Vapor-Phase Thin-Film Polymerization for Microbial-Resistant Surface Functionalization

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Abstract. The focus of this paper is the so-called functional polymer thin films deposited via all-dry vapour-phase processes including CVD, plasma-enhanced CVD, and paracyclophane-based CVD, with the aim of engineering substrate-independent microbial-resistant surfaces for a broad range of healthcare, membrane separation, food processing, and marine applications. Mechanism-organised design strategies: (1) hydration-driven passive resistance with zwitterionic and hydrophilic polymers, (2) contact-active lysis with quaternary-ammonium and cationic coatings, (3) biofilm-disrupting amphiphilic copolymers with dynamic chain reorientation at three-phase interfaces, (4) hybrid multifunctional architectures combining barrier and biocidal properties. The review highlights the capability of vapour deposition to overcome the solution-processing drawbacks, such as the provision of conformal nanoscale films on complex geometries, formulation devoid of solvents, and precise control of the resulting chemistry. Additionally, they also outline other noteworthy synthetic strategies, including post-CVD derivatisation for generating zwitterions and machine-learning (ML) guided screening of copolymers. Researchers critically evaluate multiple performance assessment practices (protein/bacteria adhesion assays, CFU enumeration, biofilm staining protocols, and LIVE/DEAD viability test) and call for their standardisation for reliable inter-study comparison. The final comments talk about the challenges of scaling up, environmental impacts of fluorinated chemicals, durability under mechanical and chemical stress, and integration possibilities with topographical patterning and stimuli-responsive release systems for the next-generation antimicrobial polymer coatings.

Keywords: Chemical vapor deposition, antibacterial coatings, polymer thin films, bio- fouling, antimicrobial surfaces, vapor-phase polymerization

1 Introduction

The presence of biofilm formation and microbial contamination continues to impact several industries, including healthcare, water treatment, food processing, and marine. Biofouling is responsible for a major impact on the global economy. For example, hull fouling in maritime transport increases fuel consumption by up to 40%. Furthermore, infection by biofouling on medical devices costs billions annually[2]. The conventional

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use of antimicrobial chemical disinfectants has become ineffective as microbes develop resistance to them and they are toxic to the environment[34]. The microbial contamination problem can be mitigated through surface modification in the use of polymer coatings. Yet, conventional solution-based coating methods suffer from serious natures including incompatibility towards the substrate, poor conformality on complex geometries, and organic solvent slum issue[27]. Vapour phase deposition methods provide remarkable advantages through all-dry processing, with no solvent issues and excellent substrate independence and conformality[18]. Chemical vapor deposition (CVD) methods started with the semiconductor industry. They have readily been adapted for organic and polymeric thin film manufacture. The development of CVD for polymer synthesis has opened up new avenues for the design of advanced anti-bacterial surfaces with practical chemical control and uniformity of the nanoscale thickness[4]. Among the various vapour deposition techniques, the initiated CVD (iCVD) method, plasma- enhanced CVD (PECVD), and paracyclophane-based CVD (parylene CVD) methods are particularly suited for conducting antimicrobial applications due to their compatibility with functional organic moieties and gentle processing conditions[12]. The main challenge in the design of antibacterial surfaces is the multi-step nature of biofouling. Bacteria will first weakly attach to the surface of the substrate. Then they will form a strong non-reversible attachment. Next, there will be the production of a biofilm and its maturation to provide a functional structure. Finally, bacteria will disperse in a controlled manner[40]. To effectively combat bacteria, meshed material design with processes involved, to prevent, eradicate and resist bacteria, plays a critical role. This review provides an overview of the recent development in vapour-deposited antibacterial polymer coatings, covering the design principles, synthesis, performance characterization, and implementation issues. Our goal is to lay out a plan for developing future antimicrobial surfaces that effectively utilize vapor-phase polymerization techniques by taking a closer look at what the research currently looks at and what it should focus on next.

2 Vapor-Phase Polymerization Techniques

Unlike conventional coating solutions, vapor-phase polymerization techniques can become the game changers for antibacterial surface functionalization. With the help of these all-dry processes, dissolvent-related limitations are eliminated with the help of these. It also enables an unprecedented amount of control over film chemistry, thickness, and conformality. The basic principles, capabilities, and comparative advantages of the main CVD techniques used for the fabrication of antibacterial coatings is investigated in this section.

