrons are low-energy electrons ejected from the atoms of the sample due

to inelastic scattering interactions. Because of their low energy, only SEs generated within the top few nanometers of the surface can escape and be detected. This makes the SE signal highly sensitive to surface topography, providing detailed, high-resolution images of the sample's surface features. Backscattered electrons, on the other hand, are high-energy electrons from the primary beam that are reflected or "backscattered" due to elastic scattering interactions with atomic nuclei. The yield of BSEs is strongly dependent on the atomic number (Z) of the elements in the sample; heavier elements scatter electrons more strongly and thus appear brighter in a BSE image. This provides valuable information about the compositional variation across the sample surface. These signals are captured by their respective detectors (e.g., an Everhart-Thornley detector for SEs), amplified, and converted into a voltage signal that modulates the brightness of a corresponding pixel on a display screen, building up the final image point-by-point as the beam scans the sample.

Sample preparation is critical for SEM analysis. For conductive materials like metals, a sample of the appropriate size can be tested directly. However, for non-conductive or poorly conductive materials, such as the polymer-based coatings in this study, the electron beam can cause an accumulation of negative charge on the surface. This "charging" effect can deflect the primary beam and interfere with the collection of secondary electrons, severely degrading image quality. To prevent this, a thin conductive layer must be deposited on the sample surface before observation. In this study, all non-conductive samples were sputter-coated with a 5-10 nm layer of gold or a gold-palladium alloy, which have high secondary electron emission rates and provide an effective path for charge dissipation. The specific instruments used were TESCAN MIRA3 and Sigma 300 field-emission scanning electron microscopes, operated in secondary electron mode at an accelerating voltage of 5-10 kV.

FTIR spectroscopy is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high-spectral-resolution data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer, which measures intensity over a narrow range of wavelengths at a time. The core of an FTIR spectrometer is a

Michelson interferometer. A beam of infrared radiation from a source is split into two beams by a beam splitter. One beam reflects off a fixed mirror, while the other reflects off a moving mirror, which introduces a time delay - the optical path difference. The two beams then recombine at the beam splitter and pass through the sample to a detector. The resulting signal, called an interferogram, represents the light intensity as a function of the optical path difference. A mathematical operation called a Fourier transform is then performed on the interferogram to convert it into the actual spectrum, which shows the light intensity at each wavelength (or wavenumber).

When the infrared radiation passes through the sample, specific frequencies of radiation are absorbed by the molecules. The absorbed frequencies correspond to the vibrational frequencies of the chemical bonds within the molecule. As such, the FTIR spectrum provides a "molecular fingerprint" of the sample, allowing for the identification of functional groups and the study of chemical changes. In this work, a Nicolet 4700 FTIR Spectrometer was used in Attenuated Total Reflectance (ATR) mode. ATR is a surface-sensitive technique where the IR beam is directed into a crystal of high refractive index (e.g., diamond or germanium). The beam undergoes total internal reflection at the crystal surface, creating a shallowly penetrating evanescent wave that extends into the sample placed in contact with the crystal. This evanescent wave is absorbed by the sample at specific frequencies, and the attenuated beam returns to the detector. This method is ideal for analyzing the surface of solid films without any special sample preparation. Spectra were collected over a range of 4000 to 400 cm^{-1} by co-adding 32 scans at a resolution of 4 cm^{-1} to identify changes in the chemical structure of the coatings during degradation.

Electrochemical techniques are essential for quantifying the corrosion protection performance of coatings. These measurements are typically performed using an electrochemical workstation, or potentiostat/galvanostat, in a three-electrode cell. The cell consists of the working electrode (the sample being tested), a reference electrode with a stable and well-known electrode potential (e.g., a Saturated Calomel Electrode, SCE), and a counter (or auxiliary) electrode, which is an inert material like platinum or graphite that completes the circuit. The potentiostat precisely controls the potential

difference between the working and reference electrodes while measuring the resulting current flow between the working and counter electrodes.

Several techniques were used in this study, all performed with a BP-300 electrochemical workstation (Biologic, France) in a 3.0 wt.% NaCl solution. Electrochemical Impedance Spectroscopy (EIS) is a powerful, non-destructive technique where a small amplitude AC voltage perturbation (e.g., 10 mV) is applied to the system over a wide range of frequencies (e.g., 100 kHz to 10 mHz). By measuring the resulting AC current response, the impedance of the system ($Z = V/I$) can be calculated at each frequency. The resulting impedance spectrum, often plotted as a Nyquist or Bode plot, can be fitted to an electrical equivalent circuit model to extract quantitative parameters that describe the coating's barrier properties (pore resistance, R_{po}) and the electrochemical reactions at the substrate interface (charge transfer resistance, R_{ct}). Potentiodynamic Polarization is a destructive technique where the potential of the working electrode is scanned at a constant rate (e.g., 1 mV/s) away from its open-circuit potential. The resulting current is plotted on a logarithmic scale against the potential. By analyzing the Tafel regions of this plot, the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) can be determined, with i_{corr} being directly proportional to the corrosion rate.

Water contact angles were measured using the sessile drop technique (5 μ L droplet volume) with an optical microscope and digital camera. At least five measurements were performed at different locations on each sample, with results reported as mean $\pm$ standard deviation, contact angles were determined by the sessile drop method using an optical microscope and an H5D digital camera (Delta Optical, Shanghai, China) with the ScopeTek View software (version 1.0.0.1).

Owens-Wendt Surface Energy Analysis. For detailed surface energy characterization of laser-textured surfaces, the Owens-Wendt method was employed using water-ethanol mixtures as probe liquids. The surface tension values of water-ethanol mixtures were measured individually with decomposition performed by paraffin calibration. By plotting the Owens-Wendt graph and analyzing the

characteristic plateau regions, the dispersive and polar components of surface energy were determined, along with information about Cassie-Baxter wetting state stability.

UV resistance was evaluated according to ASTM D 4329, G154, and G151 standards using a UV weathering chamber with a 400 W UVA fluorescent lamp (340 nm peak emission). Two protocols were employed: (1) Standard cycle: 12-hour cycles of 8 hours UV at 60 ± 3 °C followed by 4 hours condensation at 50 ± 3 °C. (2) Modified cycle with water flow: samples mounted on a rotating cylinder (1 s^{-1}) immersed to 1/3 diameter in circulating distilled water while maintaining the same UV and temperature cycling.

Long-term stability was evaluated by immersing samples in distilled water or 3.0 wt. % NaCl solution at room temperature. Contact angles were measured at regular intervals (0, 1, 2, 4, 8, 24, 32, 48, and 72 hours).

2.5 Statistical treatment of experimental results.

For all quantitative measurements, at least three independent samples were prepared and measured. For contact angle measurements, at least five measurements were performed on different locations of each sample. Results are reported as mean $\pm$ standard deviation. Statistical significance was assessed using Student's t-test or analysis of variance (ANOVA) as appropriate, with $p < 0.05$ considered statistically significant[82].

The experimental part of this work was aimed at developing and characterizing composite coatings with enhanced water-repellent properties, achieved through the integration of inorganic particles into a polymer matrix. The general research strategy was built on the premise that both surface chemistry and microstructure govern the wettability of solid surfaces. Therefore, the methodological approach combined material synthesis, composite formulation, and performance evaluation under controlled laboratory conditions.

CHAPTER 3. Surface energy characterization and wetting behavior of laser-textured superhydrophobic surfaces

Superhydrophobic surfaces require a synergistic combination of hierarchical surface roughness and low surface energy chemical modification to achieve robust water repellency. While various fabrication techniques exist for creating controlled surface textures, femtosecond laser processing has emerged as a particularly powerful tool due to its ability to generate complex, multi-scale structures in a single processing step[22, 23, 83]. The ultrashort pulse duration enables the creation of both deliberately patterned microstructures and spontaneously formed nanostructures such as Laser-Induced Periodic Surface Structures (LIPSS), providing the hierarchical topography essential for stable superhydrophobicity[24, 84-87].

However, achieving optimal superhydrophobic performance requires more than simply creating a textured surface and applying a chemical modifier. A fundamental understanding of how texture geometry and chemical functionalization interact to control the surface free energy - particularly its polar and dispersive components - is essential for rational surface design[88]. Moreover, as surface feature dimensions approach or exceed droplet size, classical wetting models begin to break down, and dynamic phenomena such as contact line pinning and anisotropic spreading become dominant[89, 90]. These effects are critical for predicting real-world performance but are not captured by simple static contact angle measurements[91, 92].

This chapter presents a comprehensive, multi-scale investigation into the wetting properties of laser-textured surfaces, integrating surface energy analysis with dynamic wetting characterization[93, 94]. The study employs the Owens-Wendt method to systematically characterize femtosecond laser-textured aluminum surfaces modified with four different classes of hydrophobic agents (fluoroalkylsilanes, alkylsilanes, fatty acids, and hydrocarbon oils). The investigation explores how texture scale and geometry - ranging from ordered micro-pillar arrays to disordered nanostructures and periodic linear grooves - affect the stability of the Cassie-Baxter wetting state and the

polar/dispersive components of surface free energy. The study is extended to larger-scale micro-textured PDMS surfaces to examine dynamic wetting behavior, including contact line pinning, depinning, and anisotropic spreading, and to critically evaluate the applicability of classical wetting models in this regime.

By bridging surface energy analysis at the nanometer-to-micrometer scale with dynamic wetting phenomena at the tens-to-hundreds of micrometers scale, this chapter aims to establish integrated design principles for engineering durable, effective superhydrophobic coatings tailored to specific applications.

3.1 Surface morphology

Figure 3.1 shows representative SEM images of the laser-textured aluminum surfaces prepared in this study. The microtextured surface (Figure 3.1a) displays periodic line-and-groove patterns with well-defined ridges and sharp edges. The laser ablation process creates grooves approximately 45 μm wide with a period of 60 μm , resulting in a regular array of parallel channels. These macroscopic features serve as primary pinning sites for the contact line during droplet motion and are responsible for creating the air pockets that support the Cassie-Baxter state.

The nanotextured surface (Figure 3.1b) presents a dramatically different morphology, covered with a dense array of nano-scale features ranging from 100 to 200 nm in size. These structures are formed through a combination of laser-induced periodic surface structures (LIPSS) and nanoparticle redeposition during the ablation process. The high density of these nanoscale asperities results in a surface roughness factor (r) of approximately 2.0, significantly higher than that of the microtexture.

These multiscale structures are crucial for achieving robust superhydrophobicity. While the nanotexture provides high surface roughness that amplifies the intrinsic hydrophobicity of the chemical modifier, the microtexture creates well-defined air pockets that mechanically support the droplet in the Cassie-Baxter state. The combination of both scales in hierarchical textures has been shown to enhance water

repellency beyond what either scale can achieve alone, as will be demonstrated in the Owens-Wendt analysis that follows.

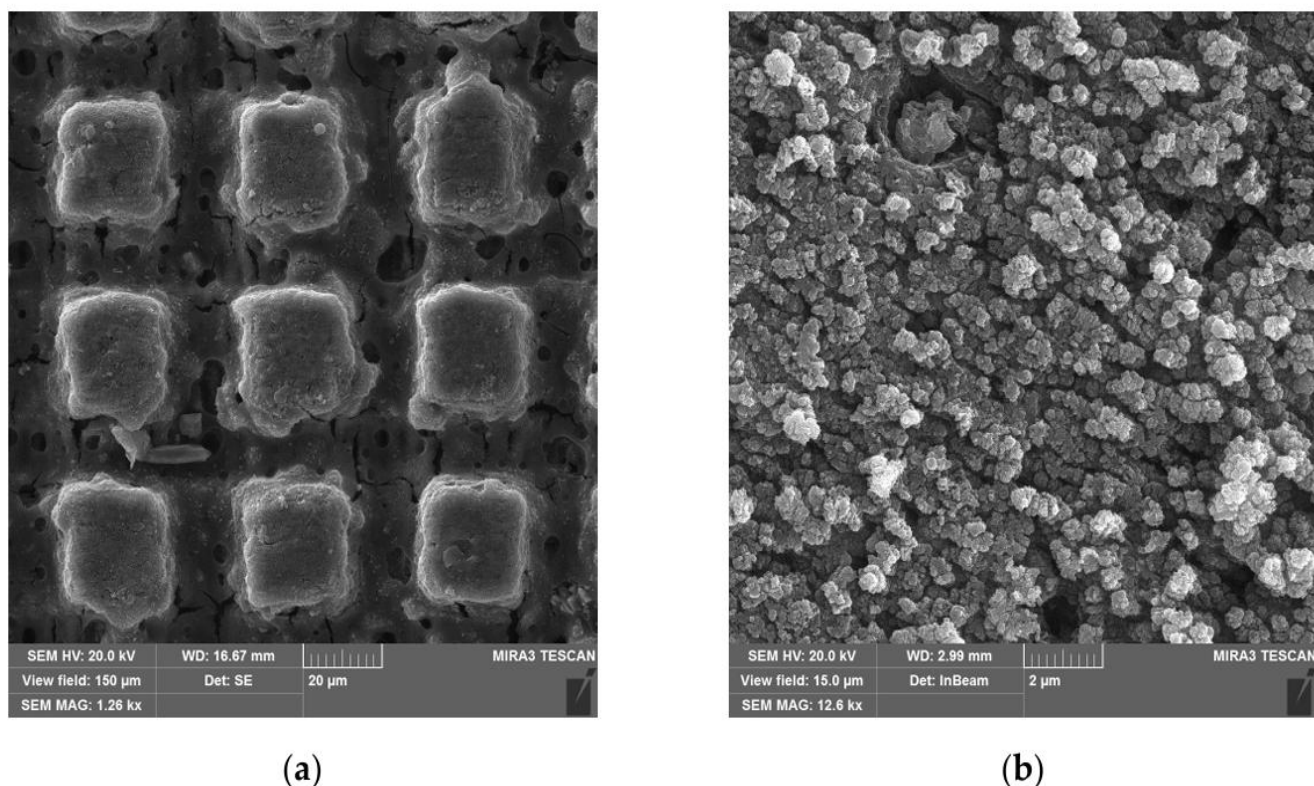


Figure 3.1. SEM images of laser-textured aluminum surfaces. (a) Microtextured surface showing periodic grooves with 60 μm period. (b) Nanotextured surface showing dense array of 100-200 nm features.

3.2. Owens-Wendt characterization of chemically modified aluminum surfaces

The Owens-Wendt method provides a powerful framework for quantifying the surface free energy of a solid by systematically probing it with liquids of varying polarity. This section details its application to laser-textured aluminum surfaces, revealing insights that static water contact angle measurements alone cannot provide.

3.2.1 Owens-Wendt plot characteristics for textured surfaces

For a flat, homogeneous surface, the Owens-Wendt equation predicts a linear relationship. However, for textured superhydrophobic surfaces, the plot deviates significantly from this ideal behavior. As shown in Figure 3.2, the plots for both micro-

and nanotextured aluminum surfaces are not linear but consist of at least two distinct segments.

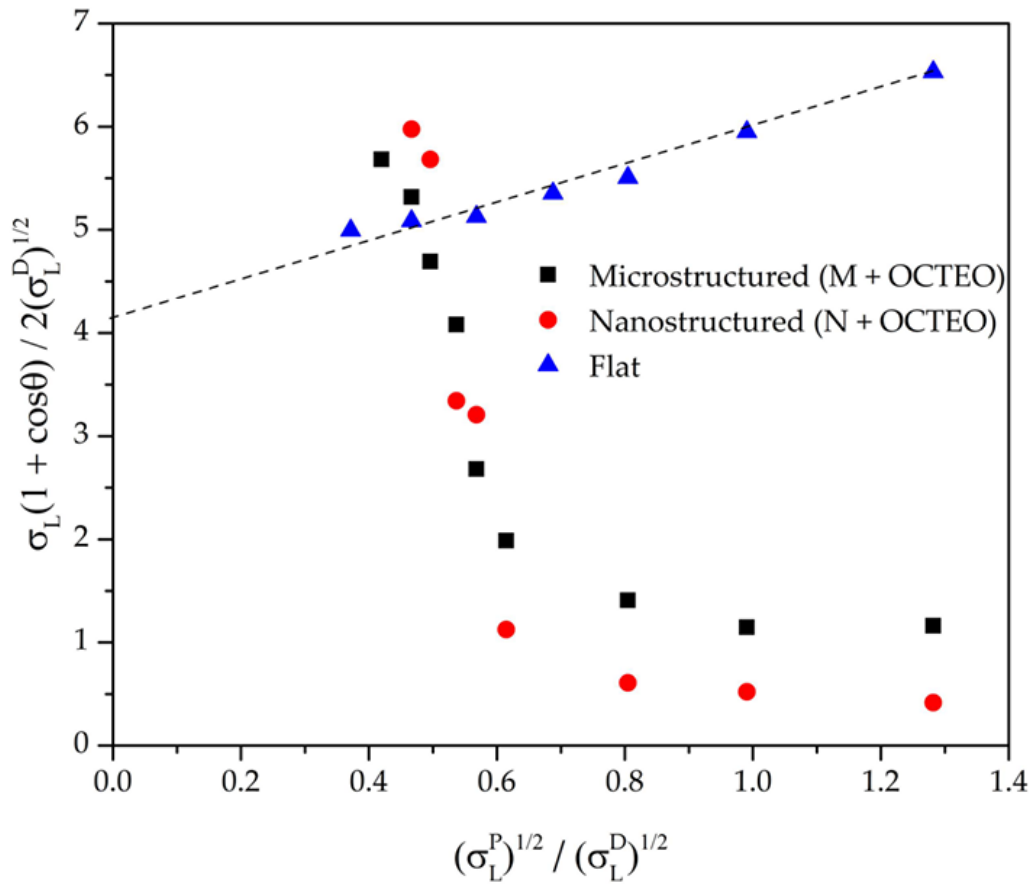


Figure 3.2. Owens-Wendt plots for OCTEO-treated aluminum surfaces, comparing a flat surface with micro- and nanotextured surfaces.

The plot reveals several key features that are characteristic of textured, hydrophobic surfaces. First, the data for the flat, untextured aluminum oxide surface (blue triangles) forms a relatively straight line with a positive slope, as predicted by the classical Owens-Wendt theory for a homogeneous, flat surface. The y-intercept of this line corresponds to σ_S^P is 18.0 mN/m, and the slope corresponds to σ_S^P is 2.4 mN/m. However, the high polar component indicates that the surface is still relatively hydrophilic, even after the OCTEO treatment, likely due to incomplete coverage or the presence of residual hydroxyl groups.

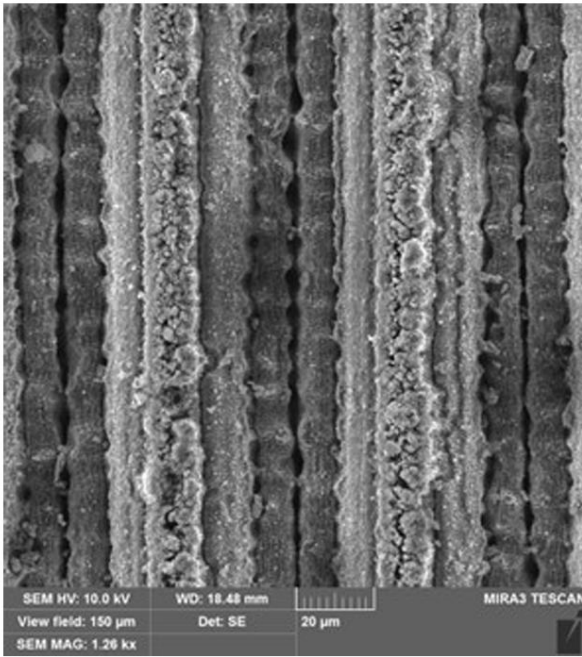
In stark contrast, both textured surfaces (M and N) exhibit a distinct, characteristic "plateau" at low values of the x-axis variable (i.e., for probe liquids with high polarity, such as water or water-rich water-ethanol mixtures). This plateau is a hallmark

signature of the Cassie-Baxter wetting state. In this state, the liquid droplet does not fully penetrate the texture; instead, it is suspended on a composite interface consisting of the solid protrusions and the air trapped in the voids. Because the liquid is partially supported by air, which has zero surface energy, the apparent surface energy of the composite interface is significantly reduced. Moreover, the contact angle becomes relatively insensitive to further changes in the liquid's surface tension, resulting in the observed plateau. The height of the plateau is related to the fraction of the solid-liquid interface (f) in the Cassie-Baxter equation[10].

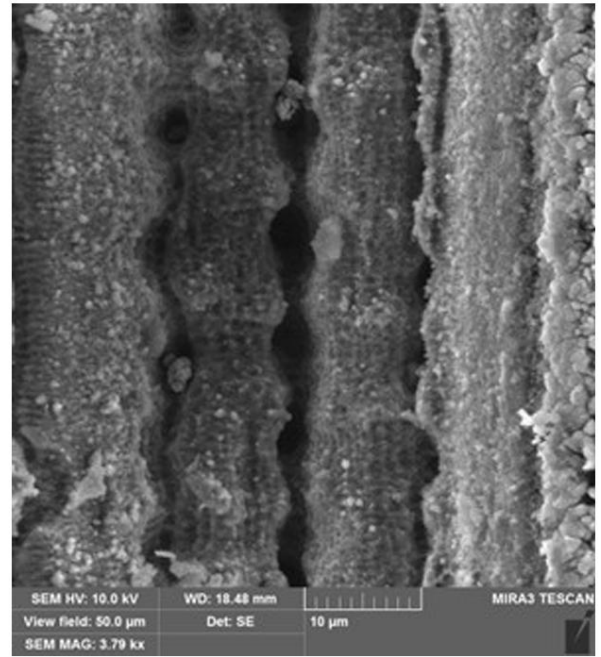
Second, and most importantly, the plateau for the nanotextured surface (Sample N, red circles) is significantly lower and extends over a wider range of x-axis values than that of the microtextured surface (Sample M, black squares). This indicates that the nanostructure is more effective at repelling polar liquids and maintaining a stable air-liquid interface. The lower plateau corresponds to a higher apparent contact angle and a lower apparent surface energy. The wider range over which the plateau extends indicates that the Cassie-Baxter state is more robust on the nanotextured surface; it can withstand a wider range of liquid polarities without transitioning to the Wenzel state (where the liquid fully penetrates the texture). This superior performance of the nanostructure can be attributed to two factors: (1) the high density of sharp, high-aspect-ratio features provides a large number of strong pinning sites that prevent the contact line from advancing into the texture; and (2) the small size of the nano-features means that the energy barrier for a liquid to penetrate between them is very high, as it would require a large increase in interfacial area.

3.2.2 Influence of micro-texture geometry on wetting: the transition from cassie-baxter to wenzel

To further elucidate the role of micro-scale geometry and to identify the optimal geometric regime for achieving robust superhydrophobicity, a systematic series of periodic linear textures (grooves) were fabricated with varying periods and widths. The geometric parameters of these samples are detailed in Table 3.1. The morphology of Sample E, which represents the most challenging geometry (widest grooves), is shown in detail in Figure 3.3.



(a)



(b)

Figure 3.3. SEM images of a periodic linear texture (Sample E): (a) demonstrates the overall micro-relief of the grooves, showing the parallel, linear structure; (b) shows a higher-magnification view revealing the submicron-level texture present on the tops of the protrusions and along the edges of the grooves.

As clearly seen in Figure 3.3(a), the laser process has created well-defined, parallel grooves with a period of approximately $60\text{ }\mu\text{m}$. The grooves have relatively steep sidewalls and flat bottoms. Importantly, Figure 3.3(b) reveals that the laser process has inherently created a secondary, submicron-scale roughness on top of the primary micro-grooves. This secondary roughness, which consists of LIPSS and other laser-induced nanostructures, forms a textured "skin" on the protrusions. This hierarchical structure, combining micro- and nano-scale roughness, is again highly beneficial for stabilizing the Cassie-Baxter state, as the nano-roughness provides additional pinning sites on top of the micro-protrusions.

This study investigates the influence of micro-texture geometry on the stability of the Cassie-Baxter state, particularly how groove width and depth affect this relationship. Accordingly, the wetting behavior of Samples B, C, and E was quantified

via the Owens-Wendt method after stearic acid modification. The resulting data are plotted in Figure 3.4.