2.1 Initiated Chemical Vapour Deposition (iCVD)

The technique of initiated CVD has proven effective at synthesising thin films of a functional polymer while retaining organic functionality. The iCVD process uses a volatile initiator species that thermally decomposes to generate free radicals. These free radical species initiate chain-growth polymerization of adsorbed monomer molecules on the cooler substrate surface[12]. The process is practically identical to a free-radical polymerisation process, but in vapor phase, leading to better retention of functional groups for the antibacterial activity. The reason why iCVD is substrate-independent is partly due to van der Waals interactions between the deposited coating and solid substrates. During the deposition process, gaseous monomers are physisorbed on the solid substrate[18]. The feature allows effective coating onto substrates and coating scales ranging from centimetre-scale medical devices to nanometer-scale membrane pores with high performance and conformality[31]. The thermal activation in iCVD which takes place at around 200-300 °C for the decomposition of the initiator, does not result in the degradation of the material. This makes it compatible with delicate substrates, such as textiles, biological scaffolds, and polymeric membranes. A major advantage of iCVD for antimicrobial applications is the potential for zwitterionic polymer coatings fabrication, using novel two-step strategies[52]. Although zwitterionic monomers do not typically display sufficient volatility for direct vapour deposition, we demonstrate their formation using iCVD through consecutive deposition of a polymer containing a tertiary amine followed by vapour- phase derivatisation with a ring-opening reagent (e.g., 1,3-propane sulfone)[5]. This approach allows access to some of the most efficient antifouling chemicals ever described, which have shown efficacy in water purification membranes, implantable devices, and marine coatings. The iCVD technique's conformal coverage functionality can be helpful in modifying complicated geometry and high-aspect-ratio structures for antibacterial applications. iCVD coating deposition within the nanoscale pores of membranes is uniform[53], on nanopillar arrays mimicking bactericidal natural surfaces [8], as well as three-dimensional designs of medical devices[45]. The ability to deposit non-line-of-sight due to Knudsen diffusion into tiny shapes overcomes a key limitation of solution-based methods in many real-world applications.

2.2 Plasma-Enhanced CVD (PECVD)

Plasma-enhanced CVD uses direct current or radio frequency power to generate low-temperature plasma to activate monomer species for polymerization[49]. The environment created by plasma is a complex mixture of ions, electrons and neutral species, due to which polymerisation and etching processes get initiated simultaneously. The film properties of the result are influenced by their dual character, including crosslink density, functional group retention and surface morphology. Photochemical

vapour deposition occurs at a pressure lower than the atmospheric pressure and also at high temperatures. The range of monomers compatible with polylactic acid has expanded the possibility of deposition of different antibacterial coatings, especially oregano secondary metabolites[39] and terpinen-4- ol [23]. Nevertheless, the aggressive plasma environment can also cause fragmentation of delicate functional groups, which may damage the biological activity of the coatings deposited. Recent advances in the PECVD process control have overcome some limitations using optimised parameters and pulsed plasma operation. Research has shown that lower power and frequency pulsed plasma modes can improve retention of antimicrobial functional groups and maintain reasonable deposition rates[24]. Moreover, systems have been developed for PECVD at atmospheric pressure to enable continuous processing of temperature-sensitive substrates, broadening the application of the technique for use in biomedical devices and flexible electronics.

PECVD has been particularly useful in the deposition of hydrophilic antifouling coatings on optical devices and sensors, where conformal coverage and optical transparency are critical. Just as with 1-vinyl-2-pyrrolidinone and poly(ethylene glycol)methacrylate coatings synthesised by PECVD on orthokeratology lenses, optical transparency was retained, and protein adsorption and bacterial adhesion inhibition was significant[50]. The notion that vapour-phase methods can alter delicate substrates without compromising their main function is a strong, unique selling point.

2.3 Paracyclophane-Based CVD

The process of CVD that makes use of paracyclophane derivatives is also known as parylene deposition or chemical vapour polymerisation (CVP). This process works with the sublimation of [2.2] paracyclophane derivatives and a pyrolysis step of the evaporated material that generates reactive quinodimethane intermediates [47]. These diradicals polymers subsequently polymerise on substrate surfaces by step-growth mechanism, forming linear poly(p-xylylene) coatings with excellent conformality and pinhole-free. Due to the fact that many different substituted paracyclophanes are now com- mercially available, it is possible to deposit functionalized parylene films with the desired chemical, mechanical and electrical characteristics [15]. Parylene C (chlorinated), Parylene D (dichlorinated) and Parylene AM (amino-functionalized) were examined extensively for biological applications because of their biocompatibility and USP Class VI certification for medical devices [13].

A deposit of initiator-functionalized films for subsequent surface-initiated polymerisation is a major innovation in parylene-based antibacterial coatings. As an illustration, bromoisobutyrate-functionalized parylene (Parylene-Br) surfaces have been found to be useful for the ATRP of zwitterionic methacryloyloxyethyl phosphorylcholine giving rise to grafted polymer brushes with excellent antifoul- ing

properties[37]. The hybrid combination of vapour-deposited parylene's superior adhesion/conformality and the chemical diversity of solution-based polymerisation.

Table 1. Vapor-Phase Polymerization (Compact)

Tech.	Activ.	FG Ret.	Conf.	Apps
iCVD	Thermal	High	Excl.	Med., sensors
PECVD	Plasma	Mod.	Good	Text., optics
Parylene	Pyrol.	High	Excl.	Implants,elec.