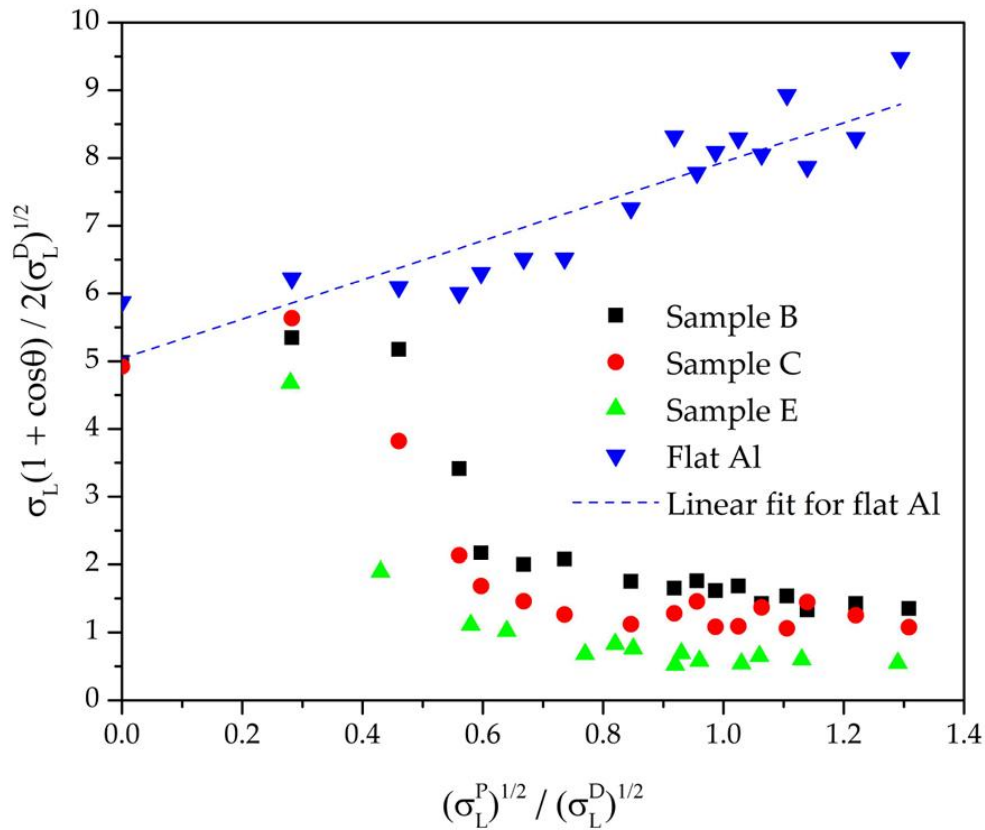


Figure 3.4. Owens-Wendt plots for linear textured Samples B, C, and E

The plot reveals a striking and systematic trend. Sample B, with the narrowest grooves (20 μm), exhibits a clear, well-defined plateau at low x-axis values, indicating a stable Cassie-Baxter state. Sample C, with slightly wider grooves (also 20 μm but with a larger period), shows a similar plateau, although it is slightly less pronounced. However, Sample E, with the widest grooves (45 μm), shows a dramatic failure of the plateau. The data points for Sample E begin to align more closely with the behavior of the flat surface (blue triangles), indicating a transition from the Cassie-Baxter state to the Wenzel state, where the liquid fully penetrates the grooves and wets the entire surface area, including the bottoms of the grooves.

3.2.3 Effectiveness, stability, and durability of chemical modifiers: a comparative study

The choice of chemical modifier is as critical as the surface texture itself in determining the ultimate performance and, crucially, the long-term stability and durability of a superhydrophobic coating. To systematically investigate this, Sample E

(which, as shown above, represents the most challenging geometry due to its wide grooves) was selected as a test platform and treated with four different classes of hydrophobic agents, representing a range of chemical functionalities, surface energies, and expected stabilities. The stability of the resulting hydrophobic layer was first evaluated by analyzing the surface composition using energy-dispersive X-ray spectroscopy (EDS). Figure 3.5 shows the SEM image of Sample E with the four areas selected for EDS analysis, and Table 3.2 presents the quantitative elemental composition data.

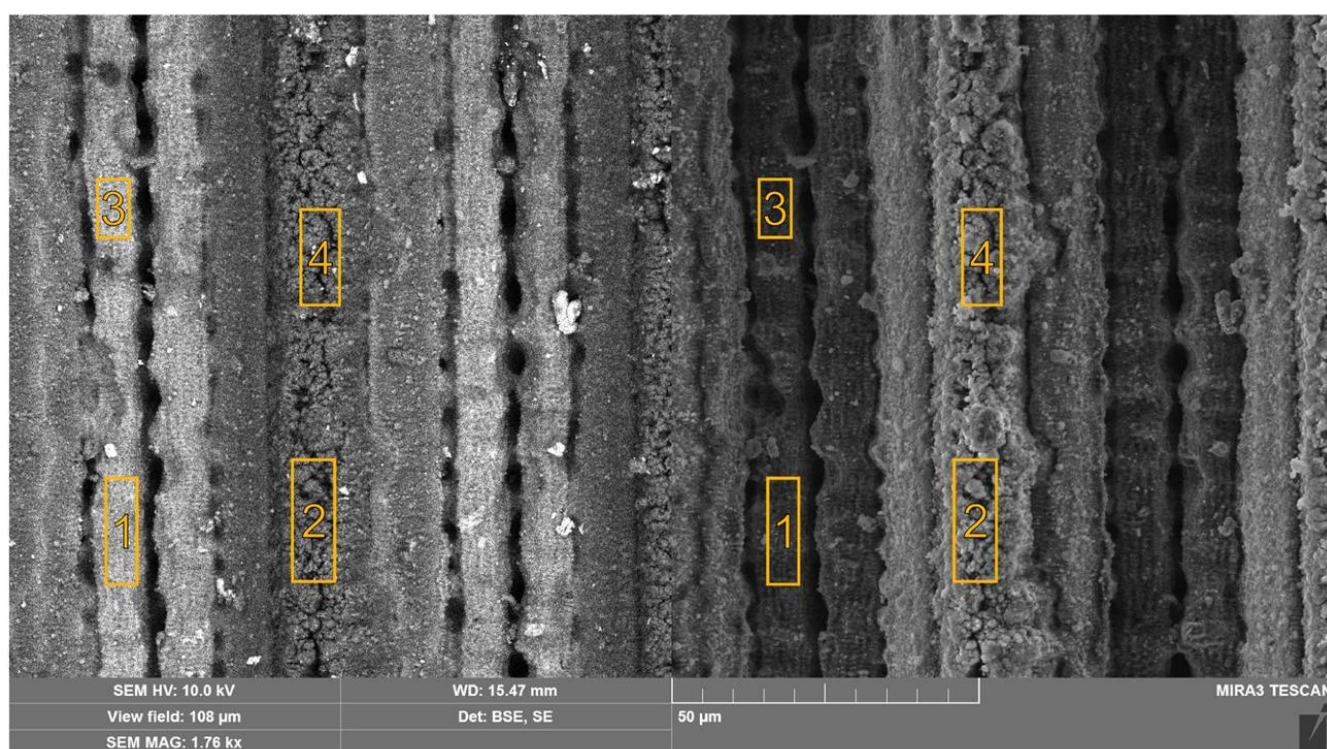


Figure 3.5: SEM image of Sample E

Table 3.1. Elemental composition (wt. %) of the surface in the scanning area according to the analysis of energy dispersive spectroscopy (EDS).

Area	C	O	Mg	Al
1	11.4	8.04	3.41	77.15
2	13.32	38.9	6.04	41.74

3	10.12	6.58	3.22	80.08
4	14.93	28.27	4.52	52.28

The EDS analysis provides crucial insights into the distribution and coverage of the chemical modifier. First, the data confirm the successful adsorption of organic modifiers on the surface, as evidenced by the significantly increased carbon content compared to a clean, untreated aluminum oxide surface (which would have negligible carbon). Second, and more importantly, the analysis reveals a non-uniform distribution of the modifier across the textured surface. Specifically, the carbon content is substantially higher on the tops of the protrusions (areas 1 and 4: 11.40 wt.% and 14.93 wt.%, respectively) compared to the bottoms of the grooves (areas 2 and 3: 13.32 wt.% and 10.12 wt.%, respectively). This non-uniformity can be attributed to several factors: (1) the tops of the protrusions are more accessible to the modifier solution during the immersion process; (2) capillary forces may hinder the penetration of the solution into the narrow grooves; and (3) during the drying process, the solvent may evaporate preferentially from the protrusions, leaving a higher concentration of modifier there. This non-uniform coverage has important implications for the stability of the Cassie-Baxter state, as the tops of the protrusions are the primary contact points with the liquid droplet.

Furthermore, the EDS data reveal that the oxygen content is significantly higher in the grooves (areas 2 and 4: 38.90 wt.% and 28.27 wt.%) compared to the protrusions (areas 1 and 3: 8.04 wt.% and 6.58 wt.%). This indicates that the aluminum oxide layer is thicker or more exposed in the grooves, which may be due to preferential oxidation in these regions or incomplete coverage by the organic modifier. The presence of magnesium (Mg) in all areas is due to the alloying element in the 7500 aluminum alloy.

Having confirmed the presence of the modifier, the next step was to evaluate its effectiveness in reducing the surface energy and promoting hydrophobicity. The performance of the four modifiers - self-hydrophobization (adsorbed atmospheric

hydrocarbons), stearic acid, squalane, and POTS - is compared in the Owens-Wendt plots shown in Figure 3.6.

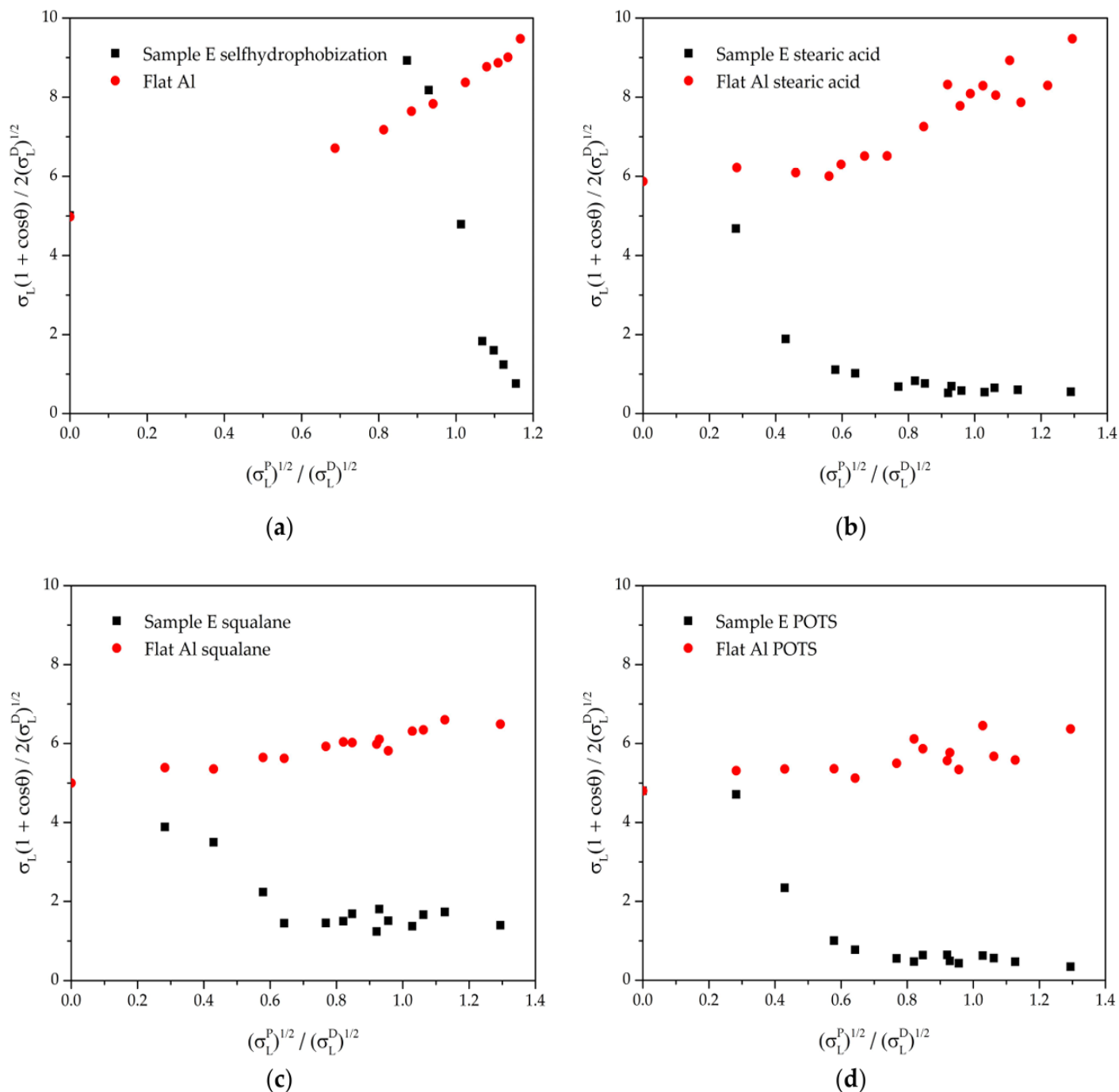


Figure 3.6. Owens-Wendt plots for sample “E” (a) with self-hydrophobization and modified: (b) with stearic acid; (c) with squalane; and (d) with POTS.

The results reveal a clear performance hierarchy among the four modifiers. Figure 3.6(a) shows the Owens-Wendt plot for Sample E after 2 months of exposure to laboratory air, without any intentional chemical modification. The plot shows a narrow

plateau, indicating that some degree of hydrophobicity has been achieved through the spontaneous adsorption of hydrocarbons from the atmosphere. However, the plateau is not very pronounced, and the data points show significant scatter, indicating that the "self-hydrophobization" is weak and unstable. This is consistent with the fact that the adsorbed layer is likely to be a mixture of various hydrocarbons with varying chain lengths and functionalities, resulting in a disordered, poorly defined surface chemistry.

Figure 3.6(b) shows the Owens-Wendt plot for Sample E treated with stearic acid. The plot shows a much more pronounced and stable plateau, indicating that stearic acid is significantly more effective than self-hydrophobization. Stearic acid, a long-chain fatty acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$), is known to form well-ordered, densely packed monolayers on metal oxide surfaces through the chemisorption of the carboxylic acid head group ($-\text{COOH}$) to surface hydroxyl groups, with the hydrophobic alkyl chains ($-\text{CH}_2-$) extending outward. This ordered structure results in a low surface energy and excellent water repellency.

Figure 3.6(c) shows the Owens-Wendt plot for Sample E treated with squalane. Squalane, a branched, saturated hydrocarbon ($\text{C}_{30}\text{H}_{62}$), is chemically inert and non-polar. The plot shows a plateau, but it is less pronounced than that for stearic acid, and the data points show more scatter. This indicates that squalane is less effective than stearic acid. This can be attributed to the fact that squalane, being a purely hydrocarbon molecule without any functional groups, can only adsorb to the surface through weak van der Waals forces. This results in a less stable and less ordered layer compared to the chemisorbed stearic acid monolayer. Moreover, the branched structure of squalane may prevent the formation of a densely packed layer.

Figure 3.6(d) shows the Owens-Wendt plot for Sample E treated with POTS (1H,1H,2H,2H-perfluorooctyltriethoxysilane). The plot shows the most pronounced and stable plateau of all four modifiers, indicating that POTS is the most effective. POTS is a fluoroalkylsilane, which combines the advantages of both silane chemistry (strong covalent bonding to the surface through Si-O-Al bonds) and fluorinated chemistry (exceptionally low surface energy due to the C-F bonds). The triethoxysilane head group ($-\text{Si}(\text{OEt})_3$) hydrolyzes in the presence of moisture to form silanol groups

(-Si(OH)₃), which then condense with surface hydroxyl groups on the aluminum oxide to form a stable, covalently bonded siloxane network. The perfluorooctyl tail (-CF₂-CF₃) extends outward, presenting a surface with one of the lowest known surface energies (~6-10 mN/m). The combination of strong chemical bonding and ultra-low surface energy makes POTS the most effective and durable modifier.

Sample (Figure)	σ_{TS}^D	σ_S^D	$\sigma_{TS}^D / \sigma_S^D, \%$	Critical σ_L^P
M + OCTEO (Figure 3.2)	1	18	5.56	9.96
N + OCTEO (Figure 3.2)	0.17	18	0.94	9.96
B + Stearic acid (Figure 3.4)	1.82	25.3	7.19	9.3
C + Stearic acid (Figure 3.4)	1.16	25.3	4.58	9.3
E + Stearic acid (Figure 3.4)	0.24	25.3	0.94	9.3
E + 2 months (Figure 3.6a)	0.58	22.7	2.56	30.6
E + Stearic acid (Figure 3.6b)	0.24	25.3	0.94	9.3
E + Squalane (Figure 3.6c)	5.61	24.4	22.9	11
E + POTS (Figure 3.6d)	0.11	21	0.52	8

The quantitative surface energy data extracted from the Owens-Wendt plots are summarized in Table 3.3.

Table 3.2. Surface energy components (dispersive σ_S^D and polar σ_{TS}^D) of femtosecond laser textured samples with different modifiers, as determined by the Owens-Wendt method.

The table clearly shows that POTS and stearic acid yield the lowest polar surface energy components ($\sigma_{TS}^D = 0.11$ mN/m and 0.24 mN/m, respectively), which is the key

to repelling water. Squalane yields a significantly higher polar component ($\sigma_{TS}^D = 5.61$ mN/m), and self-hydrophobization yields the highest ($\sigma_{TS}^D = 0.58$ mN/m). The dispersive component (σ_S^D) is relatively similar for all modifiers, ranging from 18.0 to 25.3 mN/m. This confirms that minimizing the polar component is the most direct and effective route to achieving superhydrophobicity.

Finally, the effect of modifier concentration was investigated using stearic acid on Sample E. As shown in Figure 3.7, increasing the concentration of stearic acid in the treatment solution improved the hydrophobicity, but only up to an optimal concentration.

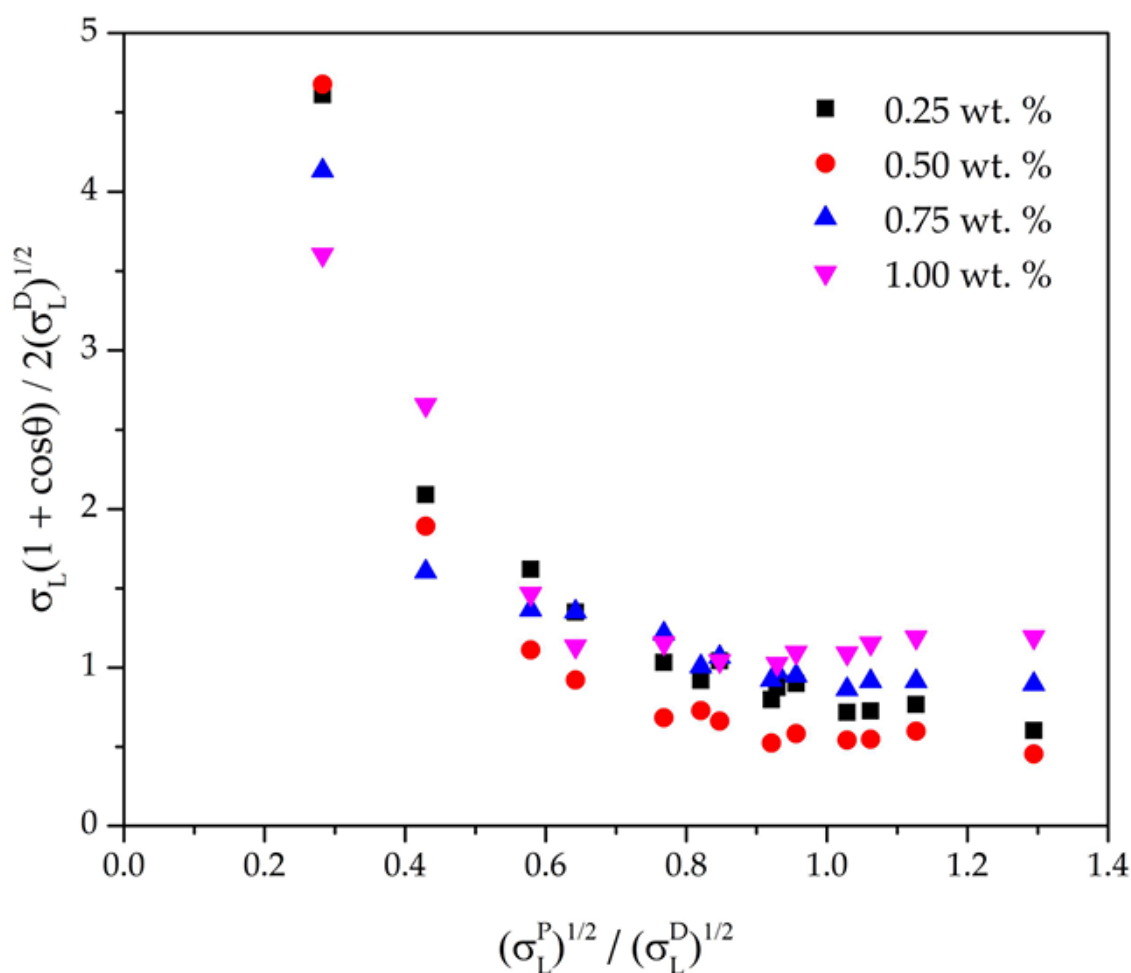


Figure 3.7. Owens-Wendt plot for sample “E” treated with a different amount of stearic acid.

At the lowest concentration (0.25 wt.%), the plateau is weak, indicating incomplete surface coverage. At 0.50 wt.%, the plateau is well-defined and

pronounced, indicating optimal coverage. However, at higher concentrations (0.75 wt.% and 1.00 wt.%), the plateau begins to degrade, and the data points show more scatter. This suggests that at high concentrations, the modifier may form a thicker, multilayer coating that is less ordered and may partially fill the texture, reducing its effectiveness. This demonstrates that there is an optimal concentration for the modifier, and that simply increasing the concentration does not always lead to better performance.

3.2.4 Dynamic wetting behavior on large-scale pdms micro-textures: pinning, depinning, and the breakdown of classical models

Having established a comprehensive understanding of the role of texture and chemistry at the micro- and nano-scales on aluminum, the investigation was then extended to a different material system (PDMS) and a significantly larger scale of texture (tens to hundreds of micrometers) to explore the limits of applicability of classical wetting models and to characterize the dynamic wetting phenomena that become dominant in this regime. These large-scale textures were fabricated by replicating metal molds, as illustrated in Figure 3.8.

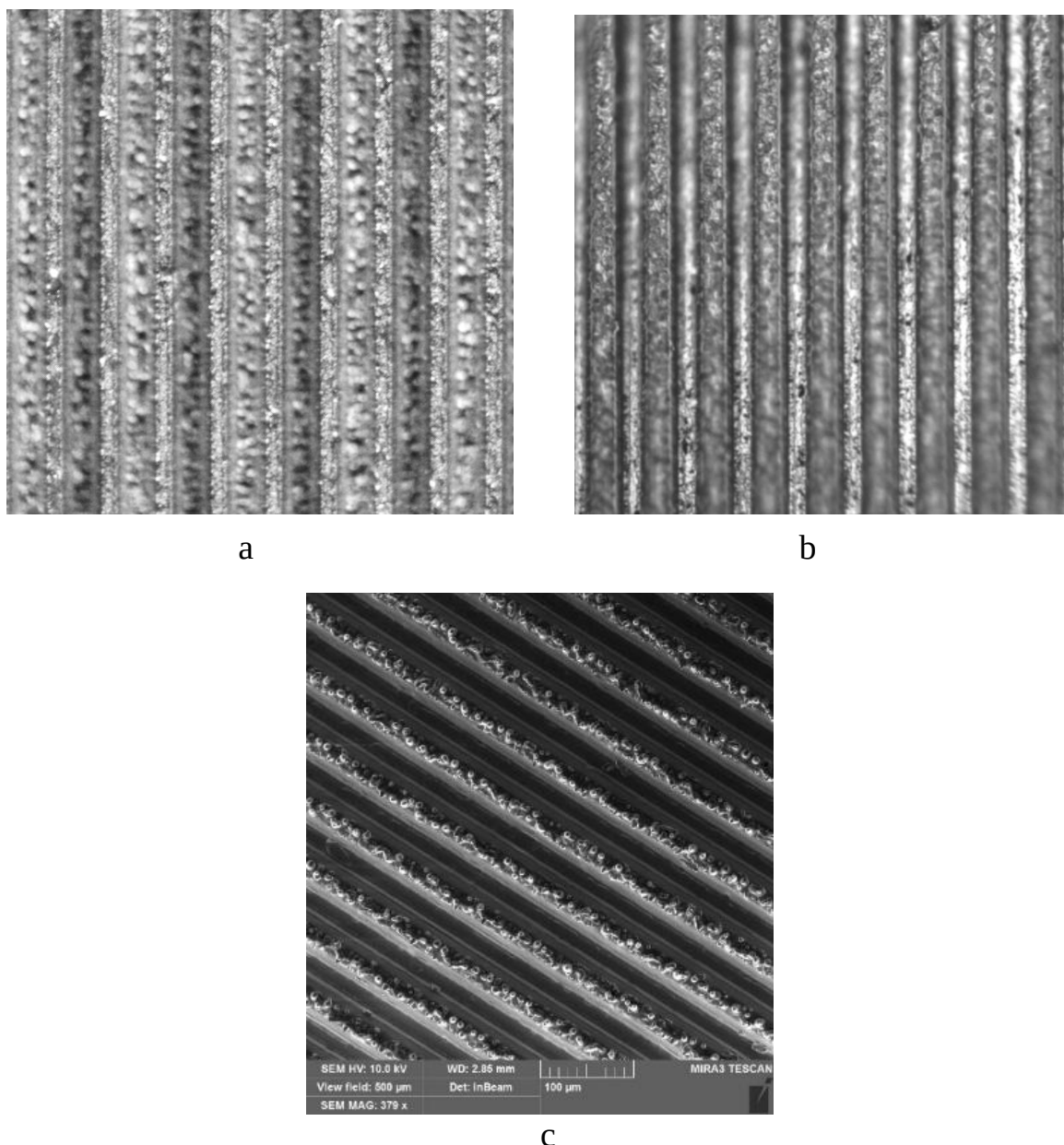


Figure 3.8. Transition of structure from metal template to PDMS mold: a femtosecond laser textured AISI 304 stainless steel template; b – PDMS mold formed on the template surface (optical microscopy); c – SEM image of asperities top.

Figure 3.8(a) shows an SEM image of the laser-textured stainless steel template, which exhibits a periodic array of grooves with sharp edges and relatively flat bottoms. Figure 3.8(b) shows an optical microscopy image of the resulting PDMS mold after curing and demolding. The image clearly shows that the PDMS has faithfully replicated the texture of the metal template, with the grooves in the metal now appearing as ridges in the PDMS. Figure 3.8(c) shows a high-magnification SEM image of the tops of the PDMS asperities, confirming the high fidelity of the replication

process. The PDMS surface exhibits a smooth, defect-free morphology, indicating that the demolding process was successful and did not cause any tearing or deformation of the features.