Recent studies also examine the ability of parylene derivatives to resist bacterial infections. Research has shown that coatings of fluorine-substituted parylene F with a reduced bacterial adhesion and stability in the marine environment [48]. In the same way, catechol and quinone-carrying parylene variants were made for the coordination chemistry immobilisation of antimicrobial enzymes and metal nanoparticles [32].

3 Antifouling Surface Designs

Surfaces subjected to antifouling treatment thwart the adhesion and accumulation of bacteria and microbial contamination. These strategies use physicochem- ical surface properties to impede microbial attachment. As a result, they avoid issues associated with toxicity and resistance, often linked to active strategies. Vapour phase polymerisation facilitates the formation of antifouling coatings of desired composition, thickness and stability.

3.1 Hydration-Based Antifouling Mechanisms

The hydration-driven antifouling strategy is the most established and effective anti-biofouling strategy. The mechanism involves the formation of tightly bound water layers that result in large enthalpic penalties against foulant displacement[25]. Zwitterionic polymers are the gold standard in hydration-based antifouling materials. These polymers bear covalently linked cationic and anion groups, which induce strong hydration via electrostatic origin and charge-neutral character[41].

The vapour-phase routes to zwitterionic polymers were a major get of polymer science CIRVD. Zwitterionic coatings, such as sulfobetaine, carboxybetaine, and phosphorylcholine-based polymers, have been fabricated using innovative, two-step synthesis schemes involving iCVD[52]. Resistance to proteins, bacteria, and marine organisms was observed in these coatings. These coatings have been shown to perform better than conventional polyethene glycol-based coatings.

New developments have increased the diversity of vapor-deposited zwitterionic coatings. In their study, Chen et al. prepared an imidazolium-based zwitterionic polymer by iCVD of 1-vinyl imidazole followed by derivatization with 1,3-propane sulfone. This polymer was shown to achieve 85% reduction in Pseudomonas aeruginosa

biofilm formation. Furthermore, the polymer was able to deactivate human coronavirus HCoV-OC43 by 86%[5]. The ability to kill harmful biofilm-forming bacteria and viruses shows that properly designed zwitterionic surfaces can have multiple uses.
Antifouling properties have also been shown via vapour-phase deposition on other hydrophilic coatings. Coatings of Poly(2-hydroxyethyl methacrylate) (PHEMA) , poly(vinylpyrrolidone) (PVP) and poly(methacrylic acid) (PMAA) produced by iCVD and PECVD showed considerable protein adsorption and bacterial adhesion reduction on various substrates[38]. The conformal nature of vapour deposition technology has been especially useful for making fragile filtration membranes antifouling while not significantly affecting their permeability and separation characteristics.

3.2 Amphiphilic and Chemically Ambiguous Surfaces

Coating surfaces with amphiphilic copolymers is another antifouling approach which exploits chemical confusion rather than bare hydrophilicity. The use of materials with both hydrophilic and hydrophobic components should create surfaces that have a high density of phase boundaries. This situation is energetically unfavourable for foulant adhesion[3]. This interferes with uniform interactions, which grant strong attachment for bacteria.

Vapour-phase growth possesses distinct advantages in the preparation of amorphous copolymers, as it dismisses the solubility constraint. CVD is solvent- free; monomers with different polarities and water affinities can be copolymerized statistically; no macroscopic phase separation occurs despite the molecular-scale heterogeneities created[9]. Because of this, amphiphilic coatings that incorporate remarkable combinations of hydrophilic and hydrophobic constituents can be developed.
A novel use of vapour-deposited amphiphilic copolymers to deal with biofilm formation at a solid-liquid-air three-phase interface, which is frequently missed by classical antifouling coatings[9]. An innovative technique has been developed by researchers to dynamically change the orientation of chain molecules in polymers. This allows surface modifications that can provide different properties at various interfaces. This ensures minimisation of surface energy on wet and dry surfaces simultaneously, thus achieving overall fouling resistance.
Recently, approaches based on machine learning were used to explore the large compositional space of amphiphilic copolymers. Feng and coworkers developed support vector regression models to predict the antibiofilm performance of copolymers synthesised by vapour and solution against P. aeruginosa. It was also found out which molecular descriptors were responsible for the fouling resistance[10]. With data-driven discovery acceleration, this method is designed to optimise copolymer composition while revealing fundamental structure-property relationships.

3.3 Stimuli-Responsive and Dynamic Interfaces

Advanced antifouling designs are equipped with dynamic and responsive features,

enabling them to adapt to changing environmental conditions or fouling threats. Stimuli-responsive vapour-deposited polymer coatings can provide on- demand fouling resistance or self-cleaning triggered by external stimuli, e.g., temperature, pH, light or electrical signals.

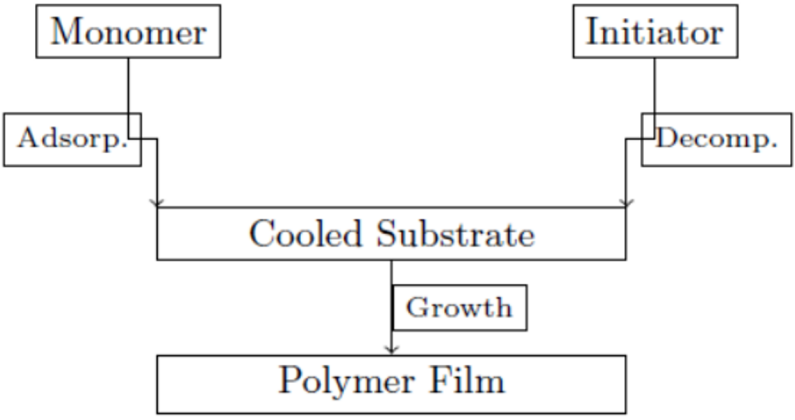

Fig. 1. iCVD process for polymer film formation on a cooled substrate.

Coatings with polysulfide grafts were synthesised using iCVD techniques to enable the antibiofilm properties attributed to the dynamic nature of the disulfide bonds which undergo reversible interchange at room temperature[22]. The biofilm formation of Escherichia coli and Staphylococcus aureus was reduced by 41-95% against control surfaces and constant release was shown until 7 days. The fouling resistance and durability overcome a major weakness of many dynamic surfaces.

Scientists have also looked at small-molecule surfactants adsorbed on functionalized CVD coatings. Chen and colleagues showed that a small amount (0.1 mM) of anionic and cationic surfactants reduced biofilm formation of P. aeruginosa on surfaces like silicon wafers, glass slides and polystyrene by 64-70% by molecular reorientation at three-phase interfaces[6]. This approach effectively improved the antibiofilm performance of existing antifouling materials without permanent chemical modification. Future trends of dynamic antifouling surfaces could also include advanced responsive elements such as shape-memory polymers, liquid crystalline materials, or biomimetic nanostructures that modify in the presence of microbes. Vapour deposition techniques allow for nanometer-precise and reproducible fabrication of such functional interfaces with accurate spatial and temporal control.

4 Contact-Active Bactericidal Surfaces

Antifouling approaches try to prevent microorganisms from attaching to a surface. In

contrast, contact-active bactericidal surfaces offer active defence by killing microorganisms upon contact. These techniques are better than release- based antimicrobial systems as the NRBCs minimise environmental spread of the biocidal compounds, which also lessen the development of resistance. Vapor- phase polymerization allows for the incorporation of bactericidal functionalities within conformal polymeric materials.

4.1 Quaternary Ammonium Compounds

Quaternary ammonium compounds (QACs) are the most studied type of contact- killing agent for antimicrobial surfaces. The electrostatic charges on these cationic polymers interact with negatively charged cell membranes to cause disruption of membrane integrity and killing of the cells[30]. The inclusion of QAC functions in vapour-deposited polymers has made the surface of the coatings antimicrobial, with slow release of the active agent.

iCVD has proven especially effective at producing QAC-based bactericidal coatings utilising copolymerization strategies. Choi et al. created coatings made of poly(4-vinylbenzyl chloride-co-DMAEMA), where the interaction of the chloride and tertiary amine groups created crosslinked networks with quaternary ammonium functionalities[7]. These surfaces killed over 99.5% of E. germs. Incubation of E coli and Corynebacterium glutamicum for 164 hours did not leach film components.

The conformal characteristics of the deposition of vapour enables the application of QAC coatings onto complex substrates relevant to infection prevention. The electrospun nanofiber filter was coated with 10 nm thick poly(DMAMS-co- EGDMA), which is suitable for face mask applications and allows for 99.98% coliform eradication. Song et al. were the authors of this study. E.coli and S. Efficient filtration which take out ¿90% E.coli[43]. Such an ability to conduct vapour-deposited bactericidal coatings indicates a potential high utility in practical uses.

Surfaces that rely on quaternary ammonium compounds (QACs) face a challenge from dead cells and debris that can foul the surface. This fouling masks active sites, which can stop the bactericidal activity of these surfaces. To overcome this limitation, Su et al. synthesised self-regenerative coatings with iCVD performed sequentially with a bactericidal poly(DMAMS-co-EGDA) biodegradable poly(methacrylic anhydride), and more bactericidal layers[45]. When the top layer was depleted, hydrolysis of the intermediate layer revealed a fresh source of bactericidal material that maintained 95% killing efficiency after the top layer was activated.