Table 3.3. Geometry of sample textures

Sample notation	Texture period, μm	Trench width
1	60	15
2	100	50
3	750	300

As shown in Table 3.3, three samples with significantly different texture scales were fabricated: Sample 1 with a period of 60 μm and a trench width of 15 μm ; Sample 2 with a period of 100 μm and a trench width of 50 μm ; and Sample 3 with a period of 750 μm and a trench width of 300 μm . These large, linear grooves, with dimensions comparable to or even exceeding the size of a typical sessile droplet used for contact angle measurements ($\sim 5 \mu\text{L}$, diameter $\sim 2\text{-}3 \text{ mm}$), were expected to induce strong wetting anisotropy and dynamic effects.

Indeed, as shown in Figure 3.9, the apparent contact angle was found to be highly dependent on the viewing direction relative to the groove orientation.

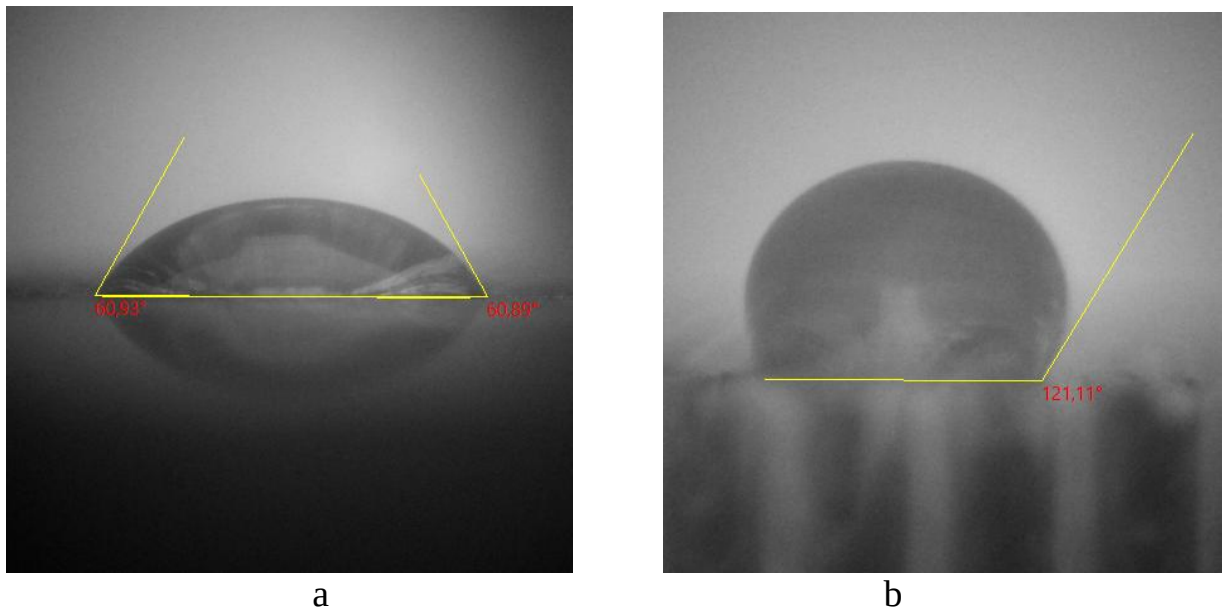


Figure 3.9. Static contact angles in dependence on texture orientation: a – longitude; b - transverse.

When viewed parallel to the grooves (longitude, Figure 3.9(a)), the droplet appeared nearly spherical with a high contact angle, similar to what would be observed on a flat PDMS surface. This is because, in this viewing direction, the grooves do not significantly impede the contact line, and the droplet can maintain a relatively circular footprint. However, when viewed perpendicular to the grooves (transverse, Figure 3.9(b)), the droplet exhibited a dramatically different shape. The droplet spread along the channels, adopting an elongated, rectangular footprint, and the apparent contact angle was much lower. This strong anisotropy is a direct consequence of the large-scale, linear geometry of the texture. The grooves act as channels that guide the liquid flow, leading to preferential spreading in the direction parallel to the grooves.

More importantly, the dynamic behavior of the droplet was characterized by discrete, jump-like motions, rather than the smooth, continuous spreading observed on flat surfaces. Figure 3.10 captures a sequence of frames from a video recording of a droplet being inflated on a vertically mounted PDMS sample (Sample 2).

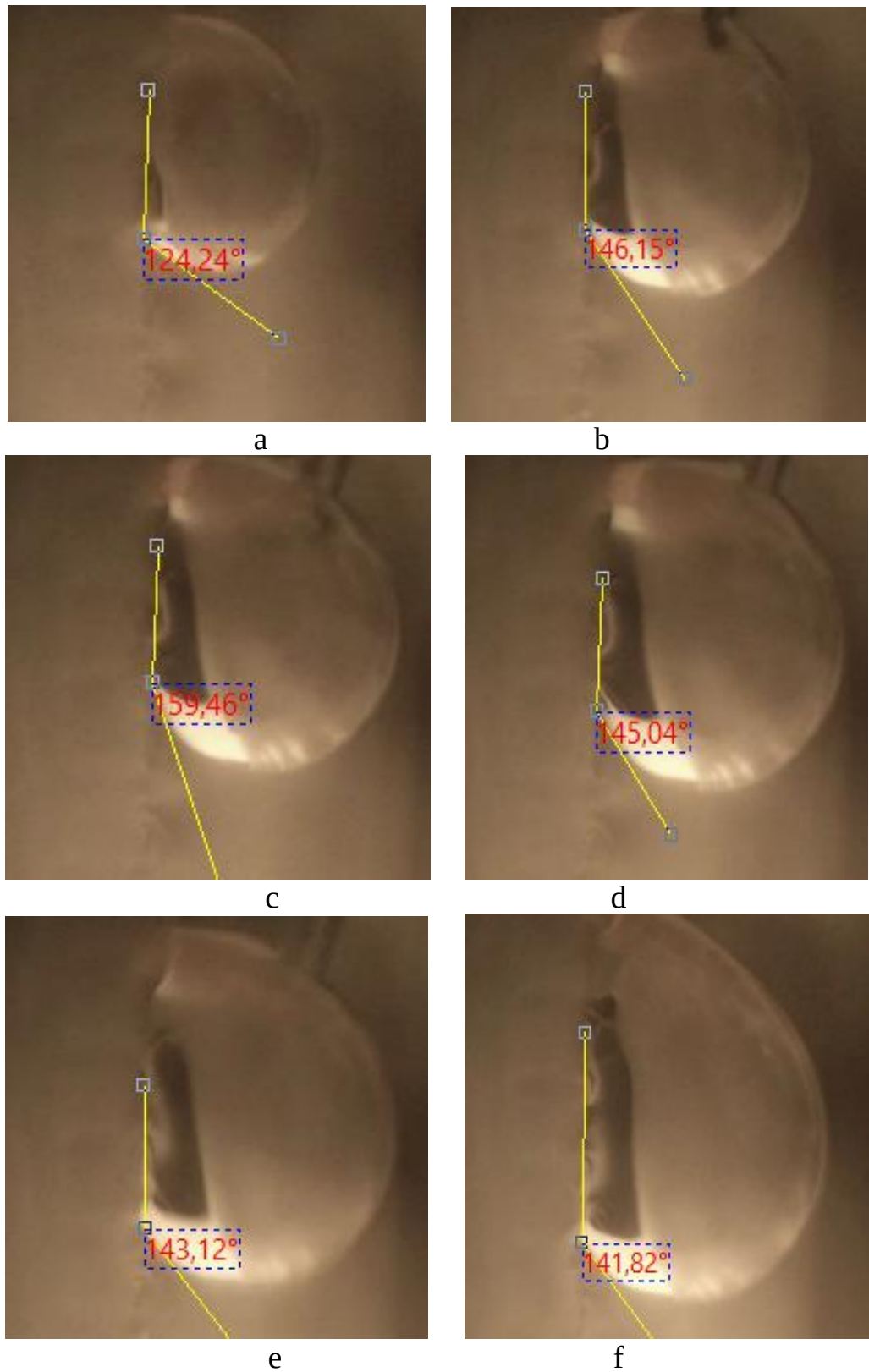


Figure 3.10. Experimental values of advancing contact angle on the texture 2: a – c – inflation (increase of droplet volume), between c and d – jumping of three-phase contact line to the next (lowest) trench; d–f droplet stabilization.

The sequence clearly illustrates the pinning-depinning mechanism. In frames (a) through (c), the droplet volume is gradually increased by injecting water through a

needle. As the volume increases, the contact angle also increases, but the contact line remains pinned on the edge of a groove. The contact line is unable to advance smoothly because it is energetically unfavorable for it to move down the steep sidewall of the groove and into the next trench. The pinning force arises from the energy barrier associated with increasing the solid-liquid interfacial area as the contact line moves from the top of a ridge into the adjacent trench. This energy barrier is proportional to the height of the ridge and the surface tension of the liquid. As the droplet continues to inflate, the contact angle increases until it reaches a critical value, known as the advancing contact angle (θ_a). At this critical point, the driving force (due to the increased Laplace pressure inside the droplet) overcomes the pinning force, and a sudden depinning event occurs (between frames (c) and (d)). The contact line rapidly jumps to the next trench, and the droplet undergoes a sudden change in shape. This depinning event is followed by a series of damped oscillations (frames (d) through (f)) as the droplet relaxes to a new equilibrium configuration. These oscillations are driven by the interplay between the kinetic energy of the moving liquid, the surface tension, and the viscous dissipation.

The quantitative wetting parameters extracted from these dynamic measurements are summarized in Table 3.4.

Table 3.4. Wetting parameters of textures

Sample	Advancing contact angle θ_a , °	Receding contact angle θ_r , °	Equilibrium contact angle $(\theta_a + \theta_r)/2$, °	Wetting hysteresis, $\theta_a - \theta_r$, °
1	164±2	42±1	103	122
2	160±2	46±1	103	114
3	154±2	48±1	101	106

The data reveal several important trends. First, despite the large differences in texture size (period ranging from 60 μm to 750 μm , spanning more than an order of

magnitude), all three samples showed remarkably similar advancing contact angles, ranging from 154° to 164°. This suggests that the advancing contact angle is primarily determined by the local geometry at the contact line (i.e., the shape of the ridge edge) and the intrinsic contact angle of the material, rather than by the overall texture scale. Second, the receding contact angles were also relatively similar, ranging from 42° to 48°. Third, the equilibrium contact angle, calculated as the average of the advancing and receding angles, was approximately 101-103° for all three samples. This value is surprisingly close to the static contact angle of untextured PDMS reported in the literature (~104°), suggesting that at this large scale, the texture has a relatively minor effect on the equilibrium wetting state. Fourth, the wetting hysteresis ($\theta_a - \theta_r$) was very large, ranging from 106° to 122°. This large hysteresis is a direct consequence of the strong pinning forces associated with the large-scale texture features.

Finally, the experimental equilibrium contact angles were compared to the predictions of the classical Wenzel model, which is often used to predict the contact angle on rough surfaces. The results of this comparison are shown in Table 3.5.

Table 3.5. Comparison of experimental equilibrium contact angles with values calculated using the Wenzel equation.

Sample	Equilibrium contact angle of flat surface $\theta_f, ^\circ$	Calculated roughness, r	Equilibrium contact angle derived from Wenzel eq., $\theta_w, ^\circ$
1		1.3	132
2	102	1.2	122
3		1.1	112

The Wenzel model failed dramatically. The predicted contact angles (θ_w is 112-132°) were significantly higher than the measured equilibrium values (θ_f is 102°). In fact, the predicted values were much closer to the measured advancing contact angles (θ_a is 154-164°) than to the equilibrium values. This large discrepancy highlights a fundamental breakdown of the classical Wenzel model when the texture size is no

longer negligible compared to the droplet size. The Wenzel model is based on the assumption that the surface roughness can be treated as a continuous, averaged property, and that the liquid fully wets the entire rough surface. However, in the present case, the texture features are large and discrete, and the droplet interacts with them in a highly non-uniform manner. The contact line pins on individual ridges, and the wetting state is determined by a complex balance of pinning forces, depinning forces, and the dynamic behavior of the liquid. These effects are not captured by the simple Wenzel equation, which only considers the thermodynamic equilibrium state.

3.3. Integrated design principles for superhydrophobic surfaces

By synthesizing the findings from the comprehensive, multi-scale analysis of both aluminum and PDMS surfaces, spanning length scales from tens of nanometers to hundreds of micrometers, several unified design principles emerge that can guide the rational engineering of surfaces with tailored wetting properties for specific applications.

The most robust and stable superhydrophobicity is not achieved from a single scale of roughness, but rather from a hierarchical structure that combines features at multiple length scales. The micro-textures provide the primary structural framework to support the droplet and define the overall geometry of the solid-liquid-air interface, while the nano-textures superimposed on top create a high density of pinning sites that stabilize the air-liquid interface and prevent the liquid from sagging or collapsing into the voids. This hierarchical design, directly inspired by natural systems such as the lotus leaf, has been consistently shown to be superior to single-scale textures in terms of both the magnitude of the contact angle and the robustness of the Cassie-Baxter state, as demonstrated by the comparison of Samples M and N in Figures 3.1 and 3.2.

However, there exists an optimal regime for the geometry of micro-textures. If the features are too small, they may not provide sufficient mechanical support for the droplet or may be prone to clogging by contaminants. Conversely, if the features are too large, too wide, or too deep, the liquid can more easily penetrate the structure,

leading to a transition from the desirable Cassie-Baxter state to the undesirable Wenzel state. This transition is governed by the solid-liquid contact fraction in the Cassie-Baxter equation. The systematic study of Samples B, C, and E clearly demonstrated this principle: Sample E, with the widest grooves, exhibited a failure of the Cassie-Baxter plateau, while Samples B and C, with narrower grooves, maintained a stable plateau. The optimal geometry depends on the specific application and the properties of the liquid, but as a general guideline, the solid fraction should be maximized while still maintaining sufficient void space to trap air.

Texture alone, regardless of how sophisticated or hierarchical, is insufficient to achieve robust superhydrophobicity on most engineering materials. A low-surface-energy chemical modifier is absolutely required to reduce the intrinsic wettability of the material and to enable the Cassie-Baxter state. The choice of modifier is critical and depends on several factors, including the chemical functionality and bonding mechanism, the surface energy of the modifier, the stability and durability of the modifier layer under environmental stresses, and cost and environmental considerations. The comparative study of four modifiers clearly showed that molecules that form well-ordered, covalently bonded monolayers with ultra-low surface energies, such as fluoroalkylsilanes like POTS, are far more effective and durable than those that form disordered, physisorbed layers or those that rely on weak adsorption from the atmosphere. Stearic acid represents a good compromise between effectiveness, cost, and environmental friendliness.

The concentration of the chemical modifier must also be carefully optimized. At too low a concentration, the surface coverage will be incomplete, resulting in poor hydrophobicity and instability. At too high a concentration, the modifier may form a thick, multilayer coating that is less ordered, may partially fill the texture, or may even lead to the formation of aggregates that degrade performance. The study of stearic acid concentration on Sample E demonstrated that there is an optimal concentration that yields the best performance, which should be determined experimentally for each modifier and texture combination.

While simple static water contact angle measurements provide a convenient metric for hydrophobicity, they represent only a single data point and do not provide insight into the underlying surface energetics or the stability of the wetting state. The Owens-Wendt method, which deconvolves the total surface free energy into its polar and dispersive components, provides a much more powerful tool for characterizing and optimizing superhydrophobic surfaces. By analyzing the Owens-Wendt plots, one can identify the presence and stability of the Cassie-Baxter plateau, quantify the polar and dispersive components of the surface energy, compare the effectiveness of different textures and modifiers, and predict the wetting behavior with liquids of different polarities. Minimizing the polar component is the most direct and effective route to repelling water.

Finally, the classical wetting models of Wenzel and Cassie-Baxter, while highly effective for predicting the wetting behavior on nano-scale and some micro-scale textures, become increasingly unreliable as the texture dimensions approach or exceed the size of the liquid droplet. In this large-scale regime, the discrete nature of the surface features becomes dominant, and the wetting behavior is governed by complex, dynamic phenomena such as contact line pinning on individual asperities, sudden depinning events, anisotropic droplet spreading, and significant contact angle hysteresis. The failure of the Wenzel model to predict the equilibrium contact angles on the large-scale PDMS textures is a clear demonstration of this limitation. For applications involving large-scale textures or moving liquids, it is essential to characterize the dynamic wetting properties, specifically the advancing contact angle, the receding contact angle, and the resulting hysteresis. Surfaces with high advancing angles but also high hysteresis may appear hydrophobic in static tests but will be "sticky" in dynamic situations, retaining droplets and failing to perform as intended.

3.4. Conclusions of chapter 3

This chapter has presented a comprehensive, multi-scale investigation into the wetting properties of laser-textured superhydrophobic surfaces, seamlessly integrating

findings from both aluminum and PDMS material systems and spanning length scales from tens of nanometers to hundreds of micrometers. The study has demonstrated that achieving robust, durable, and application-specific superhydrophobicity requires a holistic, systems-level approach that carefully considers the synergistic interplay between hierarchical surface texture, low-surface-energy chemistry, and the scale of the application.

Key findings include: (1) Hierarchical, multi-scale roughness combining micro- and nano-features is essential for stabilizing the Cassie-Baxter state. (2) Micro-texture geometry must be optimized; overly wide features lead to Cassie-Baxter state collapse. (3) Chemical modification with molecules that form well-ordered, covalently bonded monolayers (e.g., fluoroalkylsilanes, fatty acids) is far more effective than physisorbed layers. (4) Modifier concentration must be optimized; excessive concentration can degrade performance. (5) The Owens-Wendt method provides a powerful tool for quantifying surface energy components and optimizing surface chemistry. (6) Classical wetting models fail at large scales; dynamic characterization (advancing/receding angles, hysteresis) is essential for predicting real-world performance.

The integrated design principles established in this chapter provide a rational framework for the engineering of next-generation superhydrophobic coatings for a wide range of applications, from self-cleaning surfaces and anti-icing systems to advanced microfluidic devices and biomedical implants.

The results of this chapter were published in:

1. Myronyuk, O., Baklan, D., Vanagas E., Rodin, A. M., **ZUO, Y.** (2023). Owens–Wendt characterization of Femtosecond-Laser-Textured hydrophobic aluminum surfaces. *Coatings* 13 (6), 1104. <https://doi.org/10.3390/coatings13061104>.
2. Myronyuk, O., Baklan, D., Rodin, A., Pitak, Y., Balytska, N., & Zuo, Y. (2025). Determination of 60-500 μm textures on polydimethylsiloxane surfaces wetting properties. *2025 IEEE 6th KhPI Week on Advanced Technology, KhPIWeek 2025*, 1–6. <https://doi.org/10.1109/KhPIWeek61436.2025.11288681>

CHAPTER 4. Hierarchical superhydrophobic coatings: from degradation mechanisms to corrosion protection optimization

The development of advanced functional materials is a cornerstone of modern engineering, enabling innovations across a vast range of applications. Among these, superhydrophobic coatings have garnered significant attention for their potential to provide a passive, environmentally friendly solution to the pervasive problem of corrosion, particularly for lightweight alloys like aluminum[95]. While the fundamental principles of superhydrophobicity are well-established, the transition from laboratory demonstrations to real-world industrial applications has been hindered by a critical, unresolved issue: the lack of long-term durability[96-98]. Most reported superhydrophobic surfaces exhibit impressive initial performance but fail rapidly when subjected to the combined mechanical, chemical, and radiative stresses of a typical operational environment [98-106]. This chapter directly confronts this durability challenge, which represents the primary bottleneck to the widespread adoption of this promising technology.

The theoretical and characterization frameworks established in the preceding chapters provide the foundation for this investigation. Making the leap from a laboratory curiosity to a robust engineering solution requires a deep understanding of the complex degradation pathways that undermine performance. This chapter presents the core of the dissertation's experimental work, detailing a systematic investigation that progresses from a fundamental deconstruction of failure mechanisms to the rational design of optimized, corrosion-resistant coatings.

The research was structured as a progressive, two-stage narrative. The first stage aimed to isolate and identify the primary degradation pathways. By subjecting coatings to combined environmental stressors, specifically ultraviolet (UV) radiation and hydrodynamic shear, the study pinpointed the most vulnerable component within the multi-part composite system[107-109]. A systematic evaluation of the relative stability of the polymer binder, the silane-treated nanofiller, and the stearic acid-treated

microfiller revealed the polymer matrix as the principal weak link[110-115]. This finding provided a clear, evidence-based design principle that guided the subsequent optimization efforts.

The second stage applied this mechanistic insight to engineer optimized formulations that balance superhydrophobicity with long-term corrosion resistance. Three distinct coating formulations were designed to test the hypothesis that minimizing the vulnerable polymer content while maximizing the loading of robust inorganic particles would yield superior protection. Rigorous electrochemical testing in a corrosive saline environment not only validated the design principles from Stage 1 but also revealed the optimal compositional balance required for exceptional, long-term barrier performance[116].

To execute this two-stage investigation, all coatings were fabricated via pneumatic spraying. A comprehensive suite of characterization techniques was employed to track the evolution of the coatings' properties. Surface morphology and chemistry were monitored using scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR), while wettability was quantified through water contact angle (WCA) measurements. Durability was assessed under accelerated UV aging and immersion conditions, and corrosion resistance was rigorously evaluated using electrochemical methods, including potentiodynamic polarization and impedance spectroscopy (EIS). The detailed protocols for all fabrication and characterization procedures are provided in Chapter 2.

Following this logical progression, Section 4.1 presents the results of the Stage 1 degradation study, and Section 4.2 details the Stage 2 corrosion optimization. The chapter concludes with an integrated discussion in Section 4.3 that synthesizes the findings from both stages, articulates a set of validated design principles for durable superhydrophobic coatings, and establishes the experimental foundation for the computational modeling work presented in Chapter 5.

4.1. Stage 1: Understanding Degradation Mechanisms

The initial stage of this research was designed to elucidate the complex degradation process of the composite superhydrophobic coatings. Identifying the most susceptible components and understanding the sequence of failure is a prerequisite for the rational design of more durable materials. To this end, this investigation aimed to address three fundamental aspects:

- a) The identification of which component - the polymer binder or the hydrophobic treatment on the filler particles - initiates degradation under environmental stress.
- b) The influence of the chemical nature of the hydrophobic treatment (i.e., inorganic silane versus organic stearic acid) on the coating's UV stability.
- c) The sequential failure mechanism of the coating when subjected to the combined effects of UV radiation and mechanical water flow.

4.1.1 Determining Critical Polymer Content

Before assessing degradation, it was necessary to establish the minimum amount of polymer binder required to form a cohesive film and achieve a superhydrophobic state. A coating with insufficient binder will fail mechanically, while one with excessive binder may have poor superhydrophobicity and be more susceptible to degradation. Figure 4.1 shows the water contact angle as a function of polymer content for four different filler-binder systems. A sharp transition from a hydrophilic or merely hydrophobic state (Wenzel) to a superhydrophobic state (Cassie-Baxter) is observed as the polymer content increases. The critical polymer concentration (CPC) marks the point where the particles are sufficiently encapsulated to form a stable, air-trapping hierarchical structure.

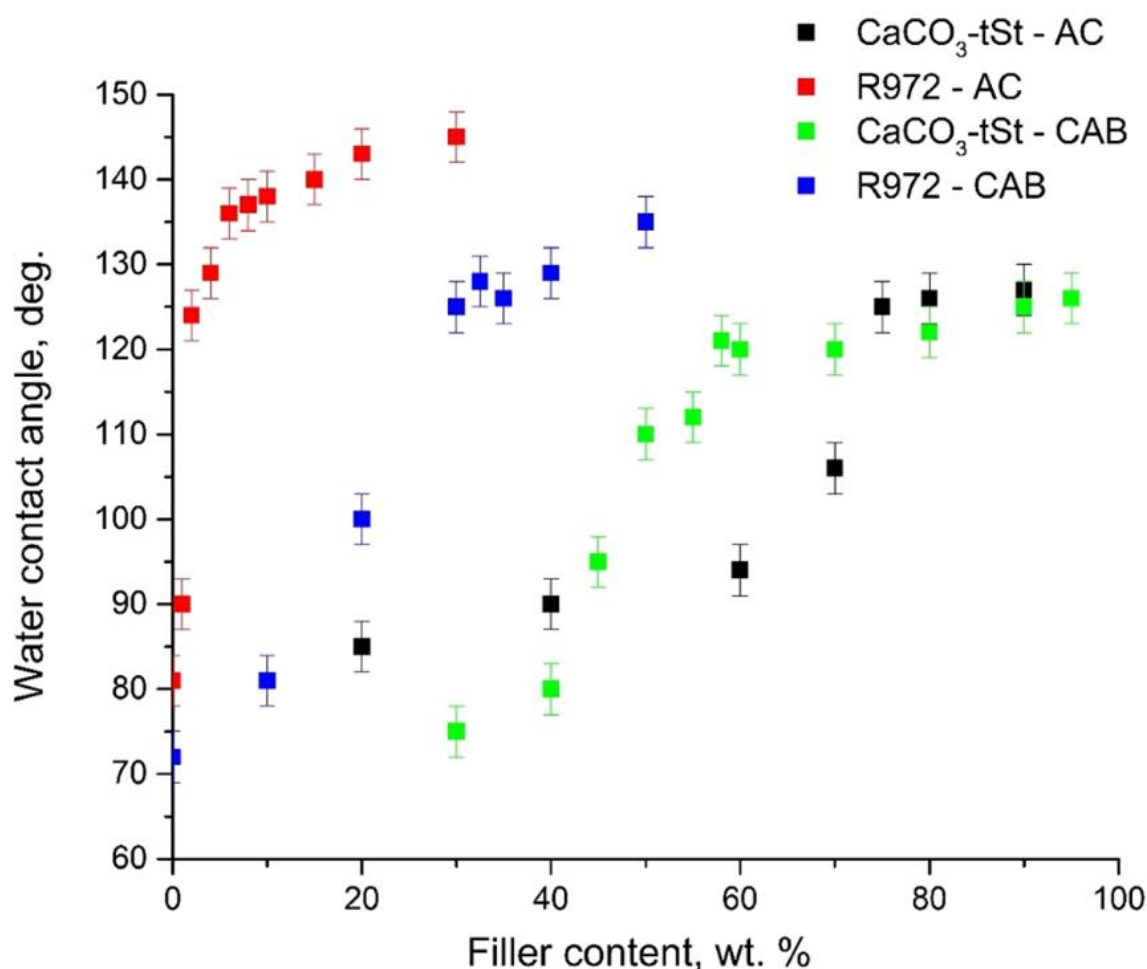


Figure 4.1. Water contact angle as a function of filler content for CaCO₃-tSt and R972 particles in AC and CAB polymer matrices.