4.2 Antimicrobial Peptides and Enzymes

The immobilisation of natural antimicrobial substances is an alternative to the synthetic biocides, using evolved defence mechanisms, which are usually less toxic. Via various conjugation chemistries, antimicrobial peptides (AMPs) and enzymes can be tethered

to functionalized vapour-deposited coatings to synthesize surfaces with particular biological activity. Hybrid peptides from the immune systems of insects, Cecropin and melitin, were immobilised on dibromomaleimide-functionalized parylene coatings by cysteine-maleimid chemistry[51]. These surfaces were effective against E. Anal- ysis revealed peptide orientations upon contact with E. coli that pointed towards a charge-based killing mechanism instead of membrane disruption. The vapour-deposited interface was stable, ensuring persistent activity without pep- tide leaching. The synthetic antimicrobial peptide SHAPI which is designed for wound treatment applications, was conjugated to poly(1,3,5,7-tetramethyl-1,3,5,7-tetravinyl cyclotetrasiloxane) (PV4D4) iCVD coatings with UV-activated thiol-ene click chemistry[16]. The surfaces created were able to kill 96% of both E. S. and E. coli aureus, showing broad-spectrum activity and a good substrate specificity. Lysozyme is an antimicrobial enzyme that attacks glycosidic linkages in Gram-positive bacterial cell walls. It was also incorporated into zwitterionic iCVD coatings via nucleophilic substitution of pentafluorophenyl moieties[19]. The invention combines mechanisms to prevent fouling and kill bacteria, thus re- ducing the adhesion of P. aeruginosa by 87% and killing 67% of adhered Bacillus subtilis. The multi-purpose function dealt with the prevention and eradication of microbes.

4.3 Natural Product-Derived Biocides

The deposition of polymers from natural antimicrobial materials is a sustainable way to create bactericidal surfaces. The incorporation of essential oil components and plant secondary metabolites in the designed coatings, through polymerisation, will ensure their durability due to bioactivity. The secondary metabolites of oregano, which are rich in carvacrol, have been subjected to polymerisation by RF-PECVD to obtain coatings with remarkable bactericidal properties[39]. The coatings produced by pulsed plasma at a power level of 50 W removed more than 99% of P. aeruginosa and more than 20% of S. Retention of activity after prolonged contact with aureus. The polymerisation process retained adequate functionality of carvacrol to ensure antimicrobial activity and generate stable films.

The two-step process has allowed for the deposition by PECVD of a com- ponent of tea tree oil, terpinen-4-ol, for use as dissolvable outer layers in self- polishing antifoulings[23]. Through purposeful incomplete polymerisation at low levels (10-25 W), coatings were made that elicited contact killing by way of monomer elution and surface renewal through dissolution of the outer layer. In marine environments, field testing demonstrated 83% fouling reduction after 7 days, and 47% after 28 days, versus unmodified surfaces. Nanocomposites with the inclusion of natural biocides and inorganic antimicrobial agents through vapour deposition are an emerging direction. Kumar et al experimented with zinc oxide nanoparticles on the PECVD coatings of terpinen-4-ol. The outcome demonstrated a synergistic effect against the marine

fouling[24]. Hybrid strategies enjoy the merits of organic antimicrobial and inorganic antimicrobials while also being conformally distributed due to vapour- phase processing techniques.

5 Multifunctional and Synergistic Approaches

The inability of single-mechanism antibacterial strategies to withstand frequent use has driven scientists to develop multifunctional surfaces that use different mechanisms to improve performance and durability. Polymerisation in the vapour phase allows for the controlled introduction of such sophisticated interfaces with tailored properties for required applications.

5.1 Antifouling-Bactericidal Combinations

Combining antifouling and bactericidal properties solves the related problems of preventing adhesion and killing microorganisms that adhere. Through gradient compositions, multilayer, and hybridisation at the molecular scale, vapour deposition methods permit these combinations.

The iCVD coatings were developed by Su et al. to have a composition gradient with bactericidal QAC-bearing PDMAMS at the base and hydrophilic VP moieties at the coating's surface[44]. This design accomplished over ninety-nine point nine per cent kill rates against both E. Escherichia coli and B. subtilis, which allows debris release via pH-activated electrostatic changes. The graded architecture exhibited a significantly high surface potential of 16 mV, notwithstanding the dilution of surface DMAMS concentration with VP, suggesting a contribution from subsurface QAC groups.

Stretchable polyampholyte hydrophilic films with compositional gradients have been prepared by Kim et al. through sequential iCVD of PV4D4 and P(2- carboxyethyl acrylate-co-2-(dimethylamino)ethyl acrylate)[21]. These coatings exhibit remarkable protein resistance (20.3 ng/cm² after 500 s exposure to human serum) and excellent antibiofilm properties (¿10-fold reduction against E. coli and S. aureus biofilms). The mechanical robustness of the underlying layer PV4D4 permitted the application to elastomeric substrates without performance impairments.