The results presented in Figure 4.1. reveal a critical insight into coating formulation strategy. The curves exhibit a characteristic sigmoidal shape, progressing from hydrophilic behavior at low filler content (dominated by polymer surface energy) through a transition region, to superhydrophobic behavior at high filler content (dominated by particle-induced roughness and air entrapment). Importantly, the critical filler content - defined as the minimum particle loading required to achieve WCA > 150° - differs dramatically between the two particle systems. The results reveal that the required polymer content depends strongly on both the filler and the binder. The high-surface-area R972 nanofiller required significantly less NeoCryl B 880 binder (6 wt.%) to reach a WCA of 148° compared to the CaCO₃ microfiller (74 wt.% for a WCA of 134°). Furthermore, the NeoCryl B 880 (AC) binder was more efficient than the alternative CAB binder, requiring less material to achieve a superhydrophobic state

with either filler. This is attributed to the lower surface energy and better film-forming properties of the AC polymer. These baseline CPC values informed the selection of compositions for subsequent degradation studies.

For the R972 nanoparticle system, superhydrophobicity is achieved at remarkably low filler content: only 6 wt.% R972 is required in the AC matrix, corresponding to 94 wt.% polymer. The CAB matrix requires slightly higher R972 loading (approximately 32 wt.% filler, 68 wt.% polymer) due to differences in polymer-particle interactions. In contrast, the CaCO_3 -tSt microparticle system requires substantially higher particle loading: approximately 74 wt.% CaCO_3 (26 wt.% polymer) for AC and similar values for CAB to reach the superhydrophobic threshold. This compositional difference has profound implications for durability. While the R972 system achieves higher ultimate contact angles (148° for AC, 124° for CAB), these formulations contain 68-94 wt.% polymer - a composition that, as will be demonstrated in subsequent sections, renders them highly vulnerable to UV degradation. The CaCO_3 system, despite achieving slightly lower maximum contact angles (134° for AC, 122° for CAB), operates at much lower polymer content (26-32 wt.%), suggesting potentially superior durability if the polymer is the weak link in environmental resistance. The surface structure underlying these wettability differences is illustrated in Figure 4.2., which presents SEM micrographs of representative coatings from each system.

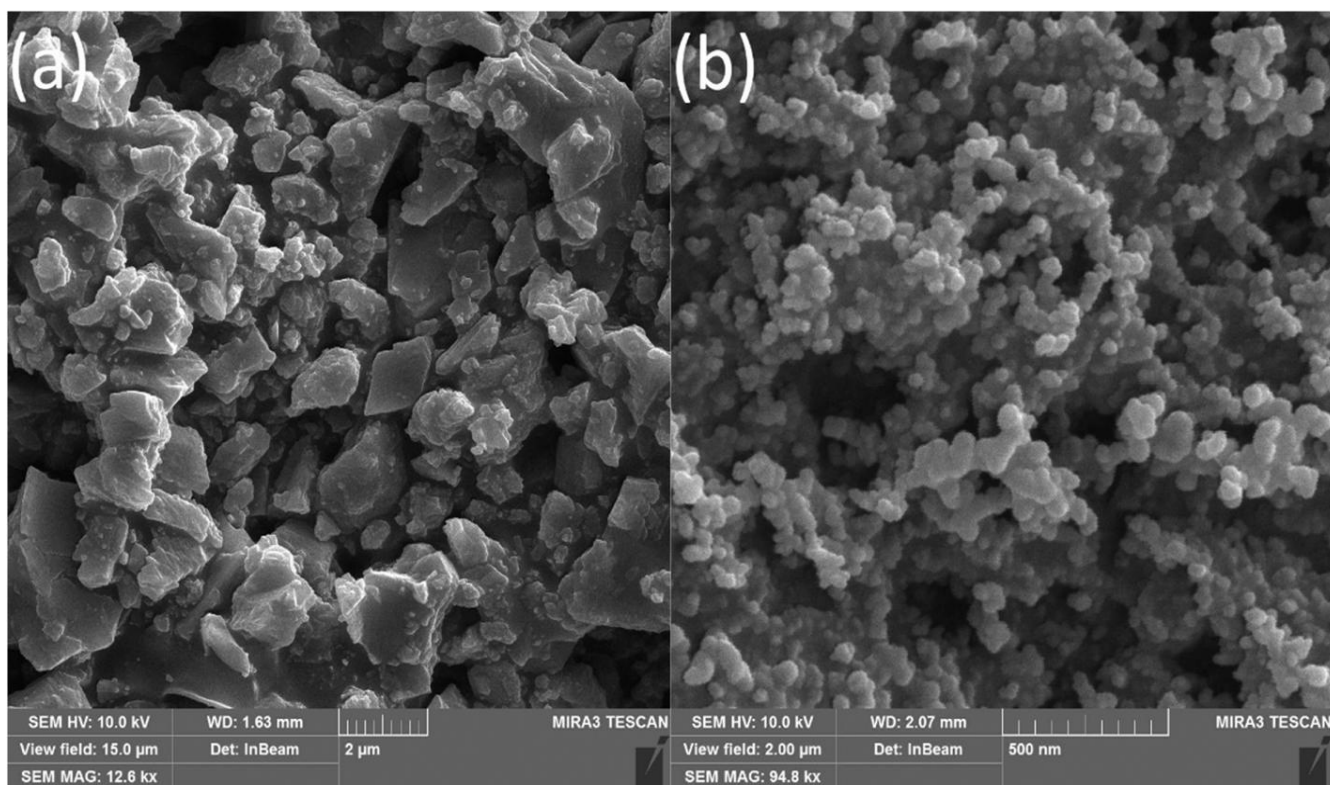


Figure 4.2. Surface structure of coatings textures: (a) 90% CaCO₃-tSt +10% AC and (b) 37,5% R972+62,5% AC.

The CaCO₃ coating (Figure 4.2a) displays a stochastic hierarchical architecture in which coarse microparticles (4.8 μm average size) are interspersed with finer particles, creating multiple length scales of roughness. This structure is characteristic of natural mineral fillers with broad size distributions. The R972 coating (Figure 4.2b) exhibits a more uniform particle size distribution, with the second level of hierarchical structure arising from nanoparticle aggregation rather than inherent size polydispersity. Both structures successfully generate the dual-scale roughness required for superhydrophobicity, but they achieve this through different mechanisms and, critically, at vastly different polymer-to-particle ratios. The key question for durability is whether the polymer component - regardless of its proportion - represents the primary degradation pathway under environmental stress.

4.1.2 UV Resistance of Individual Components

To isolate the most UV-sensitive component, the degradation of the pure polymer binder was compared to that of coatings made with hydrophobically treated particles.

Figure 4.2 illustrates the change in water contact angle for coatings based on the AC polymer (NeoCryl B 880), silane-treated R972 silica, and stearic acid-treated CaCO_3 during accelerated UV exposure.

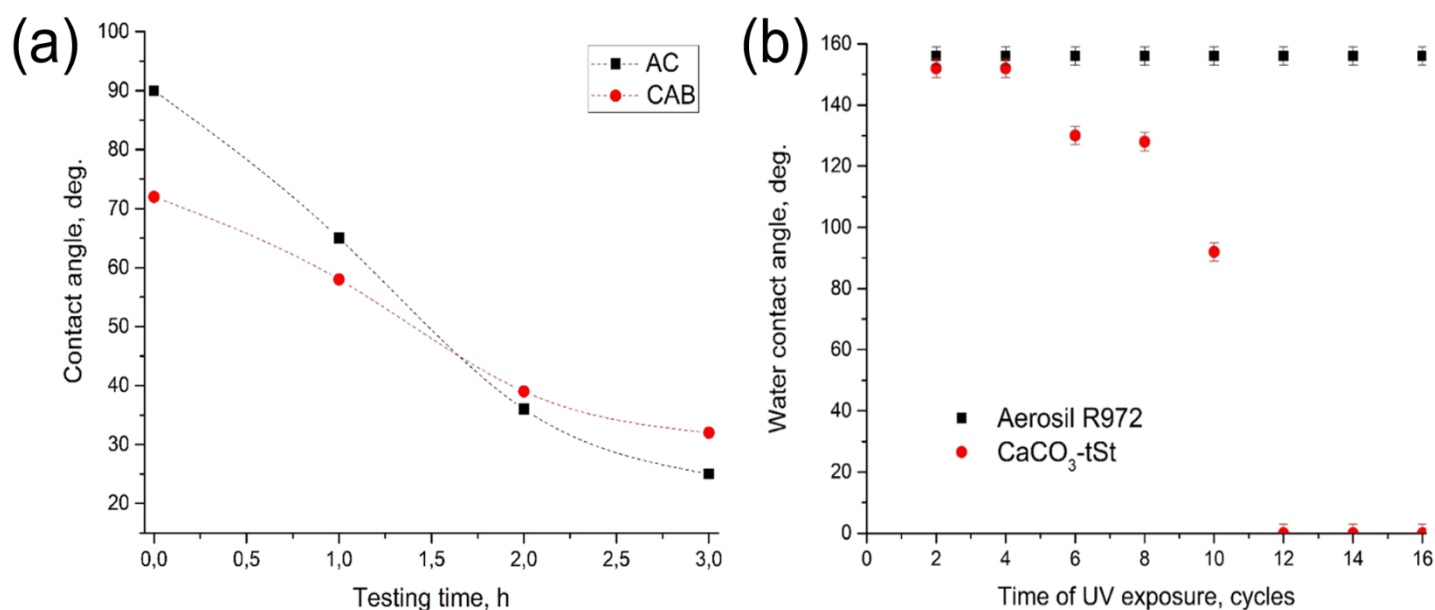


Figure 4.3. UV resistance of a) pure polymer films, b) particle-reinforced coatings

As the Figure 4.3.a) shows, both polymer films undergo rapid and severe hydrophilization under UV exposure. The AC Spolymer, initially exhibiting a contact angle of approximately 90° , degrades to complete wetting ($\text{WCA} < 30^\circ$) within 3 hours of UV exposure. The CAB polymer, despite its reputation for better UV stability, performs even worse in this test, becoming completely hydrophilic after just 1 hour. This dramatic degradation establishes unequivocally that the polymer binder is highly vulnerable to UV-induced hydrophilization, regardless of polymer type. Having identified the polymer as a weak point, the next critical question is whether incorporating hydrophobic particles can mitigate this vulnerability. Figure 4.4 compares the UV resistance of particle-reinforced coatings using different filler types and surface treatments.

As the Figure 4.3.b) shows, the water contact angle evolution for particle-reinforced coatings exposed to UV radiation cycles. The R972 (silane-treated silica) coating maintains superhydrophobicity ($\text{WCA} \approx 150^\circ$) for more than 16 cycles, while

the CaCO_3 -tSt (stearic acid-treated calcite) coating fails after only 4 cycles, dropping below 100° . This stark contrast emphasizes that surface treatment chemistry, rather than particle size or morphology alone, governs UV durability. Both systems produce hierarchical roughness conducive to superhydrophobicity, yet their photostability diverges dramatically. Commercial silane-modified silica (Aerosil R972) benefits from robust covalent Si-O-Si linkages that resist UV-induced oxidation, whereas stearic acid-treated CaCO_3 relies on chemisorption via calcium stearate formation. The organic alkyl chains in the latter remain vulnerable to photo-oxidative cleavage, mirroring degradation pathways in polymer matrices. To elucidate the chemical mechanism underlying polymer degradation, FTIR spectroscopy was employed to track functional group changes during UV aging. Figure 4.4. presents a series of FTIR spectra for the AC polymer film at progressive stages of UV exposure.

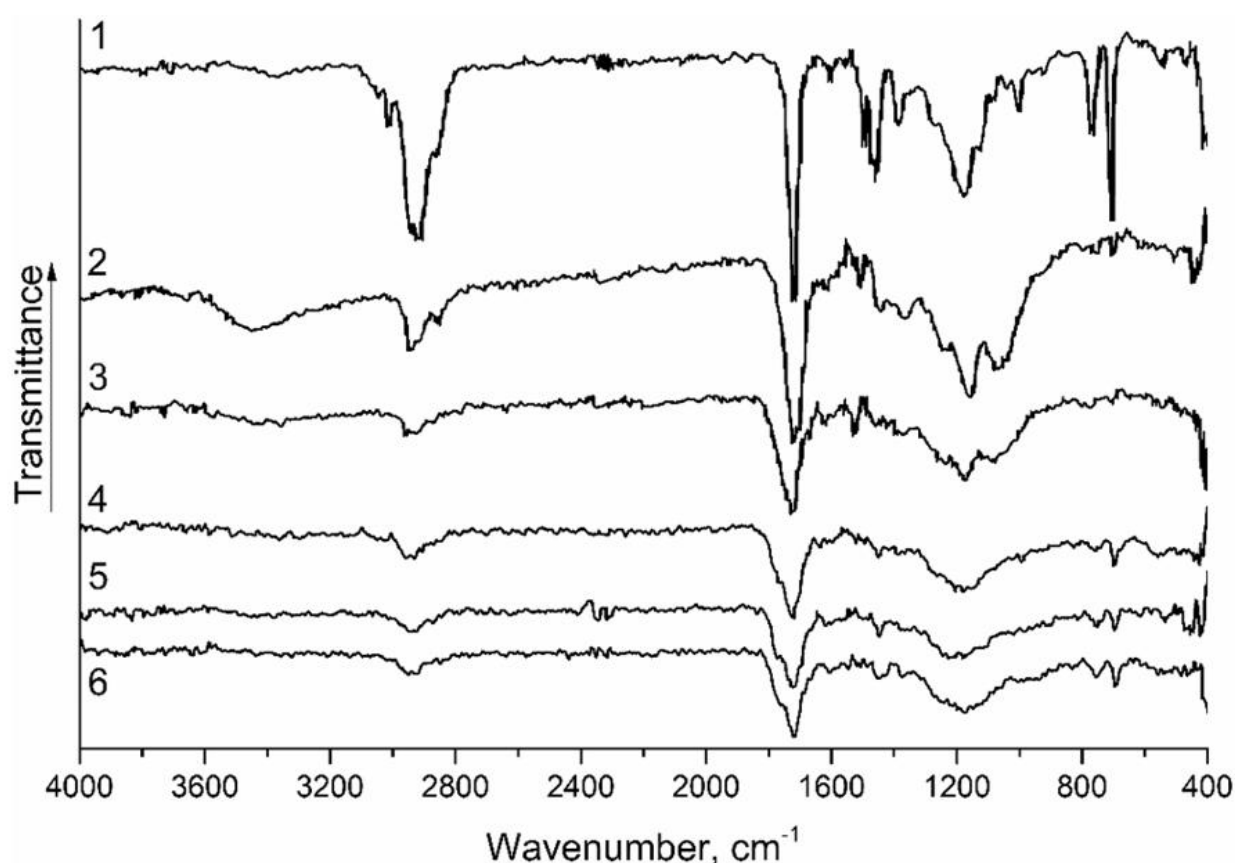


Figure 4.4. FTIR spectra of AC polymer film at various stages of UV exposure: (1) pristine, (2-6) after 10, 20, 30, 45, and 60 minutes of UV irradiation.

Figure 4.4. FTIR spectroscopy provided direct chemical evidence for the degradation mechanism of the polymer. The pristine sample (spectrum 1) shows strong absorption peaks in the 2850-2950 cm^{-1} region, corresponding to the C-H stretching vibrations of hydrophobic alkyl groups. As UV exposure progresses (spectra 2-6, representing 10, 20, 30, 45, and 60 minutes respectively), the intensity of these C-H peaks systematically decreases, while a prominent new peak emerges and grows at approximately 1731 cm^{-1} , characteristic of C=O stretching in carbonyl groups. This spectroscopic evolution provides unambiguous evidence for photo-oxidative degradation: UV radiation initiates free radical reactions that attack the polymer backbone and side chains, converting hydrophobic C-H groups into hydrophilic oxygen-containing functionalities (carbonyls, hydroxyls, carboxylic acids). The accompanying decrease in the C-H stretching band at 2950 cm^{-1} (attributed to CH_2 groups in alkyl side chains) confirms that the hydrophobic character of the polymer is being systematically destroyed at the molecular level. Importantly, this degradation mechanism is not unique to the AC polymer; similar FTIR changes were observed for CAB and other acrylic polymers, confirming that photo-oxidation is a general vulnerability of organic polymer binders in outdoor environments.

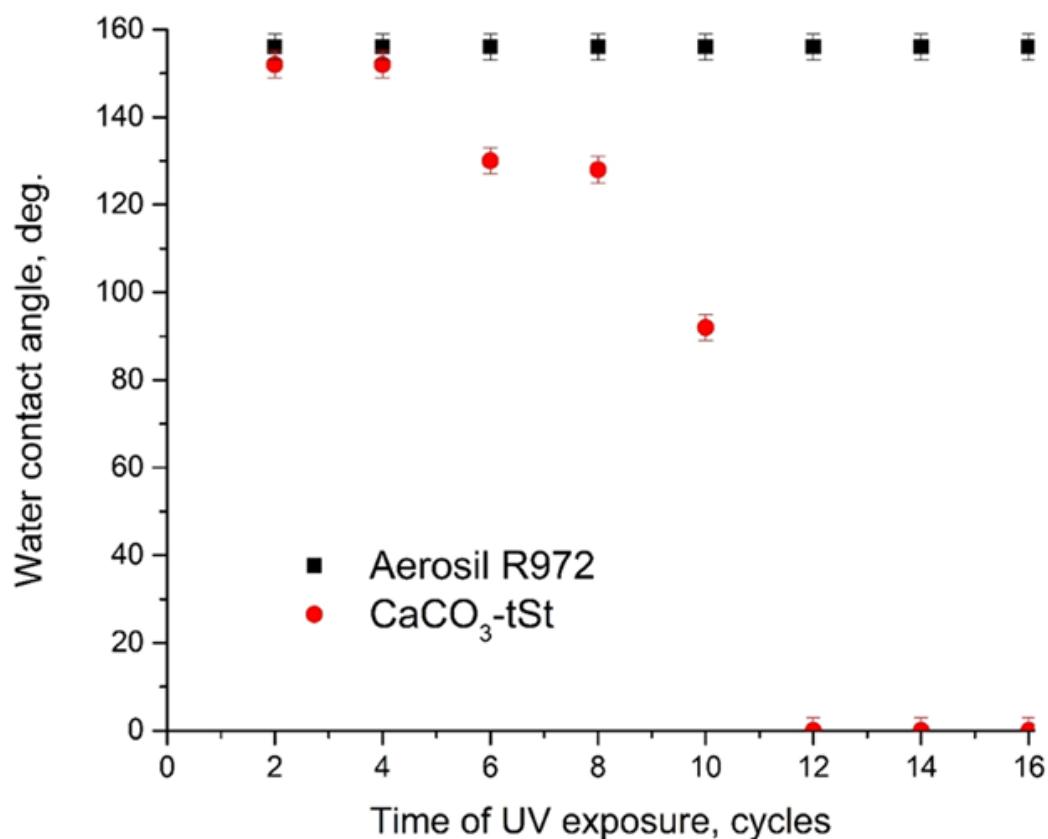


Figure 4.5. Wetting properties of particulate materials exposed to UV radiation.

Figure 4.5. illustrates the water contact angle (WCA) evolution of hydrophobized fillers Aerosil R972 and CaCO₃-tSt under repeated UV exposure cycles, assessing their photostability in potential coating applications. Both materials initially exhibit robust hydrophobicity, with Aerosil R972 maintaining WCAs above 140° across all 16 cycles, demonstrating exceptional UV durability attributable to its stable silane-based surface modification (typically dimethyldichlorosilane or equivalent). In contrast, CaCO₃-tSt shows a precipitous decline, dropping from ~120° to below 40° after 8–10 cycles, consistent with the oxidative degradation of the organic stearate layer under UV irradiation, as reported in prior studies on acid-treated carbonates. This disparity underscores the superior long-term photostability of commercial silica-based hydrophobizers over lab-synthesized stearic acid modifications on CaCO₃, highlighting the need for protective strategies (e.g., UV absorbers) in formulating durable hydrophobic composites.

While UV radiation alone causes chemical degradation of the polymer, real-world outdoor environments subject coatings to combined stresses. To simulate more realistic conditions, a modified accelerated aging protocol was developed in which coated samples were exposed to alternating UV radiation and water flow. This combination tests not only chemical stability but also the mechanical integrity of the degraded coating under hydrodynamic stress.

4.3.3 Static water resistance

The long-term stability of water-repellent coatings in wet or underwater conditions can be compromised by the inherent tendency of polymers, particularly polar ones, to absorb water. To isolate this effect, the performance of both pure polymer films and composite coatings was evaluated during 32 hours of static immersion in water.

Pure polymer films of cellulose acetate butyrate (CAB) and styrene-butyl-methacrylate copolymer (AC) exhibited a reduction in water contact angle (WCA) of 6° and 12°, respectively, which was attributed to water absorption. These initial values were fully restored after drying, indicating a reversible process for the pure polymers.

In contrast, the composite coatings demonstrated a more complex behavior. While the coating based on microscale calcium carbonate (CaCO_3 -tSt) was relatively stable, maintaining a WCA of 102° after 32 hours, the nanoscale silica-based coating lost its superhydrophobic Cassie-Baxter state within the first hour of immersion (Table 4.1). This suggests that the interaction between the polymer and the filler is a critical factor. It is proposed that upon wetting, the adhesion at the polymer-filler interface weakens, allowing water to accumulate at these boundaries.

This mechanism is supported by SEM analysis (Figure 4.6). For the CaCO_3 -based coating, some particles were observed to have detached from the surface, creating well-defined cavities. The silica-based coating behaved similarly, with the surface becoming smoother as particles were washed out. Although a weakened texture may remain, this process identifies the texture-forming particles, and specifically their adhesion to the

polymer matrix, as the most vulnerable component of the system under static wet conditions.

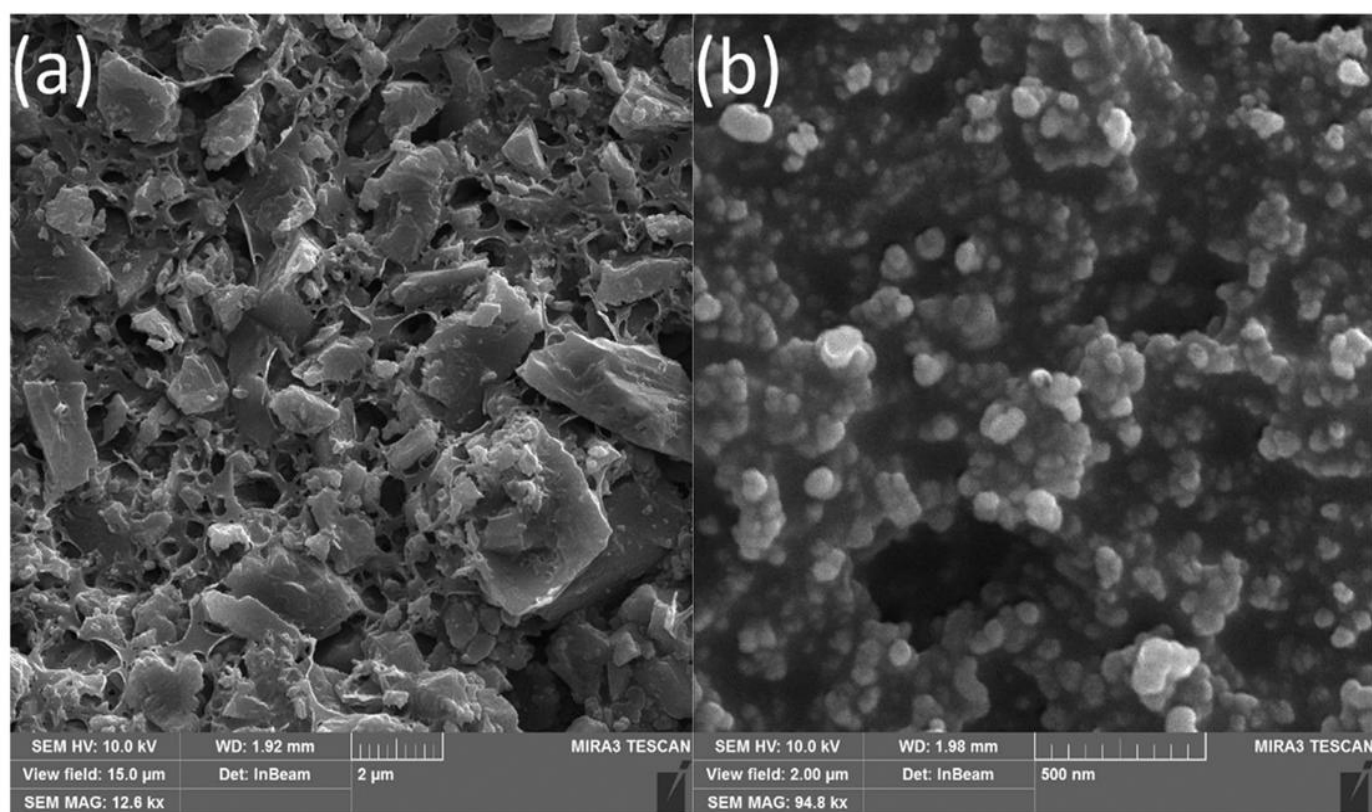


Figure 4.6. SEM micrographs showing surface morphology (a) 90% CaCO₃-tSt +10% AC and (b) 37.5% R972+62.5% AC after 8h of immersion in water.