Through the copolymerization of good ole QAC-bearing monomers with some hydrophilic components, the molecular-level integration of anti-fouling and bactericidal elements has been achieved. Statistical copolymers consisting of both DMAMS and VP units can reduce bacterial adhesion while simultaneously killing the adhered cells. The relative proportions between the two can be tuned to optimize both functions for specific applications[54]. By process of one-step vapour deposition, functionalities are evenly distributed through the thickness of the coating.

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5.2 Topographical Chemical Synergies

Bactericidal surface topographies and chemical antimicrobials may possess synergy, which can improve efficacy, making their combination powerful. Vapour deposition allows you to deposit functional coatings with 3D conformality onto the surface of complex topography without changing its shape or size.

Choi et al used iCVD-synthesised coatings made from PVBC-co-DMAEMA for the fabrication of NPA[8]. The incorporation of the QAC-containing polymer in this polymer-coated surface was found to enhance the electrostatic interactions between the bacteria and the nanopillars of the coating, resulting in a higher killing efficiency of 51% for the uncoated NPAs to 99.6% for the coated surface against S. aureus. The addition of chemical functionality preserves the nanoscale topography of the conformal coating.

When the same copolymer is applied to three-dimensional polyaniline-gold hierarchical nanostructures with secondary spikes that were cultivated on NPA, further improvement occurs[20]. The modified surfaces did well in eliminating microorganisms. The uncoated nanostructures showed 60% reduction while the flat coated surfaces caused a 160% reduction. The chemical coating increased intrinsic bactericidal activity while the hierarchical topography increased surface area and contact points. Similar methods have been used to generate microscale topographies from sandpaper on PDMS[14]. The PVBC-co-DEAEMA coating was found to log (7.0) reduction against E. coli. S. reduction of log(3.0) and coli. Their lower efficacy will be due to their thicker peptidoglycan cell wall, such as S. aureus. The unique combination of microtopography and chemical functionality led to surfaces that displayed enhanced bactericidal activity across multiple length scales.

5.3 Stimuli-Responsive Multifunctional Systems

Advanced multifunctional coatings with responsive elements exhibit modulated properties in response to environmental triggers or fouling events. These smart surfaces can toggle between antifouling and bactericidal states, release antimicrobial agents on demand, or rejuvenate their active layers upon performance degradation.

Vapour-deposited coatings that show a response to stimuli have been designed to alter their surface energy or charge characteristics with the pH, temperature, or light. When a need arises, the activation of bactericidal mechanisms can occur, while active components are preserved and non-target effects are avoided. The capability to precisely control composition and architecture by vapour deposition accommodates multiple responsive elements in the same coating systems. Another multifunctional solution includes self-polishing coatings that simultaneously discharge antimicrobial agents and renew the surface. Engineering controlled degradation rates via vapour-deposited polymer designs allows tuning of release profiles for various applications, including long-duration marine antifouling, or acute prevention of infection on medical devices. Further advances may incorporate more sophisticated feedback mechanisms to

elicit specific action, i.e. incorporation of enzyme-responsive systems that trigger the antimicrobial function only when specific bacterial secretions are present or quorum-sensing inhibitors that interrupt microbial dialogue whilst providing physical protection. Vapour deposition techniques are able to control the composition and are conformal in nature and, thus, are ideal for preparing such advanced responsive interfaces.

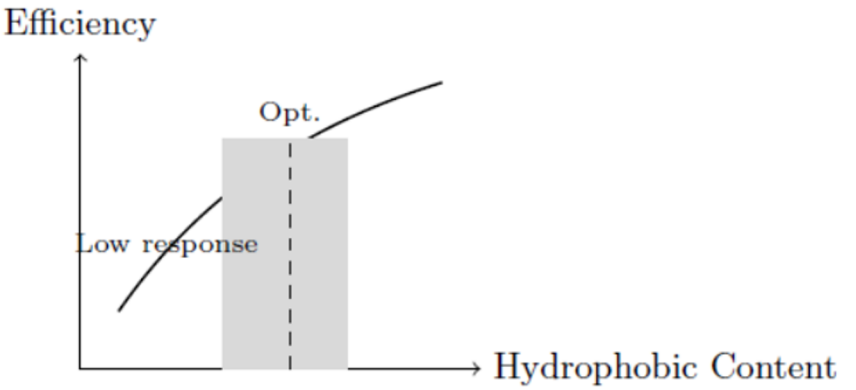

Fig. 2. Antibiofilm efficiency vs. hydrophobic content for amphiphilic coatings.

6 Performance Assessment and Standardization

Achieving antibacterial performance evaluation is vital for allowing comparison of coating systems with a robust methodology. Various mechanisms of action, target microorganisms, and application conditions necessitate comprehensive assessment strategies to multiple aspects of antimicrobial activity as well as durability.