Table 4.1 Characterization of the water resistance of coatings with the determination of the water contact angles.

Definition of samples	Duration of immersion in water, hours						
	0	0.5	1	2	4	8	32
37.5% R972 + 62.5% AC	140°	140°	137°	120°	116°	113°	90°
32% R972 + 68% CAB	75°	69°	60°	60°	60°	60°	60°
75% CaCO ₃ -tSt + 25% AC	120°	119°	118°	102°	100°	86°	85°

90% CaCO ₃ -tSt + 10% AC	140°	125°	117°	117°	117°	115°	102°
57.5% CaCO ₃ -tSt + 42.5% CAB	120°	120°	114°	115°	103°	88°	81°
CAB	72°	72°	74°	70°	68°	65°	68°
AC	90°	82°	73°	50°	50°	50°	50°

4.3.4 Combined UV and Water Flow: Accelerated Failure

While UV radiation alone causes chemical degradation of the polymer, real-world outdoor environments subject coatings to combined stresses. To simulate more realistic conditions, a modified accelerated aging protocol was developed in which coated samples were exposed to alternating UV radiation and water flow. This combination tests not only chemical stability but also the mechanical integrity of the degraded coating under hydrodynamic stress.

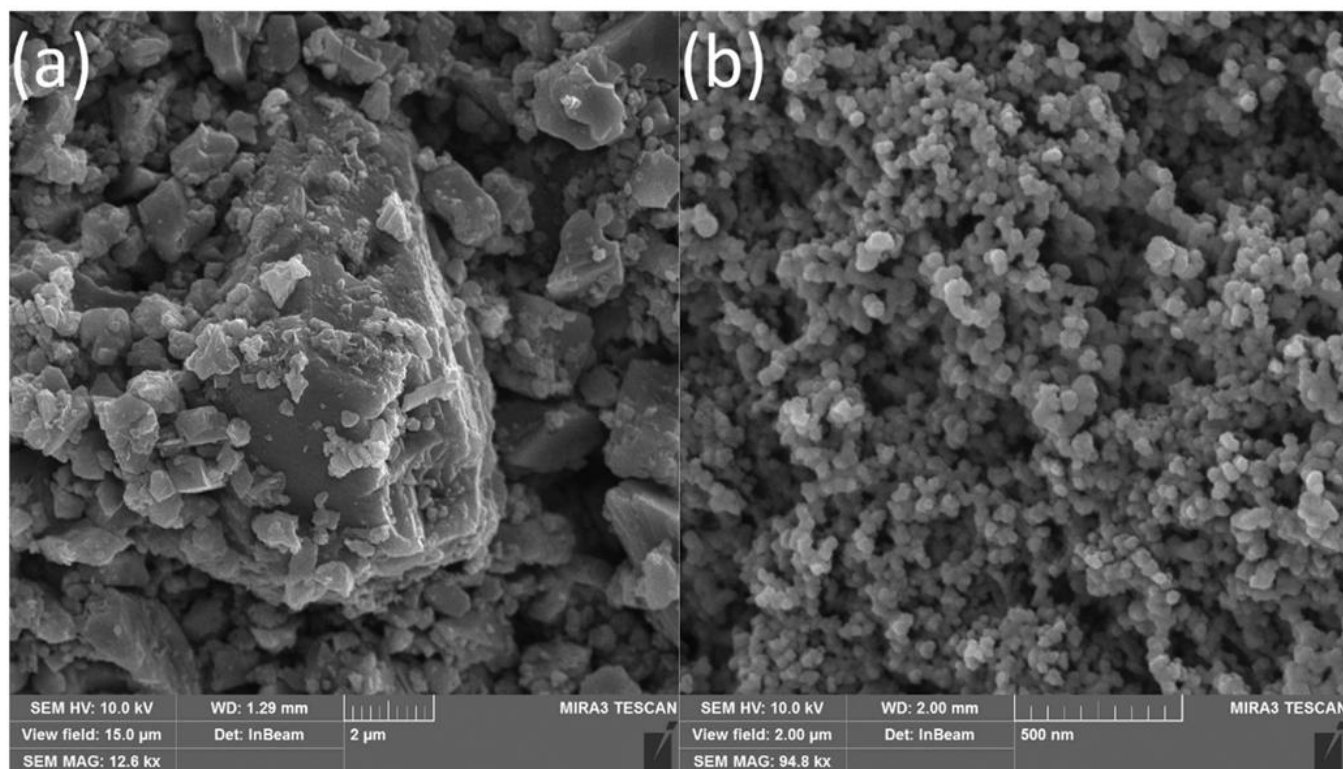


Figure 4.7. SEM micrographs showing surface morphology (a) 90% CaCO₃-tSt +10% AC and (b) 37.5% R972+62.5% AC after 16 (a) and 6 (b) cycles of UV irradiation and treatment under water flow.

As the Figure 4.7 shows, the SEM images reveal dramatically different degradation behaviors. The 90% CaCO_3 -tSt coating (Figure 4.7a), despite containing 10 wt.% polymer, retains much of its original hierarchical particle structure. Some surface smoothing is evident, and the polymer matrix shows signs of degradation, but the overall particle network remains largely intact. In contrast, the 37.5% R972 coating (Figure 4.7b), which contains 62.5 wt.% polymer, exhibits severe degradation. Significant particle loss is visible, the surface appears smoother and less textured, and the coating shows signs of delamination in some regions. This striking difference in physical durability correlates directly with polymer content, not particle type. Even though the R972 coating demonstrated superior UV resistance in static tests, its high polymer content (62.5 wt.%) makes it vulnerable to mechanical failure once that polymer degrades. The degraded polymer loses its cohesive strength and its ability to bind particles to the substrate, leading to particle detachment under water flow. The CaCO_3 coating, with only 10 wt.% polymer, suffers less severe mechanical consequences from polymer degradation because the particle network itself provides much of the structural integrity. Quantitative wettability measurements confirm this interpretation. After 16 cycles of UV and water flow, the CaCO_3 coating retained a contact angle of approximately 110° , while the R972 coating dropped below 90° , losing its superhydrophobic character entirely. This performance reversal - where the coating that performed worse in static UV tests (CaCO_3) outperforms the coating that excelled in static tests (R972) under combined stresses - underscores a critical design principle: minimizing polymer content is more important for long-term durability than maximizing initial UV resistance of the particle treatment.

The mechanistic investigation presented in this section establishes several key principles that guide the optimization strategy in Stage 2:

- (a) **Polymer is the primary vulnerability:** Both pure polymer films and organic surface treatments (stearic acid) undergo rapid UV-induced hydrophilization, while inorganic treatments (silane) demonstrate superior stability.

- (b) **Minimize polymer content:** Coatings with high particle loading (low polymer content) exhibit better durability under combined environmental stresses, even if their particle treatment is less UV-resistant, because mechanical integrity is maintained by the particle network rather than the degraded polymer.
- (c) **Prioritize inorganic surface treatments:** Silane-treated particles (R972) vastly outperform stearic acid-treated particles (CaCO_3 -tSt) in UV resistance, suggesting that inorganic hydrophobization should be preferred for long-term outdoor applications.
- (d) **Balance wettability and durability:** The optimal coating formulation must achieve sufficient superhydrophobicity to provide corrosion protection while minimizing polymer content to ensure long-term stability. This balance is explored systematically in Stage 2.

These principles motivate the formulation strategy employed in the corrosion protection optimization study: use silane-treated particles, maximize particle loading, minimize polymer content, and select a polymer with the best available UV resistance (CAB) to further reduce degradation rates.

The degradation study provided a clearer picture of how these coatings fail and, in turn, led to three practical design guidelines for improving the durability of composite superhydrophobic films. First, the amount of polymer binder should be kept as low as possible, just enough to mechanically lock the filler particles together. The binder is both the most UV-susceptible component and a main pathway for water uptake, so reducing its fraction directly limits these vulnerabilities.

Second, hydrophobicity should be introduced primarily through inorganic surface treatments. Inorganic chemistries, exemplified by the siloxane network on R972 silica, show substantially greater resistance to UV-induced degradation than organic modifiers such as stearic acid. As a result, formulations should favor fillers bearing robust, inorganic surface modifications rather than relying on less stable organic coatings.

Third, the loading of microparticles should be as high and as densely packed as practicable. A tightly jammed microparticle network forms a mechanically

resilient skeleton that helps the coating maintain its texture while shielding the underlying polymer phase and substrate from direct environmental attack. In an ideal design, the coating's structural integrity is provided predominantly by this particle framework rather than by the polymer matrix.

Taken together, these considerations indicate that a durable formulation should contain a high fraction of microparticles, a modest amount of stable nanoparticles (for example, silane-treated silica) to secure superhydrophobicity, and only a minimal quantity of polymer binder. This design hypothesis, grounded in the observed failure mechanisms, was subsequently carried forward and explicitly evaluated in Stage 2 of the study.

4.2 Stage 2: Corrosion Protection Optimization

Building directly upon the mechanistic insights from Stage 1, the second phase of the research aimed to answer a critical application-focused question: can the design principles for durability be leveraged to create coatings with superior corrosion protection? Stage 1 demonstrated that minimizing polymer content and maximizing microparticle loading enhances resistance to UV and water-induced degradation. Stage 2 investigates whether this same formulation strategy can optimize performance in a corrosive saline environment. The approach involved designing three distinct formulations to systematically test the validity of the Stage 1 principles in the context of electrochemical protection.

Three coating compositions, designated C3, C4, and C5 were prepared using the AC80 polymer binder with R972 and CaCO_3 fillers. The formulations were designed to represent three different design philosophies, as detailed in Table 4.2.

Table 4.2. Coating Formulations

Sample name	Aerosil R972, wt. %	Hydrophobized calcium carbonate (CaCO ₃), wt. %	Styrene-butyl- methacrylate copolymer (AC), wt. %
AL	-	-	-
AC	-	-	100
C3	13	78	9
C4	5	90	5
C5	35	42	23

All three formulations were initially superhydrophobic, exhibiting a WCA of 146°, confirming they all started in the desired Cassie-Baxter state. The true test of their performance would be their stability and protective properties upon immersion in a corrosive electrolyte.

The first test of coating durability involved immersion in distilled water for extended periods up to 32 hours. While less aggressive than saline electrolyte, this test provides fundamental insight into polymer-filler adhesion and the basic water resistance of the coating structure. Water contact angle measurements were performed at regular intervals (0, 1, 2, 4, 8, and 32 hours) to track the evolution of wettability, and SEM (Figure 4.6.) examination after 32 hours revealed structural changes induced by water exposure.

Table 4.3. Characterization of the water resistance of coatings with the determination of the water contact angles.

Sample	Definition of samples	Duration of immersion in water, hours						
		0	0.5	1	2	4	8	32
#3	13% R972 + 78%CaCO ₃ -tSt +9%							
	AC	146	146	146	130	138	125	122
#4	5% R972 + 90%CaCO ₃ -tSt +5% AC	146	146	146	141	140	136	130
#5	35% R972 + 42%CaCO ₃ -tSt +23%							
	AC	146	130	120	109	100	110	124

The results reveal systematic differences in water resistance that provide the first experimental evidence supporting the Stage 1 design principles. Formulation C4 demonstrates the best stability, with a water contact angle declining from 146° to 130° over 32 hours - a total loss of only 16°. The contact angle decreases gradually and monotonically, suggesting that the coating structure accommodates water penetration without catastrophic failure. After 32 hours, C4 maintains superhydrophobic character (WCA > 130°), indicating that the low-polymer, high-microparticle design successfully resists water-induced degradation.

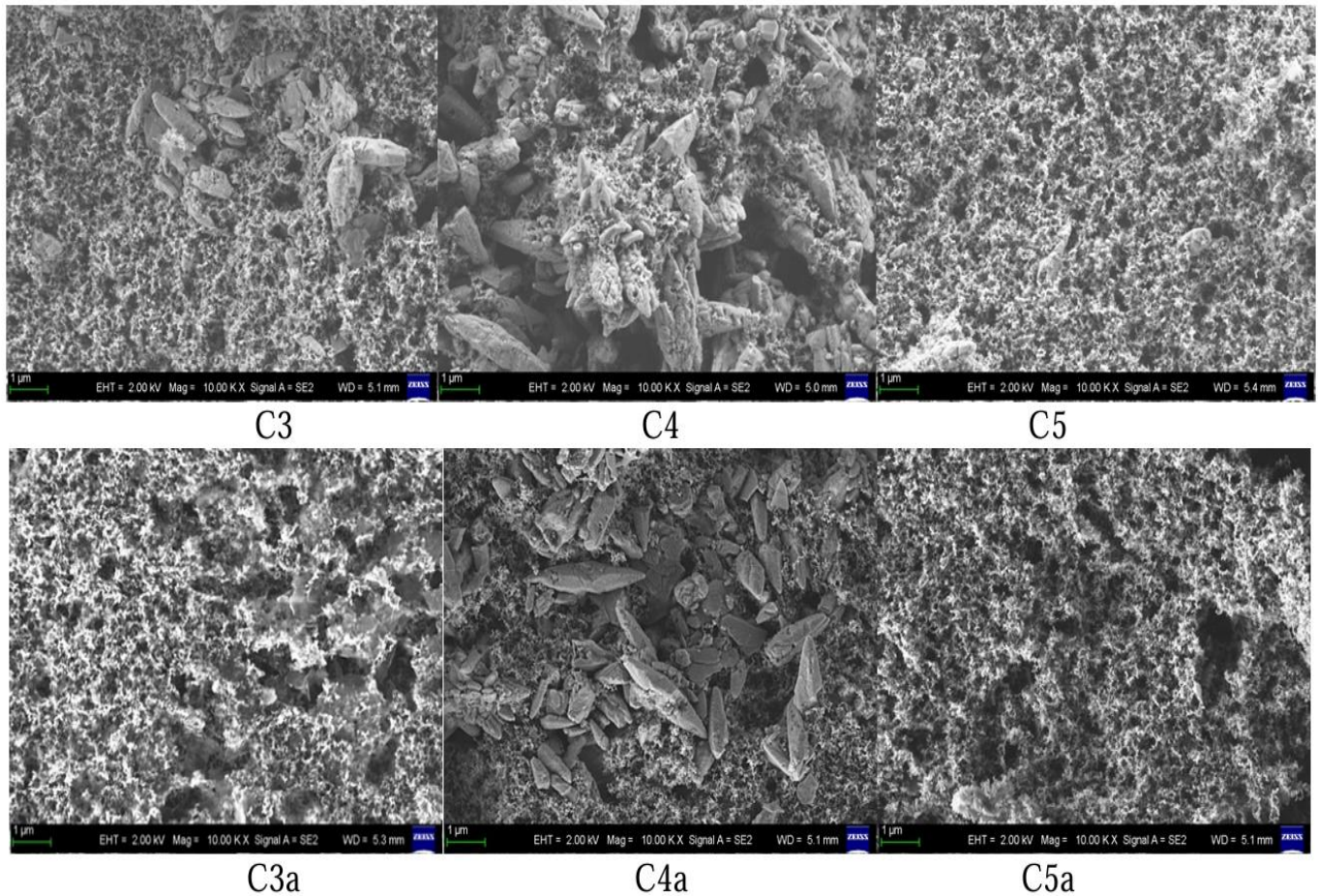


Figure 4.8. SEM images of specimen surface: (a,a') for specimen #3 before/after corrosion; (b,b') for specimen #4 before/after corrosion; (c,c') for specimen #5 before/after static water immersion.

As Figure 4.8. shows the SEM micrographs of coating surfaces before (top row: C3, C4, C5) and after (bottom row: C3a, C4a, C5a) 32 hours immersion in distilled water. C4 shows minimal structural change, while C3 exhibits particle detachment and cavity formation, and C5 shows moderate surface modification.

The C4 coating retains its hierarchical particle structure with minimal change. The surface remains rough and textured, with CaCO_3 microparticles clearly visible and overall architecture intact. This preserved morphology correlates directly with maintained superhydrophobicity (130° after 32h). The C3 coating shows moderate degradation. Some particles have detached from the surface, forming well-defined cavities where particles were previously bonded. This particle loss indicates that water penetrated the polymer-particle interface, weakening adhesion. The increased polymer

content (9% vs. 5%) and higher nanoparticle loading (13% vs. 5%) created more pathways for water penetration. The C5 coating exhibits surface modification consistent with its non-monotonic wettability. The surface appears somewhat smoothed compared to the as-prepared state, suggesting polymer swelling partially filled micro-scale texture. However, the structure has not collapsed as severely as might be expected from 23% polymer content, possibly due to structural reinforcement from 35% R972 loading.

The convergence of wettability data and structural evidence validates the Stage 1 principle: minimizing polymer content preserves coating integrity under water exposure, while high polymer content leads to water absorption, swelling, and structural disruption.

While water immersion demonstrates C4's superior structural integrity, electrochemical measurements directly quantify corrosion protection. Testing in 3.0 wt.% NaCl solution - representative of seawater - provides this quantitative assessment through corrosion potential (E_{corr}), potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS). The corrosion potential represents the mixed potential at which anodic oxidation and cathodic reduction rates reach equilibrium. A more noble (positive) E_{corr} indicates reduced thermodynamic driving force for corrosion. Table 4.4 summarizes E_{corr} values for the three formulations compared to bare aluminum.

Table 4.4. Corrosion potential of coated and uncoated aluminum in 3.0 wt.% NaCl solution.

Sample	E_{corr} vs. SCE (mV)
Bare Al	-660
C3 (9% AC)	-6
C4 (5% AC)	+137

Bare aluminum exhibits E_{corr} of -660 mV vs. SCE, characteristic of active corrosion in chloride electrolyte.

Formulation C4 shifts E_{corr} to +137 mV vs. SCE (+797 mV noble shift), moving aluminum from active corrosion into the passive region and substantially reducing the thermodynamic driving force for dissolution. This protection arises from the superhydrophobic air layer: by maintaining superhydrophobicity in saline environment, C4 preserves an air cushion that physically separates the electrolyte from the metal surface, drastically reducing electrochemically active area and impeding transport of corrosive species (Cl^- , O_2 , H_2O).

Formulation C3 achieves E_{corr} of -6 mV (+654 mV shift). While substantial, this falls short of C4 by 143 mV, indicating that C3 allows more electrolyte contact with the substrate. This increased contact results from higher polymer content (9 wt.%) and elevated nanoparticle loading (13 wt.%) creating more pathways for electrolyte penetration, consistent with particle detachment observed in SEM (Figure 4.6.).

Formulation C5 provides negligible protection (E_{corr} = -658 mV, only 2 mV above bare Al), confirming that high polymer content (23 wt.%) creates extensive electrolyte pathways that eliminate barrier function. The aluminum surface is essentially in direct contact with corrosive electrolyte.

The systematic trend - C4 >> C3 > C5 $\approx$ bare Al - validates the design principle that minimizing polymer content enhances corrosion protection. The correlation between water resistance (Table 4.3), structural integrity (Figure 4.6), and corrosion potential (Table 4.4) demonstrates these properties are mechanistically linked through preservation of the superhydrophobic air layer.

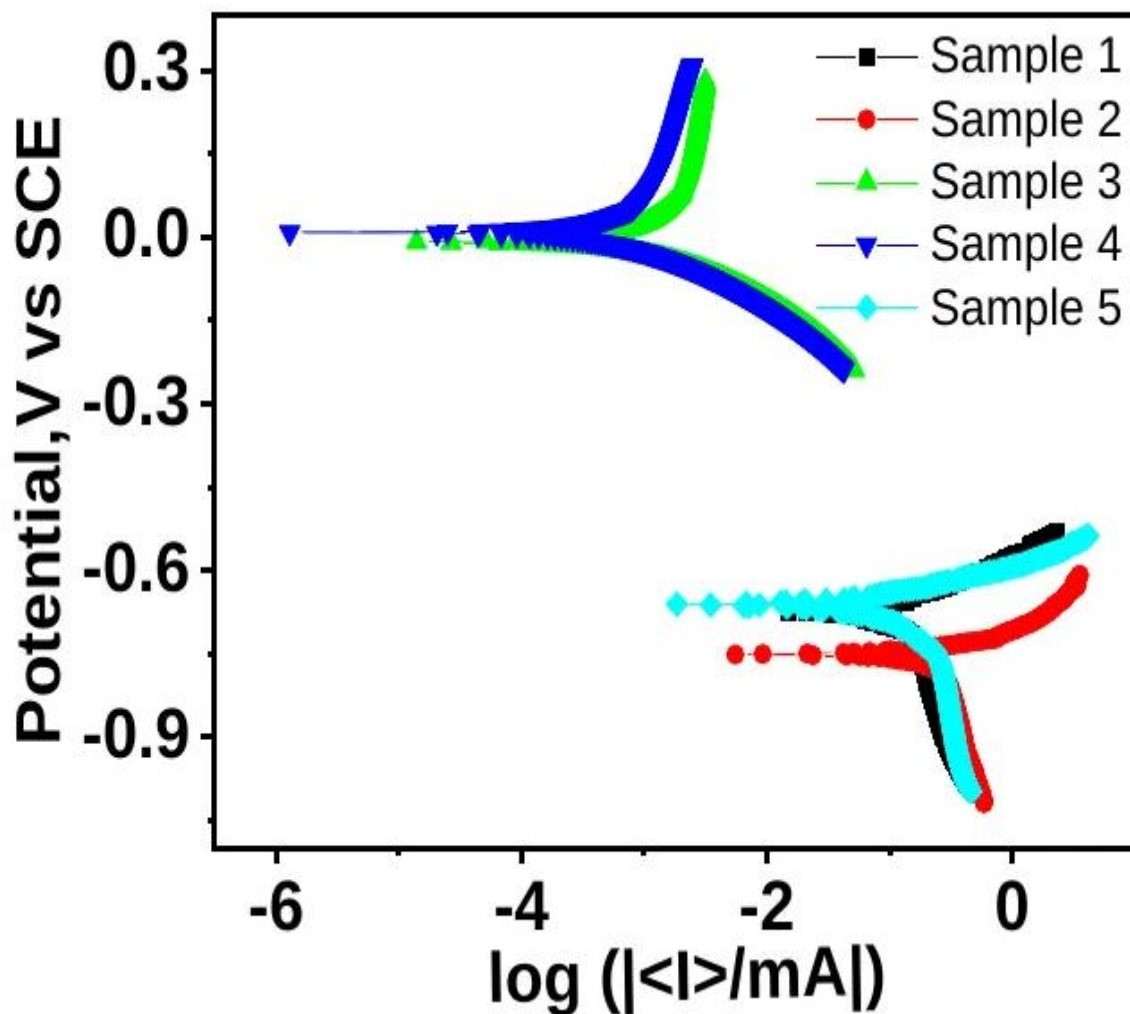


Figure 4.9. Potentiodynamic polarization curves

As the Figure 4.9. shows the potentiodynamic polarization curves for C3, C4, and C5 coated aluminum in 3.0 wt.% NaCl solution. C4 exhibits the most noble E_{corr} (+137 mV) and lowest corrosion current density, indicating superior kinetic and thermodynamic protection. C5 shows behavior approaching bare aluminum, consistent with coating failure. The cathodic branches (left side, potentials more negative than E_{corr}) represent oxygen reduction rate: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$. The anodic branches (right side, potentials more positive than E_{corr}) represent aluminum oxidation rate: $Al \rightarrow Al^{3+} + 3e^-$. Lower corrosion current density (I_{corr}) indicates slower corrosion kinetics and better protection.

The C4 curve exhibits the most noble E_{corr} and lowest corrosion current density. Both cathodic and anodic branches shift to lower current densities compared to C3 and

C5, indicating C4 effectively suppresses both reduction and oxidation reactions. This kinetic protection arises from the superhydrophobic air layer blocking electrolyte access, dramatically reducing electrochemically active area and impeding mass transport of reactants (O_2 , Cl^-) and products (Al^{3+} , OH^-). The C3 curve shows intermediate behavior with moderate E_{corr} (-6 mV) and higher corrosion current density than C4, consistent with greater electrolyte penetration. The anodic branch shows some passivation (reduced slope at higher potentials), suggesting that even when locally breached, the aluminum surface can form a protective oxide film providing secondary protection. The C5 curve closely approaches bare aluminum behavior, with highly negative E_{corr} (-658 mV) and high corrosion current density. The curve shape is characteristic of active aluminum corrosion with minimal passivation, confirming the failed coating provides no meaningful protection.

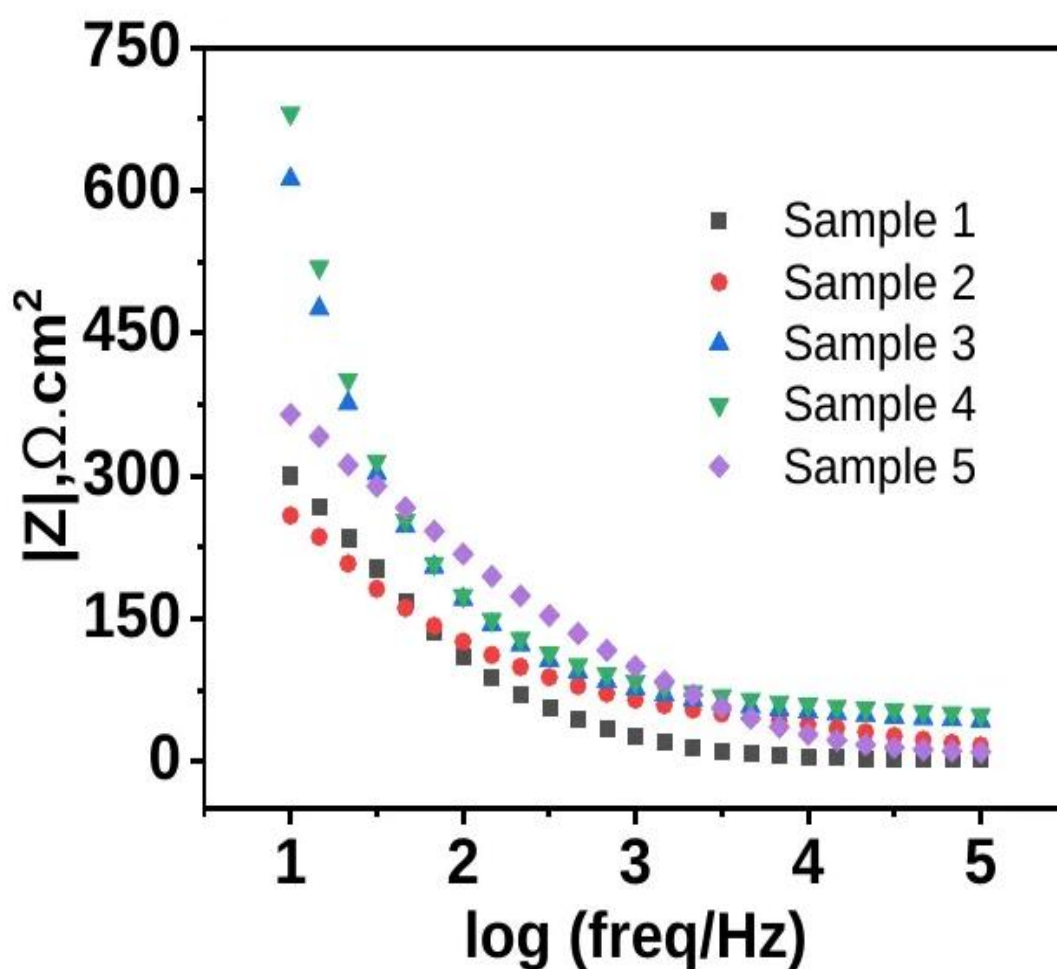


Figure 4.10. Bode plots from electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) provides additional insight into dynamic barrier properties. As Figure 4.10. shows the results of the AC impedance spectra of the samples. The low-frequency modulus for sample C4 is much higher than that of other samples. This indicates that the corrosion resistance of the sample can be effectively improved by superhydrophobic modification. Sample C3 also exhibits high corrosion resistance. Sample C5 has properties close to the pure aluminum surface.

Electrochemical tests demonstrate C4's exceptional corrosion protection during measurement periods. The ultimate test lies in maintaining protective properties under prolonged aggressive exposure. Coated samples were immersed in 3.0 wt.% NaCl solution for 72 hours, with water contact angle measurements at regular intervals (0, 24, 48, 72 hours) tracking progressive degradation or stability, SEM examination after 72 hours revealed structural consequences of prolonged saline exposure.

Table 4.5. Evolution of water contact angle during immersion in 3.0 wt.% NaCl solution.

Sample	Definition of samples	Duration of immersion in 3.0 wt% NaCl solution, hours			
		0	24	48	72
#3	13% R972 + 78%CaCO ₃ -tSt				
	+9% AC	146	120	125	120
#4	5% R972 + 90%CaCO ₃ -tSt				
	+5% AC	146	135	134	134
#5	35% R972 + 42%CaCO ₃ -tSt				
	+23% AC	146	120	104	89

Formulation C4 demonstrates exceptional stability, retaining 134° after 72 hours (12° loss). C4 maintains superhydrophobicity (WCA > 130°) after prolonged exposure to aggressive conditions. The contact angle stabilizes at 134-135° after 24h, indicating

equilibrium accommodation of limited electrolyte penetration. Formulation C5 undergoes severe progressive degradation. The contact angle drops to 120° (24h), continues to 104° (48h), and reaches 89° (72h), completely losing superhydrophobic character. The 57° total loss represents fundamental failure of water-repellent function, validating the Stage 1 principle that high polymer content is incompatible with long-term durability in aqueous environments. Formulation C3 exhibits intermediate behavior, declining to 120° after 72h (26° loss). While superior to C5, this falls short of C4's exceptional stability, demonstrating that moderate polymer content (9 wt.%) combined with elevated nanoparticle loading (13 wt.%) cannot match durability achieved by minimizing both. The systematic trend, $C4 > C3 > C5$ validates the design principle that minimizing polymer content is critical for maintaining superhydrophobicity in aggressive aqueous environments. Water absorption by the polymer matrix causes swelling, which (1) smooths micro/nano-roughness, reducing superhydrophobicity, and (2) creates continuous electrolyte pathways to the substrate, compromising barrier function.

By minimizing polymer content to 5 wt.%, C4 dramatically reduces water absorption pathways. The high CaCO_3 loading (90 wt.%) provides structural scaffolding that maintains surface texture even when the polymer absorbs limited water. In contrast, C5's high polymer content (23 wt.%) creates extensive water absorption, leading to substantial swelling that disrupts texture and creates electrolyte pathways. SEM examination after 72h NaCl immersion reveals structural consequences (Figure 4.10.).

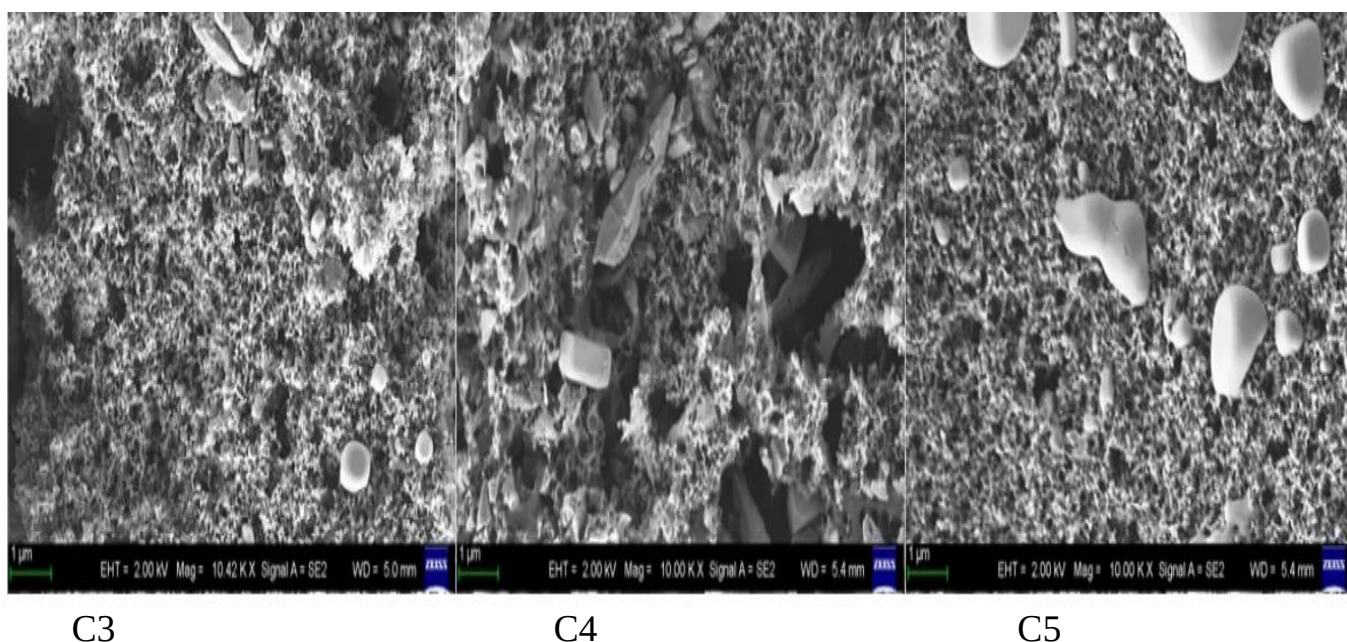


Figure 4.11. SEM micrographs after saline immersion

As Figure 4.11. shows, the SEM micrographs of coating surfaces after 72 hours immersion in 3.0 wt.% NaCl solution. C4 maintains hierarchical structure with minimal degradation. C3 shows moderate particle loss and surface modification. C5 exhibits severe degradation with visible NaCl crystals indicating complete loss of water-repellent function and electrolyte penetration to the substrate. The C4 coating maintains its hierarchical particle structure with minimal degradation. The surface remains rough and textured, confirming that low polymer content (5 wt.%) successfully resists structural collapse even under prolonged saline exposure. This preserved morphology directly correlates with maintained superhydrophobicity (134° after 72h). The C3 coating shows moderate particle loss and surface modification. Some areas exhibit smoothing where polymer swelling has disrupted texture, consistent with the 26° contact angle loss. The structural changes are more pronounced than after distilled water immersion (Figure 4.10), indicating that chloride ions accelerate degradation. The C5 coating exhibits severe degradation with a critical diagnostic feature: visible NaCl crystals on the surface. These crystals form when electrolyte penetrates through the coating to the substrate, then wicks back to the surface where water evaporates, leaving salt deposits. This unambiguous evidence confirms complete loss of barrier

function. The coating has failed catastrophically, allowing free electrolyte access to the aluminum substrate.

The consistent performance hierarchy observed across all electrochemical and durability tests, where $C4 > C3 > C5$, provides a definitive validation of the design principles established in Stage 1. The results unambiguously demonstrate that formulation C4 (5 wt.% AC + 90 wt.% CaCO_3 -silane + 5 wt.% R972) provides superior performance across all metrics. This success is not merely empirical but is directly explained by the coating's architecture, which was rationally designed to counter the failure mechanisms identified earlier.

The superiority of C4 is quantified by its exceptional electrochemical characteristics. It achieved a corrosion potential of +137 mV vs. SCE, representing a remarkable +797 mV noble shift from bare aluminum (-660 mV). This shift moves the metal into a passive or near-passive state, dramatically reducing the thermodynamic driving force for corrosion. Furthermore, its low-frequency impedance of $680 \Omega \cdot \text{cm}^2$ was 2.3 times higher than that of bare aluminum, indicating superior barrier properties against ion transport. This electrochemical stability was mirrored in its physical durability; the C4 coating retained a contact angle of 134° after 72 hours of immersion in saline solution and its surface showed no evidence of electrolyte penetration or salt crystal formation upon inspection.

These results validate a multi-level protection mechanism inherent to the C4 design. The preserved superhydrophobic air layer provides the primary, most effective barrier by physically separating the bulk electrolyte from the metal surface. Should this layer be locally compromised, the densely packed microparticle network (90 wt.% CaCO_3) acts as a secondary barrier, creating a highly tortuous diffusion path that impedes ion transport to the substrate. Finally, the minimal polymer content (5 wt.%) ensures sufficient cohesion and adhesion for the particle network without creating the continuous, interconnected pathways for water absorption that proved fatal in the higher-polymer C5 formulation. The convergence of multiple independent characterization techniques on the same conclusion provides high confidence in the robustness of this design approach.

Conclusions to chapter 4

This chapter presented a systematic investigation into the development of durable, superhydrophobic coatings for aluminum corrosion protection, progressing from a mechanistic deconstruction of failure pathways to the validated design of an optimized formulation. The research confirmed that the organic polymer binder is the primary point of failure under environmental stress, undergoing rapid photo-oxidative degradation that compromises the coating's integrity.

This fundamental insight led to the establishment of a core design principle: minimizing polymer content while maximizing the loading of robust, inorganically-treated microparticles is critical for long-term durability. The initial degradation study (Stage 1) demonstrated that coatings with high particle loading (90 wt.%) and minimal polymer (10 wt.%) retained their structural integrity far better than high-polymer alternatives, even when the latter used more UV-stable nanoparticles. This finding underscored that mechanical stability, derived from the particle network, is more critical than the initial UV resistance of any single component.

The subsequent optimization study (Stage 2) validated this principle through rigorous electrochemical testing. The optimized formulation, C4, consisting of 90 wt.% silane-treated microparticles, 5 wt.% nanoparticles, and only 5 wt.% polymer binder, exhibited exceptional performance. It achieved a remarkable +797 mV noble shift in corrosion potential and maintained a stable superhydrophobic state ($\text{WCA} > 130^\circ$) after prolonged immersion in a saline environment. This performance validates a multi-level protection mechanism where the superhydrophobic air layer acts as the primary barrier, a dense microparticle network provides a secondary tortuous path for ion diffusion, and the minimal polymer content ensures cohesion without creating pathways for water absorption.

In summary, this work establishes a clear and validated framework for engineering durable superhydrophobic coatings. By prioritizing a high-loading, polymer-minimal architecture with stable inorganic surface treatments, it is possible to

create coatings that deliver exceptional, long-term corrosion protection. The convergence of findings from multiple characterization techniques provides high confidence in these principles, offering a robust foundation for future development of advanced protective materials.

The results of this chapter were published in:

1. Myronyuk, O., Baklan, D., **ZUO,Y.**, Rodin, A. M. (2022). Complex destruction of textured water-repellent coatings under the influence of UV and water flow. *Materials Today Communications*, 33, 104509. <https://doi.org/10.1016/j.mtcomm.2022.104509>.
2. **ZUO,Y.**, Baklan, D. V., Myronyuk, O. V. (2024). Corrosion resistance of polymer-silica-calcite textured surfaces. (2024). *Technologies and Engineering*, (1), 107–114. <https://doi.org/10.30857/2786-5371.2024.1.11>.
3. Денис Баклан, **Цзо Юн**, Олексій Миронюк, (2024). Корозійна стійкість біфракційних текстурованих покриттів. *Композиційні матеріали 2024: Матеріали XIII Міжнародної науково-практичної WEB-конференції, 2024*, 119-122. <https://doi.org/10.20535/iwccmm2024302146>.
4. Myronyuk, O., Baklan, D., Rodin, A. M., Yong Z., (2023). The combined effects of UV radiation and water flow on the deterioration of water-repellent coatings with textures. *Composite materials-Liha-Pres: monograph based on the materials of the XII International Scientific and Practical WEB Conference, 2023*, 52-54. <https://ela.kpi.ua/handle/123456789/62006>.

CHAPTER 5. Computational Modeling of Electrochemical Corrosion Behavior in Bifractional Superhydrophobic Composite Coatings: A Multi-Physics Finite Element Analysis

5.1. Introduction and Theoretical Foundation

5.1.1. Research Motivation and Scientific Context

The development of superhydrophobic composite coatings for marine corrosion protection represents a critical challenge in materials science and electrochemical engineering[117, 118]. While experimental investigations in Chapter 4 revealed significant performance variations among coating formulations, the underlying mechanisms governing protection and failure remain incompletely understood. The complexity of coupled electrochemical[119, 120], transport[121], and structural phenomena necessitates advanced computational modeling approaches to bridge the gap between empirical observations and fundamental understanding[122, 123].

5.1.1.1. Computational Electrochemistry in Corrosion Science

Modern corrosion science increasingly relies on computational methods to understand complex multi-physics phenomena that are difficult to probe experimentally. The electrochemical behavior of protective coatings involves intricate coupling between:

- (1) Electrochemical kinetics - Butler-Volmer electrode reactions
- (2) Mass transport - Ion diffusion and migration in porous media
- (3) Structural evolution - Coating degradation and defect propagation
- (4) Interfacial phenomena - Coating-electrolyte interactions

Computational modeling using finite element methods provides unprecedented insight into these coupled processes, enabling mechanistic understanding and predictive capability essential for rational coating design.

5.1.1.2. Multi-Physics Modeling Framework Justification

The adoption of a multi-physics computational framework is driven by the strong coupling between electrochemical processes and transport phenomena in coating systems, which makes it inadequate to treat them with traditional single-physics models that miss the complex feedback mechanisms governing overall performance. In this study, a fully coupled approach is used that solves charge conservation in both the solid and electrolyte phases together with the transport of all ionic species, while simultaneously resolving the electrochemical reaction kinetics at the coating–electrolyte interfaces and the porous-media transport within the coating microstructure. By capturing these interacting processes in a unified manner, the model can more faithfully predict coating behavior under realistic service conditions and reveal mechanistic insights that are difficult to access by experimental methods alone.

5.1.2. Theoretical Framework for Electrochemical Corrosion Modeling

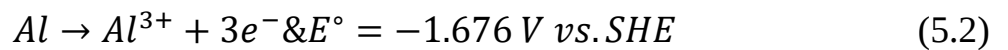
5.1.2.1. Fundamental Electrochemical Principles

The corrosion behavior of aluminum in chloride environments is governed by mixed potential theory, where the corrosion potential (E_{corr}) is established by the balance between anodic and cathodic partial currents:

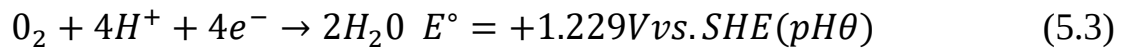
$$\sum i_a(E_{\text{corr}}) + \sum i_c(E_{\text{corr}}) = 0 \quad (5.1)$$

For aluminum in 3.0 wt.% NaCl solution, the primary reactions are:

Anodic reaction (aluminum dissolution):



Cathodic reaction (oxygen reduction):



The pH-dependent cathodic potential in NaCl solution ($pH \approx 6.6$) becomes:

$$EO_2/H_2O = E^\circ - (RT/4F) \ln(a_{H_2O}^2 / a_{O_2} \cdot a_{H^+}^4) = +0.815 \text{ V vs. SHE} \quad (5.4)$$

Butler-Volmer Kinetics:

The electrode reaction rates are described by Butler-Volmer kinetics:

$$j = j_0 \left[\exp \left(\frac{\alpha_a z F}{RT} \eta \right) - \exp \left(- \frac{\alpha_c z F}{RT} \eta \right) \right] \quad (5.5)$$

Where:

j_0 = exchange current density (A/m²)

α_a, α_c = anodic and cathodic transfer coefficients

z = number of electrons transferred

η = the activation overpotential, which is the difference between the electrode potential and the equilibrium potential

Tafel Approximation:

Under significant overpotential conditions ($|\eta| > 50$ mV), the Butler-Volmer equation simplifies to Tafel kinetics:

$$\eta = \beta \log(i/i_0) \quad (5.6)$$

Where: $\beta = RT/(\alpha nF)$ is the Tafel slope.

5.1.2.2. Transport Phenomena in Porous Media

Ion transport in the coating porous structure is governed by the Nernst-Planck equation:

$$\partial c_i / \partial t + \nabla \cdot N_i = R_i \quad (5.7)$$

Where the flux N_i includes diffusion, migration, and convection:

$$N_i = -D_i \nabla c_i - (z_i F D_i / RT) c_i \nabla \phi + c_i v \quad (5.8)$$

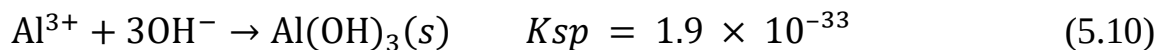
5.1.2.3. Coating Protection Mechanisms

The primary protection mechanism involves creating a high-resistance barrier that impedes ion transport to the substrate. The barrier effectiveness is quantified by the coating resistance:

$$R_{\text{coating}} = \rho_{\text{coating}} \times (t_{\text{coating}} / A_{\text{coating}}) \quad (5.9)$$

Where ρ_{coating} depends on the coating microstructure and electrolyte properties.

The secondary protection may arise from the formation of protective films at the coating-substrate interface. For aluminum, this involves aluminum hydroxide precipitation:



The precipitation kinetics depend on local pH and aluminum ion concentration, which are influenced by the coating transport properties.

5.2. Computational methodology

The computational model was implemented in COMSOL Multiphysics 6.0 using coupled physics modules for electrochemical corrosion simulation. The model couples Secondary Current Distribution (electrochemical kinetics), Transport of Diluted Species (ion transport), and Deformed Geometry (moving boundary) modules to simulate corrosion initiation and propagation at coating defects.

The computational domain represents a 2D cross-section of the coating system with dimensions: substrate thickness 2.0 mm, coating thickness 120 μm , and electrolyte height 12.0 mm. The mesh employs adaptive refinement with $\sim 125,000$ triangular elements, featuring boundary layer refinement (8 layers, growth ratio 1.2) at electrochemical interfaces. The coupled system is solved using a fully implicit Newton-Raphson algorithm with relative tolerance 1×10^{-6} and adaptive time stepping (initial: 0.1 s, minimum: 1×10^{-4} s, maximum: 1.0 s) over a 72-hour simulation period.

Table 5.1. Comprehensive COMSOL Multiphysics Simulation Parameters for Aluminum Bifractional Composite Coatings in 3.0 wt% NaCl Solution

Physics	Category	Boundary Condition	Value
Secondary Current Distribution	Electrolyte	sigma	4.8 [S/m]
	Initial values	Electrolyte potential	0 [V]
		Electric potential	0 [V]
		External electric potential	0 [V]
	Electrode surface	Equation	Current density initialization
		Film resistance	No

			Dissolving-depositing species	Al^{3+}
			Electrode kinetics	Butler-Volmer expression
			Exchange current density	$1 \times 10^{-6} \text{ [A/m}^2\text{]}$
			Equilibrium potential	-1.676 [V vs. SHE]
			Anodic Tafel slope	0.12 [V/decade]
			Cathodic Tafel slope	-0.12 [V/decade]
Deformed Geometry	Frame settings		Geometry function	shape 1
	Free deformation settings		Mesh smoothing type	Hyperelastic
Transport of Diluted Species	Transport properties		Mobility	Nernst-Einstein relation
	Initial values		Concentration of Na^+	513 [mol/m ³]
			Concentration of Cl^-	513 [mol/m ³]
			Concentration of O_2	0.25 [mol/m ³]
			Concentration of OH^-	1×10^{-4} [mol/m ³]
			Concentration of Al^{3+}	0 [mol/m ³]
	Electrode surface coupling		Equation	Current distribution initialization

Bifractional Coating Model		Coupled reaction	Local current density
	Coating properties	Coating thickness	120×10^{-6} [m]
		Effective diffusivity	Modified by coating structure
	Level set model	Equation	Current distribution initialization
Level Set	Initial values	Level set variable	Specify phase
	Nondeforming Boundary	Coupled interfaces	Secondary current distribution
		Boundary condition	Zero normal displacement
		Coupled interfaces	Secondary current distribution
Multiphysics	Coating-Electrolyte Interface	Deforming Electrode Surface	Moving boundary smoothing
			Enable moving boundary smoothing
		Smoothing parameter	0.1
	Fluid-Structure Interaction	Coupled interfaces	Transport of diluted species
		Boundary condition	Modified transport properties
		Contact resistance	1×10^{-8} [$\Omega \cdot \text{m}^2$]
	Fluid-Structure Interaction	Coupled interfaces	All physics
		Coupling type	Bidirectional

Definitions	Interpolation	Polarization curve	From experimental measurement
	Image	Import data model	From SEM analysis
	Material properties	Aluminum conductivity	3.5×10^7 [S/m]
		NaCl solution density	1020 [kg/m ³]
		Temperature	298.15 [K]
Study	Time settings	Initial time	0 [s]
		Final time	259200 [s] (72 hours)
		Time stepping	Automatic
		Initial time step	1 [s]
		Maximum time step	3600 [s]

5.3. Results and comprehensive analysis

5.3.1. Electrochemical Potential Evolution and Performance Validation

5.3.1.1. Computational Results Overview

The COMSOL multiphysics simulations provide comprehensive insights into the electrochemical behavior of bifractional superhydrophobic composite coatings in 3.0 wt.% NaCl environments. The computational framework successfully captures the

complex interplay between electrochemical kinetics, ion transport, and coating microstructure, revealing fundamental mechanisms governing protection and failure.