6.1 Antifouling Assessment Methods

Antifouling performance is evaluated based on the measurement of the prevention of adhesion in laboratory situations. Protein adsorption is a primary parameter. Bovine serum albumin, fibrinogen, and lysozyme are widely regarded as model foulants due to their relevance to real-world fouling [42]. BCA and other colourimetric protein assays can sensitively quantify surface- adsorbed proteins through reduction of Cu^{2} ion peptide bonds[19]. Although BCA assays are simple to use and compatible with different substrates, they may exhibit interference from reducing agents and membrane lipids. Appropriate controls and validation are therefore essential.

The Protein shotgun technique suits large-scale analysis of molecular complexes. In this technique, proteins are digested with protease. The resultant proteolytic peptide fragments are washed away. Functionally, it resembles antibody crosslinking. The process, in the form of mass spectrometry, identifies polypeptide sequences. Finally, it

also finds utility in non-covalent protein complex analysis, such as N-Acetyl-Muramidase[29]. By distinguishing among the different protein components of conditioning films, it is possible to gain insights into fouling mechanisms that refer to more than just total protein accumulation. The surface plasmon resonance (SPR) spectroscopy can, in real time and in real life, monitor the occurrence of protein adsorption. The spectroscopy assists in retrieving the values of the subsequent: – the rate of adsorption – the affinity of binding – and the rate of surface coverage [19]. Due to the high sensitivity of SPR, fouling (such as hydrocarbons) at the nanoscale can be detected, making it useful to characterise ultrathin (vapour-deposited) coatings.

Bacterial adhesion assays utilise fluorescent staining with nucleic acid dyes (e.g., SYTO 9) followed by enumeration by microscopy[35]. Including e. standard test strains. Escherichia coli, Pseudomonas aeruginosa, Staphylococcus Bacillus aureus and B. subtilis indicates the presence of a variety of organisms, both Gram-positive and Gram-negative, that act alone and in sex. They exhibit diverse adhesion mechanisms and surface preferences.

6.2 Bactericidal Efficacy Evaluation

After exposure to the surface, there is a reduction in the viability of microbes that are being tested in this test. The process of LIVE/DEAD staining utilises fluorescent viability indicators (typically SYTO 9 and propidium iodide) to see and count live and dead cells on the surface, which is being tested[29]. This technique provides information spatially about killing efficiency and potential heterogeneity on the surface. Colony-forming units (CFU) counting is the gold standard for quantifying bactericidal activity because of its high sensitivity and statistical robustness[1]. The standard protocols incubate a surface with a bacterial suspension, recovery of attached cells by vortexing or sonication, serial dilution and plating for counting. Typically, results are reported as log reduction values relative to controls.

LIVE/DEAD staining and CFU counting have their own pros and cons. Methods based on fluorescence can give direct information about viability ratios but can suffer from the artifacts of staining and quantification issues. Upon counting CFU, excellent quantification is achievable, but not all surface-associated cells may be recovered. Furthermore, the recovery process may cause some cell viability loss.

Recent advancements in microbiological evaluation involve the standardization of protocols for antimicrobial surface evaluation. Combining flow cytometry for accurate viability monitoring, isothermal microcalorimetry for real-time measurement of microbial metabolic activity, and molecular approaches to assess virulence expression, further elucidates the mechanism of action of antimicrobials beyond viability.

6.3 Biofilm Formation Analysis

In assessing biofilms, methodological approaches should be developed that will take into account the structured microbial communities with protective extracellular matrix. The O'Toole protocol is the most common method for biofilm quantification using

crystal violet staining of total biomass[33]. Although this approach does provide robust, high-throughput screening capability, it does not differentiate between living and dead biomass.

A detailed understanding of the antibiofilm characteristics of the substance can be achieved by advanced biofilm characterisation using a number of complementary techniques. Three-dimensional structure and physiological variation of biofilm can be visualised by confocal laser scanning microscopy[17]. Scanning electron microscopy gives topological information of high quality, but its investigation requires the sample preparation change the architecture of natural biofilms.

Molecular approaches comprising the qPCR of genes involved in biofilm, RNA sequencing for transcriptional profiling, and metabolomic analyses are involved in the understanding of biofilm community responses to antimicrobial surfaces [11]. By using these methods, we reveal sublethal effects, adaptation mechanisms and virulence changes which are undetected by just biomass quantification.

The biofilm culture conditions need to be standardised to facilitate reliable cross-study comparison. The formation of biofilms depends a lot on the composition of the medium, flow conditions, incubation time and geometries of the biofilm's interface. It is important that these parameters are managed and documented carefully. Standard strains, such as P. aeruginosa PAO1, as well as submerged and interface biofilm culture guideline-based growth, would increase reproducibility in the field.

7 Challenges and Future Perspectives

Despite major improvements in vapour-deposited antibacterial coatings, there are still issues that need to be solved. Overcoming these disadvantages and seizing new opportunities, this will contribute to the further development of antimicrobial surfaces.