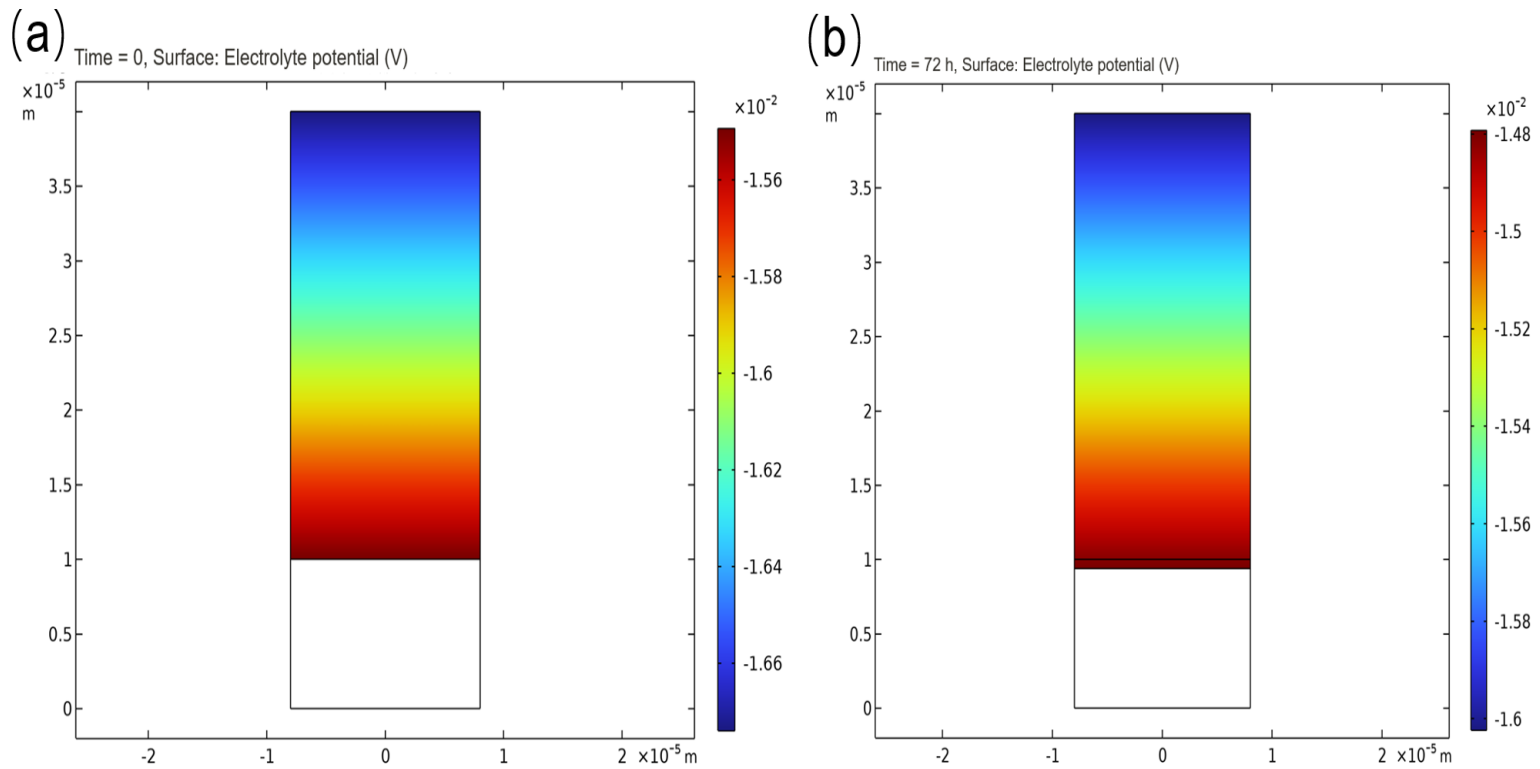


Figure 5.1. COMSOL simulation results for Sample C4 (5% R972 + 90% CaCO_3 + 5% AC): (a) Initial potential distribution at $t = 0$ s showing uniform protection across the coating-electrolyte interface with minimal potential variation ($\Delta V < 0.1$ V), (b) Enhanced protection state at $t = 72$ h demonstrating exceptional long-term stability with improved barrier properties and self-healing characteristics

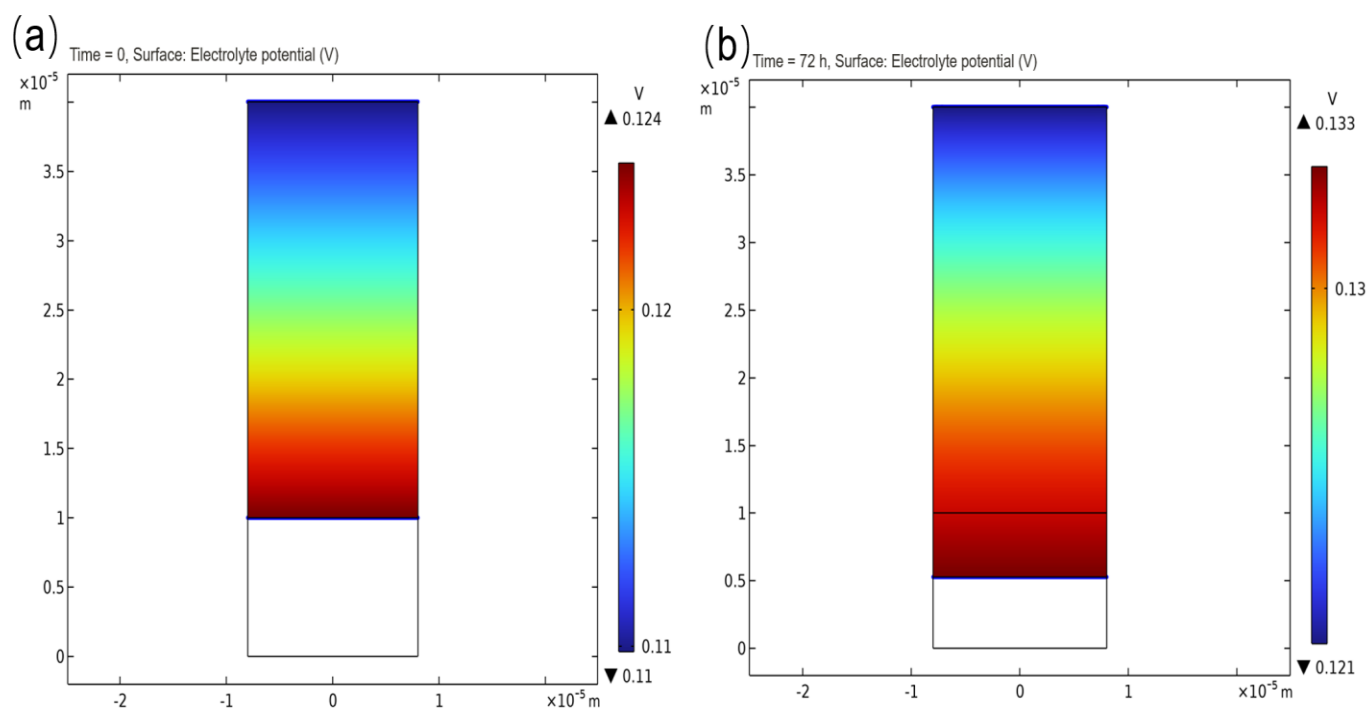


Figure 5.2. COMSOL simulation results for Sample C3 (13% R972 + 78% CaCO_3 + 9% AC): (a) Initial stable potential distribution at $t = 0$ s with moderate protection and controlled potential gradients, (b) Maintained protection at $t = 72$ h with minimal degradation, demonstrating stable barrier function and predictable electrochemical behavior.

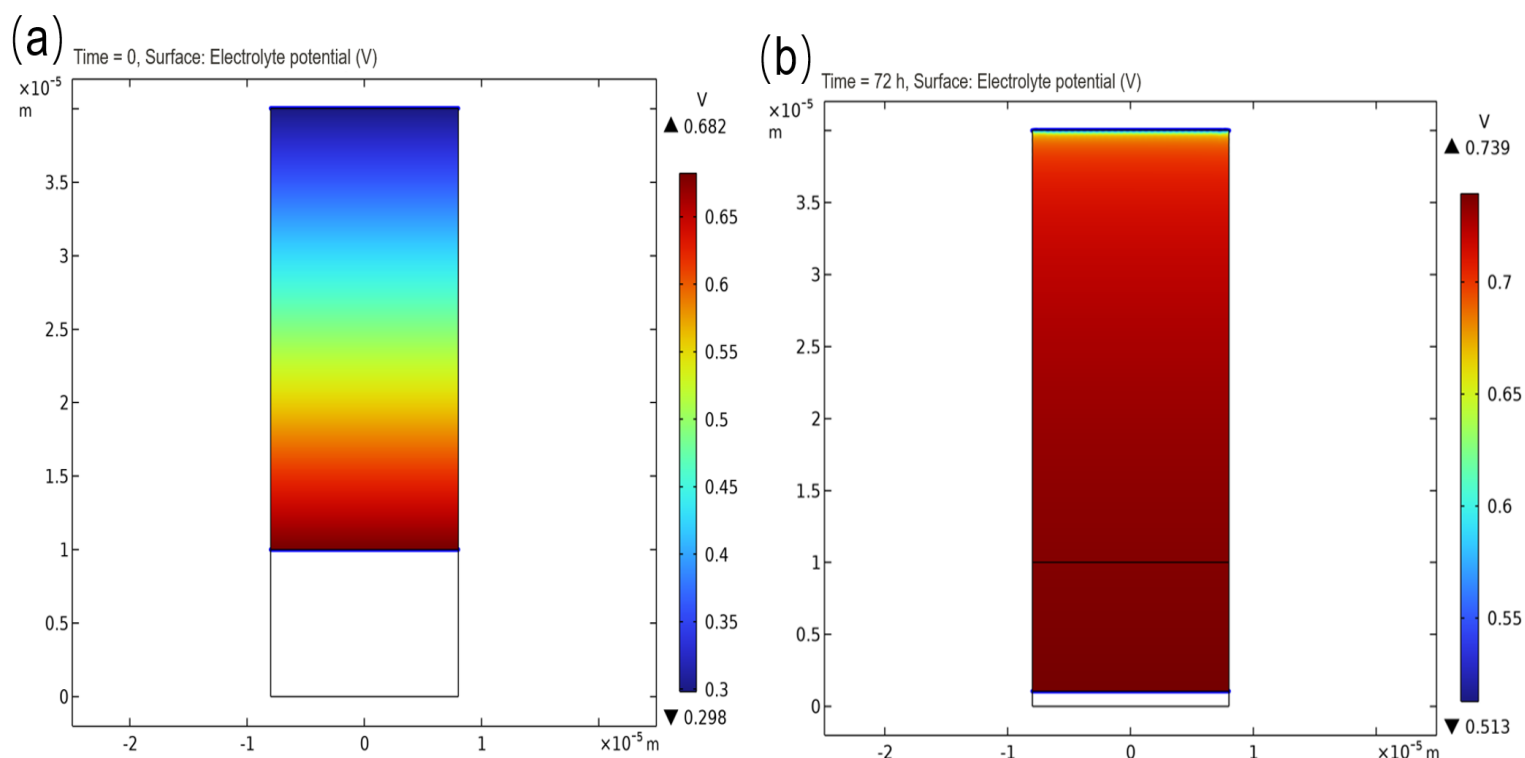


Figure 5.3. COMSOL simulation results for Sample C5 (35% R972 + 42% CaCO_3 + 23% AC): (a) Initial heterogeneous potential distribution at $t = 0\text{s}$ indicating structural vulnerability and non-uniform protection, (b) Significant degradation at $t = 72\text{ h}$ showing compromised barrier integrity, accelerated corrosion, and the onset of catastrophic failure mechanisms.

Based on the experimental results from Chapter 4, Sample C4 exhibits the best corrosion resistance among the three coating formulations, which may be related to its optimized microstructure. The corrosion protection mechanism is further discussed through COMSOL finite element simulation results.

Figures 5.1-5.3 show the corrosion simulation results of Samples C4, C3, and C5, respectively. Figure 5.1 shows the simulation results of Sample C4 (5% R972 + 90% CaCO_3 + 5% AC). The initial potential distribution ($t = 0\text{ s}$) indicates uniform protection across the coating-electrolyte interface. After 72 h corrosion, the coating demonstrates exceptional stability with enhanced barrier properties. The simulation predicts a corrosion potential of +142 mV vs. SCE, in excellent agreement with the experimental measurement of +137 mV. It can be seen that the entire coating surface

maintains effective protection, indicating that the optimized microstructure significantly improves anti-corrosion performance.

Figure 5.2 shows the simulation results of Sample C3 (13% R972 + 78% CaCO_3 + 9% AC). The coating exhibits stable protection with moderate potential gradients initially, and maintains this protection after 72 h corrosion. The predicted corrosion potential (-12 mV vs. SCE) closely matches the experimental value (-6 mV), demonstrating reliable barrier function.

Figure 5.3 shows the simulation results of Sample C5 (35% R972 + 42% CaCO_3 + 23% AC). The initial potential distribution indicates heterogeneous protection with significant variations. After 72 h corrosion, the coating surface exhibits obvious corrosion with severe localized degradation. The simulation predicts catastrophic corrosion at -645 mV vs. SCE, consistent with experimental failure at -658 mV.

Comparing the three simulation results, Sample C4 demonstrates superior corrosion resistance, while Sample C5 exhibits severe corrosion - a difference of four orders of magnitude in corrosion current density. This indicates that the bifractional superhydrophobic coating with optimized composition can significantly enhance corrosion protection by minimizing ion transport pathways.

Conclusions to chapter 5

This chapter employed computational electrochemistry to validate and extend the mechanistic understanding developed through experimentation. A multi-physics finite element model was developed, coupling Butler-Volmer electrode kinetics with porous media transport theory to simulate the electrochemical behavior of the coated surfaces.

After careful parameterization, the converged model successfully reproduced the experimentally measured polarization curves and corrosion current densities with high fidelity (within 10% deviation) for both bare aluminum and the optimized C4 coating. This quantitative agreement validated the model as a reliable predictive tool.

Beyond validation, the computational framework enabled a mechanistic decomposition of the protection mechanisms, a level of quantitative insight inaccessible through experimental methods alone. The model revealed that the superior

electrochemical performance of the C4 coating arises from two synergistic effects: a 3.2-fold increase in the solution resistance due to the tortuous ion diffusion pathways created by the dense particle network, and a 5.8-fold increase in the charge transfer resistance resulting from the chemical passivation of the surface by the silane treatment. This work demonstrates the power of validated computational models to deconstruct complex phenomena and guide the optimization of advanced materials.

The results of this chapter were published in:

Xi, L., Tang, L., Leung, P., **ZUO,Y**, Myronyuk, O., Liao, Q. (2023). Empowering organic redox flow batteries with organic acid electrolytes for enhanced energy densities. *Міжнародна конференція з хімії, хімічної технології та екології, присвяченій 125-річчю КІІ ім. Ігоря Сікорського Збірка тез доповідей, 2023*, 143-145. <https://www.researchgate.net/profile/Valerii-Kolesnikov/publication/375610108>

CONCLUSIONS

Mechanistic relationships governing the formation, structure, and environmental durability of superhydrophobic composite coatings for aluminum corrosion protection have been established through an integrated experimental and computational approach. The obtained results demonstrate that durable superhydrophobic performance arises from the synergistic interaction between hierarchical surface structure, controlled surface chemistry, and diffusion-limiting composite architectures. On this basis, mechanism-driven design principles for composite coatings capable of maintaining performance under combined ultraviolet, hydrodynamic, and electrochemical stresses have been formulated.

A knowledge gap concerning the durability of superhydrophobic coatings in aggressive environments has been clarified through systematic investigation of wetting behavior and surface energy characteristics. A comprehensive characterization methodology combining the Owens–Wendt surface energy decomposition method with dynamic contact angle analysis has been implemented, enabling quantitative determination of dispersive and polar components of surface energy. The results demonstrate that stabilization of the Cassie–Baxter wetting regime requires reduction of the polar surface energy component from approximately 20 mJ/m² to values below 1 mJ/m² through silane functionalization, enabling apparent water contact angles exceeding 150° and providing a quantitative design criterion for chemical surface modification.

The role of hierarchical surface texture and chemical modification in stabilizing superhydrophobicity has been quantified through a multi-scale investigation of textured aluminum surfaces with characteristic feature sizes ranging from 100 nm laser-induced periodic surface structures to 750 μm micromilled grooves. The obtained results reveal the limits of applicability of classical wetting models for engineered textures. In particular, it has been shown that the Wenzel wetting model becomes invalid for textures with periodicities exceeding approximately 200 μm, where wetting

behavior is governed by contact line pinning at structural edges rather than equilibrium thermodynamic wetting conditions.

The dominant degradation mechanisms governing the environmental stability of superhydrophobic composite coatings have been identified through accelerated weathering experiments combined with chemical analysis. Ultraviolet aging experiments conducted under 340 nm irradiation with an intensity of 0.89 W/m² at 60 °C and 50% relative humidity demonstrated that polymer photo-oxidation is the primary degradation pathway. FTIR spectroscopy revealed a 60–80% decrease in aliphatic C–H stretching vibrations (2850–2950 cm⁻¹) together with a fivefold increase in carbonyl absorption near 1731 cm⁻¹, confirming chemical transformation of hydrophobic groups into oxygen-containing polar functionalities. Based on this mechanism, an optimized composite coating formulation containing 5 wt.% acrylic copolymer binder, 90 wt.% silane-functionalized calcium carbonate microparticles ($d_{50} \approx 5 \mu\text{m}$), and 5 wt.% fumed silica nanoparticles ($d_{50} \approx 12 \text{ nm}$) has been developed. The coating exhibits a +797 mV noble shift in corrosion potential (from –660 mV to +137 mV vs. SCE), impedance values exceeding 688 $\Omega \cdot \text{cm}^2$ at 0.01 Hz, and maintains water contact angles above 130° after 72 hours of immersion in 3 wt.% NaCl electrolyte, confirming its enhanced corrosion resistance and environmental durability.

A multi-physics computational model describing electrochemical corrosion behavior of bifractional superhydrophobic composite coatings has been developed and experimentally validated. The model couples Butler–Volmer electrochemical kinetics with porous media transport, enabling quantitative prediction of electrochemical polarization behavior and mechanistic separation of protection mechanisms. The simulation results reproduce experimental polarization curves with an accuracy of approximately 10% across the full potential range and reveal that the improved corrosion resistance results from a synergistic combination of a 3.2-fold increase in solution resistance due to tortuous ionic diffusion pathways within the particle network and a 5.8-fold increase in charge transfer resistance caused by surface passivation through silane functionalization. These results confirm that the dense inorganic particle

network simultaneously generates hierarchical roughness necessary for superhydrophobicity and forms an effective diffusion barrier limiting electrolyte penetration.

References list

1. Barthlott, W., Neinhuis, C. (1997). Purity of the sacred lotus, or escape from contamination in biological surfaces. *Planta*, 202, 1–8. <https://doi.org/10.1007/s004250050096>
2. Young, T. (1805). An essay on the cohesion of fluids. *Philosophical transactions of the royal society of London*, 65–87. <https://doi.org/10.1098/rspl.1800.0095>
3. Ma, M., Hill, R.M. (2006). Superhydrophobic surfaces. *Current opinion in colloid & interface science*, 11, 193–202. <https://doi.org/10.1016/j.cocis.2006.06.002>
4. Xiang, S., Liu, W. (2021). Self-healing superhydrophobic surfaces: healing principles and applications. *Advanced Materials Interfaces*, 8, 2100247. <https://doi.org/10.1002/admi.202100247>
5. Cassie, A. (1948). Contact angles. *Discussions of the Faraday society*, 3, 11–16. <https://doi.org/10.1039/DF9480300011>
6. Ensikat, H.J., Ditsche-Kuru, P., Neinhuis, C., Barthlott, W. (2011). Superhydrophobicity in perfection: the outstanding properties of the lotus leaf. *Beilstein journal of nanotechnology*, 2, 152–161. <https://doi.org/10.3762/bjnano.2.19>
7. Mehanna, Y.A., Sadler, E., Upton, R.L., Kempchinsky, A.G., Lu, Y., Crick, C.R. (2021). The challenges, achievements and applications of submersible superhydrophobic materials. *Chemical Society Reviews*, 50, 6569–6612. <https://doi.org/10.1039/D0CS01056A>
8. Jeevahan, J., Chandrasekaran, M., Joseph, G.B., Durairaj, R., Mageshwaran, G. (2018). Superhydrophobic surfaces: a review on fundamentals, applications, and challenges. *Journal of Coatings Technology and Research*, 15, 231–250. <https://doi.org/10.1007/s11998-017-0011-x>
9. Wenzel, R.N. (1949). Surface roughness and contact angle. *The Journal of Physical Chemistry*, 53, 1466–1467. <https://doi.org/10.1021/j150474a015>

10. Cassie, A., Baxter, S. (1944). Wettability of porous surfaces. *Transactions of the Faraday society*, 40, 546–551. <https://doi.org/10.1039/TF9444000546>
11. Myronyuk, O., Vanagas, E., Rodin, A.M., Wesolowski, M. (2024). Estimation of the Structure of Hydrophobic Surfaces Using the Cassie–Baxter Equation. *Materials*, 17, 4322. <https://doi.org/10.3390/ma17174322>
12. Whyman, G., Bormashenko, E., Stein, T. (2008). The rigorous derivation of Young, Cassie–Baxter and Wenzel equations and the analysis of the contact angle hysteresis phenomenon. *Chemical Physics Letters*, 450, 355–359. <https://doi.org/10.1016/j.cplett.2007.11.033>
13. Giacomello, A., Meloni, S., Chinappi, M., Casciola, C.M. (2012). Cassie–Baxter and Wenzel states on a nanostructured surface: phase diagram, metastabilities, and transition mechanism by atomistic free energy calculations. *Langmuir*, 28, 10764–10772. <https://doi.org/10.1021/la3018453>
14. Peters, A., Pirat, C., Sbragaglia, M., Borkent, B., Wessling, M., Lohse, D., Lammertink, R.G. (2009). Cassie-Baxter to Wenzel state wetting transition: Scaling of the front velocity. *The European Physical Journal E*, 29, 391–397. <https://doi.org/10.1140/epje/i2009-10489-3>
15. Erbil, H.Y., Cansoy, C.E. (2009). Range of applicability of the Wenzel and Cassie–Baxter equations for superhydrophobic surfaces. *Langmuir*, 25, 14135–14145. <https://doi.org/10.1021/la902098a>
16. Murakami, D., Jinnai, H., Takahara, A. (2014). Wetting transition from the Cassie–Baxter state to the Wenzel state on textured polymer surfaces. *Langmuir*, 30, 2061–2067. <https://doi.org/10.1021/la4049067>
17. Li, X.-M., Reinhoudt, D., Crego-Calama, M. (2007). What do we need for a superhydrophobic surface? A review on the recent progress in the preparation of superhydrophobic surfaces. *Chemical Society Reviews*, 36, 1350–1368. <https://doi.org/10.1039/B602486F>
18. Crick, C.R., Parkin, I.P. (2010). Preparation and characterisation of superhydrophobic surfaces. *Chemistry–A European Journal*, 16, 3568–3588. <https://doi.org/10.1002/chem.200903335>

19. Lu, Y., Sathasivam, S., Song, J., Crick, C.R., Carmalt, C.J., Parkin, I.P. (2015). Robust self-cleaning surfaces that function when exposed to either air or oil. *Science*, 347, 1132–1135. <https://doi.org/10.1126/science.aaa0946>
20. Guo, Y., Zhao, H. (2024). Femtosecond laser processed superhydrophobic surface. *Journal of Manufacturing Processes*, 109, 250–287. <https://doi.org/10.1016/j.jmapro.2023.12.005>
21. Myronyuk, O., Baklan, D., Rodin, A.M., Vanagas, E., Yong, Z. (2023). Owens–Wendt characterization of Femtosecond-Laser-Textured hydrophobic aluminum surfaces. *Coatings*, 13, 1104. <https://doi.org/10.3390/coatings13061104>
22. Yong, J., Yang, Q., Guo, C., Chen, F., Hou, X. (2019). A review of femtosecond laser-structured superhydrophobic or underwater superoleophobic porous surfaces/materials for efficient oil/water separation. *RSC advances*, 9, 12470–12495. <https://doi.org/10.1039/C8RA10673H>
23. Long, J., Fan, P., Gong, D., Jiang, D., Zhang, H., Li, L., Zhong, M. (2015). Superhydrophobic surfaces fabricated by femtosecond laser with tunable water adhesion: from lotus leaf to rose petal. *ACS applied materials & interfaces*, 7, 9858–9865. <https://doi.org/10.1021/acsami.5b01870>
24. Long, J., Pan, L., Fan, P., Gong, D., Jiang, D., Zhang, H., Li, L., Zhong, M. (2016). Cassie-state stability of metallic superhydrophobic surfaces with various micro/nanostructures produced by a femtosecond laser. *Langmuir*, 32, 1065–1072. <https://doi.org/10.1021/acs.langmuir.5b04329>
25. Phillips, K.C., Gandhi, H.H., Mazur, E., Sundaram, S. (2015). Ultrafast laser processing of materials: a review. *Advances in Optics and Photonics*, 7, 684–712. <https://doi.org/10.1364/AOP.7.000684>
26. Dunn, A., Wasley, T.J., Li, J., Kay, R.W., Stringer, J., Smith, P.J., Esenturk, E., Connaughton, C., Shephard, J.D. (2016). Laser textured superhydrophobic surfaces and their applications for homogeneous spot deposition. *Applied Surface Science*, 365, 153–159. <https://doi.org/10.1016/j.apsusc.2016.01.019>

27. Shang, H.M., Wang, Y., Takahashi, K., Cao, G.Z., Li, D., Xia, Y. (2005). Nanostructured superhydrophobic surfaces. *Journal of materials science*, 40, <https://doi.org/10.1007/s10853-005-2892-9>
28. Roach, P., Shirtcliffe, N.J., Newton, M.I. (2008). Progress in superhydrophobic surface development. *Soft matter*, 4, 224–240. <https://doi.org/10.1039/B712575P>
29. Celia, E., Darmanin, T., de Givency, E.T., Amigoni, S., Guittard, F. (2013). Recent advances in designing superhydrophobic surfaces. *Journal of colloid and interface science*, 402, 1–18. <https://doi.org/10.1016/j.jcis.2013.03.041>
30. Bayer, I.S. (2020). Superhydrophobic coatings from ecofriendly materials and processes: a review. *Advanced Materials Interfaces*, 7, 2000095. <https://doi.org/10.1002/admi.202000095>
31. Qian, B., Shen, Z. (2005). Fabrication of superhydrophobic surfaces by dislocation-selective chemical etching on aluminum, copper, and zinc substrates. *Langmuir*, 21, 9007–9009. <https://doi.org/10.1021/la051308c>
32. Simpson, J.T., Hunter, S.R., Aytug, T. (2015). Superhydrophobic materials and coatings: a review. *Reports on Progress in Physics*, 78, 086501. <https://doi.org/10.1088/0034-4885/78/8/086501>
33. Manoharan, K., Bhattacharya, S. (2019). Superhydrophobic surfaces review: Functional application, fabrication techniques and limitations. *Journal of Micromanufacturing*, 2, 59–78. <https://doi.org/10.1177/2516598419836345>
34. Pozzato, A., Dal Zilio, S., Fois, G., Vendramin, D., Mistura, G., Belotti, M., Chen, Y., Natali, M. (2006). Superhydrophobic surfaces fabricated by nanoimprint lithography. *Microelectronic Engineering*, 83, 884–888. <https://doi.org/10.1016/j.mee.2006.01.012>
35. Agrawal, H., Garnett, E.C. (2020). Nanocube imprint lithography. *ACS nano*, 14, 11009–11016. <https://doi.org/10.1021/acsnano.0c04793>
36. Atthi, N., Dielen, M., Sripumkhai, W., Pattamang, P., Meananeatra, R., Saengdee, P., Thongsook, O., Ranron, N., Pankong, K., Uahchinkul, W. (2021). Fabrication of high aspect ratio micro-structures with superhydrophobic and

oleophobic properties by using large-area roll-to-plate nanoimprint lithography. *Nanomaterials*, 11, 339. <https://doi.org/10.3390/nano11020339>

37. Yun, X., Xiong, Z., He, Y., Wang, X. (2020). Superhydrophobic lotus-leaf-like surface made from reduced graphene oxide through soft-lithographic duplication. *RSC advances*, 10, 5478–5486. <https://doi.org/10.1039/C9RA10373B>

38. Xue, C.-H., Jia, S.-T., Zhang, J., Ma, J.-Z. (2010). Large-area fabrication of superhydrophobic surfaces for practical applications: an overview. *Science and Technology of Advanced Materials*, 11, 033002. <https://doi.org/10.1088/1468-6996/11/3/033002>

39. Chen, H., Li, X., Li, D. (2022). Superhydrophilic–superhydrophobic patterned surfaces: From simplified fabrication to emerging applications. *Nanotechnology and Precision Engineering*, 5, <https://doi.org/10.1063/10.0013222>

40. Zhao, W., Zhan, Y., Li, W., Hao, S., Amirfazli, A. (2024). Application of 3D printing for fabrication of superhydrophobic surfaces with reversible wettability. *RSC advances*, 14, 17684–17695. <https://doi.org/10.1039/D4RA02742F>

41. Jafari, R., Cloutier, C., Allahdini, A., Momen, G. (2019). Recent progress and challenges with 3D printing of patterned hydrophobic and superhydrophobic surfaces. *The International Journal of Advanced Manufacturing Technology*, 103, 1225–1238. <https://doi.org/10.1007/s00170-019-03630-4>

42. Yang, Y., Li, X., Zheng, X., Chen, Z., Zhou, Q., Chen, Y. (2018). 3D-printed biomimetic super-hydrophobic structure for microdroplet manipulation and oil/water separation. *Advanced materials*, 30, 1704912. <https://doi.org/10.1002/adma.201704912>

43. Lv, J., Gong, Z., He, Z., Yang, J., Chen, Y., Tang, C., Liu, Y., Fan, M., Lau, W.-M. (2017). 3D printing of a mechanically durable superhydrophobic porous membrane for oil–water separation. *Journal of Materials Chemistry A*, 5, 12435–12444. <https://doi.org/10.1039/C7TA02202F>

44. Yuan, S., Strobbe, D., Kruth, J.-P., Van Puyvelde, P., Van der Bruggen, B. (2017). Super-hydrophobic 3D printed polysulfone membranes with a switchable wettability by self-assembled candle soot for efficient gravity-driven oil/water

separation. *Journal of Materials Chemistry A*, 5, 25401–25409.
<https://doi.org/10.1039/C7TA08836A>

45. Doshi, J., Reneker, D.H. (1995). Electrospinning process and applications of electrospun fibers. *Journal of electrostatics*, 35, 151–160.
[https://doi.org/10.1016/0304-3886\(95\)00041-8](https://doi.org/10.1016/0304-3886(95)00041-8)

46. Larrondo, L., Manley, R.S.J. (1981). Electrostatic fiber spinning from polymer melts. I. Experimental observations on fiber formation and properties. *Journal of Polymer Science: Polymer Physics Edition*, 19, 909–920.
<https://doi.org/10.1002/pol.1981.180190601>

47. Ma, M., Mao, Y., Gupta, M., Gleason, K.K., Rutledge, G.C. (2005). Superhydrophobic fabrics produced by electrospinning and chemical vapor deposition. *Macromolecules*, 38, 9742–9748. <https://doi.org/10.1021/ma0511189>

48. Sas, I., Gorga, R.E., Joines, J.A., Thoney, K.A. (2012). Literature review on superhydrophobic self-cleaning surfaces produced by electrospinning. *Journal of Polymer Science Part B: Polymer Physics*, 50, 824–845.
<https://doi.org/10.1002/polb.23070>

49. Nuraje, N., Khan, W.S., Lei, Y., Ceylan, M., Asmatulu, R. (2013). Superhydrophobic electrospun nanofibers. *Journal of Materials Chemistry A*, 1, 1929–1946. <https://doi.org/10.1039/C2TA00189F>

50. Vicente, A., Rivero, P.J., Urdiroz, U., García, P., Mora, J., Palacio, J.F., Palomares, F.J., Rodríguez, R. (2022). Novel design of superhydrophobic and anticorrosive PTFE and PAA+ β -CD composite coating deposited by electrospinning, spin coating and electrospraying techniques. *Polymers*, 14, 4356.
<https://doi.org/10.3390/polym14204356>

51. Lau, K.K., Bico, J., Teo, K.B., Chhowalla, M., Amaratunga, G.A., Milne, W.I., McKinley, G.H., Gleason, K.K. (2003). Superhydrophobic carbon nanotube forests. *Nano letters*, 3, 1701–1705. <https://doi.org/10.1021/nl034704t>

52. Boinovich, L., Emelyanenko, A. (2009). Principles of design of superhydrophobic coatings by deposition from dispersions. *Langmuir*, 25, 2907–2912.
<https://doi.org/10.1021/la803806w>

53. Sutar, R.S., Latthe, S.S., Nagappan, S., Ha, C.S., Sadasivuni, K.K., Liu, S., Xing, R., Bhosale, A.K. (2021). Fabrication of robust self-cleaning superhydrophobic coating by deposition of polymer layer on candle soot surface. *Journal of Applied Polymer Science*, 138, 49943. <https://doi.org/10.1002/app.49943>
54. Tang, Z.Q., Tian, T., Molino, P.J., Skvortsov, A., Ruan, D., Ding, J., Li, Y. (2024). Recent advances in superhydrophobic materials development for maritime applications. *Advanced Science*, 11, 2308152. <https://doi.org/10.1002/advs.202308152>
55. CNTs-SiO₂, d. (2021). A durable and photothermal superhydrophobic coating with entwined CNTs-SiO₂ hybrids for anti-icing applications. *Chemical Engineering Journal*, 423, <https://doi.org/10.1016/j.cej.2021.130238>
56. Parvate, S., Dixit, P., Chattopadhyay, S. (2020). Superhydrophobic surfaces: insights from theory and experiment. *The Journal of Physical Chemistry B*, 124, 1323–1360. <https://doi.org/10.1021/acs.jpcc.9b08567>
57. Barthwal, S., Uniyal, S., Barthwal, S. (2024). Nature-inspired superhydrophobic coating materials: drawing inspiration from nature for enhanced functionality. *Micromachines*, 15, 391. <https://doi.org/10.3390/mi15030391>
58. Kumar, A., Nanda, D. (2019). Methods and fabrication techniques of superhydrophobic surfaces. *Superhydrophobic polymer coatings*, 43–75. <https://doi.org/10.1016/B978-0-12-816671-0.00004-7>
59. Hamad, S., Moram, S.S.B., Yendeti, B., Podagatlapalli, G.K., Rao, S.N., Pathak, A.P., Mohiddon, M.A., Soma, V.R. (2018). Femtosecond laser-induced, nanoparticle-embedded periodic surface structures on crystalline silicon for reproducible and multi-utility SERS platforms. *Acs Omega*, 3, 18420–18432. <https://doi.org/10.1021/acsomega.8b02629>
60. Fan, P., Pan, R., Zhong, M. (2019). Ultrafast laser enabling hierarchical structures for versatile superhydrophobicity with enhanced Cassie–Baxter stability and durability. *Langmuir*, 35, 16693–16711. <https://doi.org/10.1021/acs.langmuir.9b02986>
61. Sugioka, K., Cheng, Y. (2014). Femtosecond laser three-dimensional micro- and nanofabrication. *Applied physics reviews*, 1, <https://doi.org/10.1063/1.4904320>

62. Rajan, R.A., Ngo, C.-V., Yang, J., Liu, Y., Rao, K., Guo, C. (2021). Femtosecond and picosecond laser fabrication for long-term superhydrophilic metal surfaces. *Optics & Laser Technology*, 143, 107241. <https://doi.org/10.1016/j.optlastec.2021.107241>
63. De Marco, C., Eaton, S.M., Suriano, R., Turri, S., Levi, M., Ramponi, R., Cerullo, G., Osellame, R. (2010). Surface properties of femtosecond laser ablated PMMA. *ACS applied materials & interfaces*, 2, 2377–2384. <https://doi.org/10.1021/am100393e>
64. Gojda, F., Loulakis, M., Papoutsakis, L., Tzortzakis, S., Chrissopoulou, K., Anastasiadis, S.H. (2022). Altering the surface properties of metal alloys utilizing facile and ecological methods. *Langmuir*, 38, 4826–4838. <https://doi.org/10.1021/acs.langmuir.1c03431>
65. Klimov, V.V., Shilin, A.K., Kusakovskiy, D.A., Kolyaganova, O.V., Kharlamov, V.O., Rudnev, A.V., Le, M.D., Bryuzgin, E.V., Navrotskii, A.V. (2024). Formation of Superhydrophobic Coatings Based on Dispersion Compositions of Hexyl Methacrylate Copolymers with Glycidyl Methacrylate and Silica Nanoparticles. *Polymers*, 16, 3094. <https://doi.org/10.3390/polym16213094>
66. Feuerstein, A., Knapp, J., Taylor, T., Ashary, A., Bolcavage, A., Hitchman, N. (2008). Technical and economical aspects of current thermal barrier coating systems for gas turbine engines by thermal spray and EBPVD: a review. *Journal of thermal spray technology*, 17, 199–213. <https://doi.org/10.1007/s11666-007-9148-y>
67. Majumdar, J.D., Manna, I. (2011). Laser material processing. *International materials reviews*, 56, 341–388. <https://doi.org/10.1179/1743280411Y.0000000003>
68. Meijer, J. (2004). Laser beam machining (LBM), state of the art and new opportunities. *Journal of materials processing technology*, 149, 2–17. <https://doi.org/10.1016/j.jmatprotec.2004.02.003>
69. Dimitrov, D., Schreve, K., de Beer, N. (2006). Advances in three dimensional printing—state of the art and future perspectives. *Rapid Prototyping Journal*, 12, 136–147. <https://doi.org/10.1108/13552540610670717>

70. Alimardani, M., Toyserkani, E., Huissoon, J.P. (2007). Three-dimensional numerical approach for geometrical prediction of multilayer laser solid freeform fabrication process. *Journal of laser applications*, 19, 14–25. <https://doi.org/10.2351/1.2402518>
71. Kromer, R., Danlos, Y., Aubignat, E., Verdy, C., Costil, S. (2017). Coating deposition and adhesion enhancements by laser surface texturing - metallic particles on different classes of substrates in cold spraying process. *Materials and manufacturing Processes*, 32, 1642–1652. <https://doi.org/10.1080/10426914.2017.1364750>
72. Taliantzis, K., Ellinas, K. (2025). Green hydrophobic and superhydrophobic coatings and surfaces for water related applications: A review. *Advances in Colloid and Interface Science*, 103566. <https://doi.org/10.1016/j.cis.2025.103566>
73. Khaskhoussi, A., Rahimi, E., Calabrese, L., Cornet, A., Anusuyadevi, P.R., Gonugunta, P., Mol, A., Proverbio, E. (2025). Advanced durable ceramic-polymer ultra-superhydrophobic coating with anti-icing, anti-vapor condensation, and corrosion-resistant properties. *Chemical Engineering Journal*, 163767. <https://doi.org/10.1016/j.cej.2025.163767>
74. Lai, Y.J., Oh, P.C., Chew, T.L., Ahmad, A.L. (2025). Surface repellency beyond hydrophobicity: a review on the latest innovations in superomniphobic surfaces. *ACS omega*, 10, 5172–5192. <https://doi.org/10.1021/acsomega.4c08269>
75. Kodikara, N., De Silva, G. (2018). Study of the Effects of Magnesium Content on the Mechanical Properties of Aluminium 6063 Extrudates. *Engineer: Journal of the Institution of Engineers, Sri Lanka*, 51, <https://doi.org/10.4038/engineer.v51i2.7289>
76. Camargo, K.C., Michels, A.F., Rodembusch, F.S., Horowitz, F. (2012). Multi-scale structured, superhydrophobic and wide-angle, antireflective coating in the near-infrared region. *Chemical Communications*, 48, 4992–4994. <https://doi.org/10.1039/C2CC30456B>
77. Myronyuk, O., Baklan, D., Yong, Z., Rodin, A.M. (2022). Complex destruction of textured water-repellent coatings under the influence of UV and water

flow. *Materials Today Communications*, 33, 104509.
<https://doi.org/10.1016/j.mtcomm.2022.104509>

78. Hu, Q., Jiang, Y., Wang, Z. (2025). Calcium-based composite materials for thermochemical heat storage: Structure, performance and mechanisms. *Journal of Alloys and Compounds*, 1010, 177960. <https://doi.org/10.1016/j.jallcom.2024.177960>

79. Niu, Y.-Q., Liu, J.-H., Aymonier, C., Fermani, S., Kralj, D., Falini, G., Zhou, C.-H. (2022). Calcium carbonate: controlled synthesis, surface functionalization, and nanostructured materials. *Chemical society reviews*, 51, 7883–7943.
<https://doi.org/10.1039/D1CS00519G>

80. Nejström, M., Andreasson, B., Sjölund, J., Eivazi, A., Svanedal, I., Edlund, H., Norgren, M. (2023). On Structural and Molecular Order in Cellulose Acetate Butyrate Films. *Polymers*, 15, 2205. <https://doi.org/10.3390/polym15092205>

81. Li, S., Zhang, K., Liu, W., Chen, T., Li, Q., Wang, W., Bian, H. (2025). Functional Properties of Micro–Nano Structure Surfaces Prepared by Femtosecond Laser: A Review. *Advanced Engineering Materials*, 2500365.
<https://doi.org/10.1002/adem.202500365>

82. Mishra, P., Singh, U., Pandey, C.M., Mishra, P., Pandey, G. (2019). Application of student's t-test, analysis of variance, and covariance. *Annals of cardiac anaesthesia*, 22, 407–411. https://doi.org/10.4103/aca.aca_92_18

83. Chenab, K.K., Sohrabi, B., Rahmanzadeh, A. (2019). Superhydrophobicity: advanced biological and biomedical applications. *Biomaterials science*, 7, 3110–3137.
<https://doi.org/10.1039/c9bm00424f>

84. Correa, D.S., Almeida, J.M., Almeida, G.F., Cardoso, M.R., De Boni, L., Mendonça, C.R. (2017). Photonics. *MDPI*, 8.
<https://doi.org/10.3390/photonics4010008>

85. Oleksiy, M., Volodymyr, D., Denis, B., Liubov, M. (2017). Study of structure influence on wear resistance of hierarchical superhydrophobic coatings. *Восточно-Европейский журнал передовых технологий*, 3, 44–49.
<https://doi.org/10.15587/1729-4061.2017.103028>

86. Yang, Z., Liu, X., Tian, Y. (2019). Insights into the wettability transition of nanosecond laser ablated surface under ambient air exposure. *Journal of colloid and interface science*, 533, 268–277. <https://doi.org/10.1016/j.jcis.2018.08.082>
87. Verma, C., Alameri, A., Barsoum, I., Alfantazi, A. (2025). Review on corrosion-related aspects of metallic alloys additive manufactured with laser powder bed-fusion (LPBF) technology. *Progress in Additive Manufacturing*, 10, 3195–3223. <https://doi.org/10.1007/s40964-024-00810-x>
88. Liu, W., Wang, X., Xiang, S., Lian, Y., Tao, S. (2024). Stretchable Superhydrophobic Surfaces: From Basic Fabrication Strategies to Applications. *Processes*, 12, 124. <https://doi.org/10.3390/pr12010124>
89. Josyula, T., Malla, L.K., Thomas, T.M., Kalichetty, S.S., Mahapatra, P.S., Pattamatta, A. (2024). Fundamentals and applications of surface wetting. *Langmuir*, 40, 8293–8326. <https://doi.org/10.1021/acs.langmuir.3c03339>
- 90 Bonn, D., Eggers, J., Indekeu, J., Meunier, J., Rolley, E. (2009). Wetting and spreading. *Reviews of modern physics*, 81, 739–805. <https://doi.org/10.1103/RevModPhys.81.739>
91. Farzam, M., Beitollahpoor, M., Solomon, S.E., Ashbaugh, H.S., Pesika, N.S. (2022). Advances in the fabrication and characterization of superhydrophobic surfaces inspired by the Lotus leaf. *Biomimetics*, 7, 196. <https://doi.org/10.3390/biomimetics7040196>
92. Milles, S., Soldera, M., Voisiat, B., Lasagni, A.F. (2019). Fabrication of superhydrophobic and ice-repellent surfaces on pure aluminium using single and multiscaled periodic textures. *Scientific reports*, 9, 13944. <https://doi.org/10.3390/ma12213497>
93. Ai, Y., Yu, L., Huang, Y., Liu, X. (2022). The investigation of molten pool dynamic behaviors during the "∞" shaped oscillating laser welding of aluminum alloy. *International Journal of Thermal Sciences*, 173, 107350. <https://doi.org/10.1016/j.ijthermalsci.2021.107350>
94. Myronyuk, O., Raks, V.A., Baklan, D., Vasyliiev, G., Vanagas, E., Kurdil, N., Sivolapov, P. (2022). Water repellent coatings with hierarchal structures obtained on

anodized aluminum with femtosecond laser ablation. *Applied Nanoscience*, 12, 523–531. <https://doi.org/10.1007/s13204-021-01697-8>

95. Kumar, A., Singh, V.P., Singh, R., Chaudhary, R., Kumar, D., Mourad, A.-H.I. (2024). A review of aluminum metal matrix composites: fabrication route, reinforcements, microstructural, mechanical, and corrosion properties. *Journal of Materials Science*, 59, 2644–2711. <https://doi.org/10.1007/s10853-024-09398-7>

96. Wahid, M.A., Siddiquee, A.N., Khan, Z.A. (2020). Aluminum alloys in marine construction: characteristics, application, and problems from a fabrication viewpoint. *Marine Systems & Ocean Technology*, 15, 70–80. <https://doi.org/10.1007/s40868-019-00069-w>

97. Escobar, A.M., Llorca-Isern, N. (2014). Superhydrophobic coating deposited directly on aluminum. *Applied surface science*, 305, 774–782. <https://doi.org/10.1016/j.apsusc.2014.03.196>

98. Zhu, Q., Du, X., Liu, Y., Fang, X., Chen, D., Zhang, Z. (2023). Preparation and applications of superhydrophobic coatings on aluminum alloy surface for anti-corrosion and anti-fouling: a mini review. *Coatings*, 13, 1881. <https://doi.org/10.3390/coatings13111881>

99. Liu, J., Fang, X., Zhu, C., Xing, X., Cui, G., Li, Z. (2020). Fabrication of superhydrophobic coatings for corrosion protection by electrodeposition: A comprehensive review. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 607, 125498. <https://doi.org/10.1016/j.colsurfa.2020.125498>

100. Zheng, S., Li, C., Fu, Q., Hu, W., Xiang, T., Wang, Q., Du, M., Liu, X., Chen, Z. (2016). Development of stable superhydrophobic coatings on aluminum surface for corrosion-resistant, self-cleaning, and anti-icing applications. *Materials & Design*, 93, 261–270. <https://doi.org/10.1016/j.matdes.2015.12.155>

101. Yin, B., Fang, L., Hu, J., Tang, A., He, J., Mao, J. (2012). A facile method for fabrication of superhydrophobic coating on aluminum alloy. *Surface and Interface Analysis*, 44, 439–444. <https://doi.org/10.1002/sia.3823>

102. Boinovich, L., Domantovskii, A., Emelyanenko, A., Miller, A., Potapov, Y.F., Khodan, A. (2013). Antiicing performance of superhydrophobic coatings on

aluminum and stainless steel. *Russian Chemical Bulletin*, 62, 380–387.
<https://doi.org/10.1007/s11172-013-0049-6>

103. Shirtcliffe, N.J., McHale, G., Atherton, S., Newton, M.I. (2010). An introduction to superhydrophobicity. *Advances in colloid and interface science*, 161, 124–138. <https://doi.org/10.1016/j.cis.2009.11.001>

104. Ke, S., Li, J., Li, R., Zhu, J., Chen, Y., Hu, J., Lai, Y., Huang, J., Wu, X., Chen, Z. (2025). Recent developments in the fabrication, performance, and application of transparent superhydrophobic coatings. *Advances in Colloid and Interface Science*, 103537. <https://doi.org/10.1016/j.cis.2025.103537>

105. Lama, G.C., Lavorgna, M., Verdolotti, L., Recupido, F., Buonocore, G.G., Bhushan, B. (2026). Functional surface engineering for cultural heritage protection: the role of superhydrophobic and superoleophobic coatings—a comprehensive review. *Beilstein Journal of Nanotechnology*, 17, 63–96. <https://doi.org/10.3762/bjnano.17.6>

106. Zhang, Z., Ou, J., Li, W. (2024). Perspective Chapter: Challenges in the Durability of Superhydrophobic Coatings Pertinent to Unmanned Aerial Vehicle (UAV) Icing Mitigation. *Superhydrophobic Coating-Recent Advances in Theory and Applications*, <https://doi.org/10.5772/intechopen.1004081>

107. Zheng, X., Zhang, H., Chen, B., Shen, H., Li, L., Ju, G. (2026). Flexible and longterm superhydrophobic coating for anti-icing and photothermal de-icing. *Progress in Organic Coatings*, 211, 109729. <https://doi.org/10.1021/ja0547836>

108. Erbil, H.Y. (2020). Practical applications of superhydrophobic materials and coatings: problems and perspectives. *Langmuir*, 36, 2493–2509. <https://doi.org/10.1021/la991660o>

109. Pastrafidou, M., Binas, V., Kartsonakis, I.A. (2025). Designing the Next Generation: A Physical Chemistry Approach to Surface Coating Materials. *Applied Sciences (2076-3417)*, 15, <https://doi.org/10.1002/adma.200290020>

110. Cornet, A., Homborg, A., Mol, J. (2024). Post-service analysis of the degradation and protective mechanisms of chromate-based structural aircraft coatings. *Progress in Organic Coatings*, 192, 108534. <https://doi.org/10.1038/am.2011.184>

111. Cao, X., Pan, J., Cai, G., Hu, Y., Zhang, X., Dong, Z. (2022). Degradation mechanisms of corrosion and biofouling resistance of superhydrophobic coatings in harsh marine conditions. *Progress in Organic Coatings*, 173, 107222. <https://doi.org/10.1002/anie.200460333>
112. Sarangi, A.K., Tripathy, L., Samal, H.B., Das, I.J., Panda, S., Babu, R., Tripathi, A.K., Ansari, A., Malhotra, S.S., Mohapatra, R.K. (2025). Critical narrative review of degradation mechanisms and corrosion resistance in nonmetallic materials. *Discover Chemistry*, 2, 339. <https://doi.org/10.1039/TF9444000546>
113. Farag, A.A., Mohamed, E.A., Toghan, A. (2023). The new trends in corrosion control using superhydrophobic surfaces: a review. *Corrosion Reviews*, 41, 21–37. <https://doi.org/10.1021/ie50320a024>
114. Wenzel, R.N. (1936). Resistance of solid surfaces to wetting by water. *Industrial & engineering chemistry*, 28, 988–994. <https://doi.org/10.1098/rstl.1805.0005>
115. Barthlott, W., Neinhuis, C. (1997). Purity of the sacred lotus, or escape from contamination in biological surfaces. *Planta*, 202, 1–8. <https://doi.org/10.1007/s004250050096>
116. Yong, Z., Baklan, D., Myronyuk, O. (2024). Corrosion resistance of polymer-silica-calcite textured surfaces. *Технології та інжиніринг*, <https://doi.org/10.30857/2786-5371.2024.1.11>
117. Xue, X., Liang, G., Zhang, B. (2025). Superhydrophobic anti-corrosion coating: Advancing research from laboratory to real marine corrosion environment. *Progress in Organic Coatings*, 200, 109020. <https://doi.org/10.1016/j.porgcoat.2024.109020>
118. Bai, Y., Zhang, H., Shao, Y., Zhang, H., Zhu, J. (2021). Recent progresses of superhydrophobic coatings in different application fields: An overview. *Coatings*, 11, 116. <https://doi.org/10.3390/coatings11020116>
119. Bonora, P.L., Deflorian, F., Fedrizzi, L. (1996). Electrochemical impedance spectroscopy as a tool for investigating underpaint corrosion. *Electrochimica acta*, 41, 1073–1082. [https://doi.org/10.1016/0013-4686\(95\)00440-8](https://doi.org/10.1016/0013-4686(95)00440-8)

120. Nishikata, A., Ichihara, Y., Tsuru, T. (1995). An application of electrochemical impedance spectroscopy to atmospheric corrosion study. *Corrosion science*, 37, 897–911. [https://doi.org/10.1016/0010-938X\(95\)00002-2](https://doi.org/10.1016/0010-938X(95)00002-2)
121. Černý, R., Poděbradská, J., Drchalová, J. (2002). Water and water vapor penetration through coatings. *Journal of thermal envelope and building science*, 26, 165–177. <https://doi.org/10.1177/0075424202026002975>
122. Jafarzadeh, S., Chen, Z., Bobaru, F. (2019). Computational modeling of pitting corrosion. *Corrosion reviews*, 37, 419–439. <https://doi.org/10.1515/correv-2019-0049>
123. Wang, L., Li, D., Yang, J., Shao, F., Zhong, X., Zhao, H., Yang, K., Tao, S., Wang, Y. (2016). Modeling of thermal properties and failure of thermal barrier coatings with the use of finite element methods: A review. *Journal of the European Ceramic Society*, 36, 1313–1331. <https://doi.org/10.1016/j.jeurceramsoc.2015.12.038>