7.1 Material Chemistry Expansion

Vapour-deposited polymerisations have less accessible chemistry space than solution-based synthesis, which is mainly due to volatility requirements for vapour phase delivery[12]. Even though new methods like the two-step zwitterion synthesis are great developments, more diversification of compatible functional groups will allow new antibacterial mechanisms and better performance. Using vapour-phase solvation strategies is a promising way to expand the iCVD-compatible monomer library[6]. By employing hexafluoroisopropyl alcohol as a hydrogen-bonding carrier, the volatility and adsorption characteristics of polar monomers can be improved, thereby permitting the deposition of polymers that are not amenable to vapour processing. Antibacterial applications may become more accessible due to the opening of functional groups with various properties.

Alternative methods of monomer delivery, such as precursor bubblers and ultrasonic

evaporation baths, provide options to source less volatile compounds for PECVD and parylene-based systems[49]. Thermally labile protecting groups for sensitive functionalities, so compatible with deposition, followed by mild deprotection of these functionalities, will reveal active antimicrobial functionalities.
Another under-researched area for improving vapour-deposited coatings is functional crosslinkers. Crosslinkers are usually used for mechanical stabilisation only. The development of crosslinking agents with intrinsic antimicrobial activity or other stimuli-responsive elements may create multifunctional networks with improved durability and sophisticated responses.

7.2 Environmental and Safety Considerations

Antimicrobial coatings are getting more and more attention in terms of their environmental impact for large-scale applications and (marine antifouling and water treatment membranes[36]. Due to their toxicity and ability to accumulate in ecosystems, regulators are disallowing traditional biocidal coatings made from copper, silver or organic biocides. Zwitterionic polymer-based Coatings can Release Marine Fouling Organisms. They are spoiling ship and Boat Hulls due to Fouling[26]. Nonetheless, an environmental analysis of the fate and degradation products of synthetic polymer coatings, in particular, fluorinated ones applied in amphiphilic designs must be carefully studied.

Biodegradable vapour-deposited coatings represent a new development aimed at end-of-life solutions. In nature-derived polymers, terpinen-4-ol has the potential for environmental friendliness and antifouling effectiveness [23]. Creating coatings that can degrade at pre-designed speeds intended for their use (application) life could limit environmental persistence. However, coatings must maintain functional durability during their use.

Assessment of toxicity is necessary for biomedical applications beyond anti- microbial efficacy. A thorough evaluation of cytocompatibility through relevant cell lines, hemocompatibility testing of blood-contacting devices, and in vivo im- plantation studies provides safety information[13]. The all-dry nature of vapour deposition reduces residual solvent concerns, but verification of the suitability of polymers for biology is needed.

7.3 Durability and Scale-Up Challenges

The long-term stability of vapor-deposited antibacterial coatings under real- life conditions is a major implementation hurdle. To be practically applicable, evidence of mechanical durability against abrasion, chemical stability in various environments and prolonged antimicrobial activity must be shown.

When coatings are applied to substrates with enhanced adhesion, it lowers their chance of cracking under flexing or mechanical stress[21]. Adhesion promoters, gradient

compositions and covalent bonding strategies can be engineered into the interface to improve retention without loss of antimicrobial function.

The technical challenges and economic feasibility of scaling up vapour deposition operations from lab to industry. A continuous processing system with faster processes in terms of enhanced deposition rates and more efficient precursor utilisation would enhance commercial viability[53]. The manufacturing flexibility would improve when utilizing modular reactor designs adaptable to various substrates.

Vapour-deposited antibacterial coatings will benefit from standard quality control methods, which will allow for technology transfer. Several tools could be developed to help ensure consistent manufacturing and reliable products; non-destructive thickness measurement techniques, chemical composition verification methods and functional performance parameters specific to the application.

7.4 Integration with Emerging Technologies

The combination of vapour-deposited antibacterial coatings with other advanced technologies opens exciting prospects for next-generation functional surfaces. Integrating topographical patterning, either via substrate deposition or direct patterning during growth, may enhance efficacy through synergistic physical and chemical effects[8]. The combination with stimuli-responsive systems allows smart coatings to start their antimicrobial activity when needed or as a function of the environment. Combining components such as photothermal agents, piezoelectric materials, or shape-memory materials, we can create surfaces that induce antifouling and bactericidal activity[24]. The incorporation of biological elements beyond mere immobilisation is a new frontier for advanced antimicrobial materials. Microbial communities that may be useful, biofilm-based systems that allow controlled biological functions, or synthetic biology approaches for dynamic response engineered living materials may open entirely new ways of sustaining surface protection[11]. Technologies like machine learning to speed up materials discovery, IoT sensors for real-time performance monitoring, and feedback systems for controlling deposition automatically could revolutionize vapor-deposited antibacterial coatings development and implementation. By using adaptive responses to changing conditions, these integrated approaches will enable optimal performance of surface systems.

8 Conclusion

Vapor-phase polymerization has established itself as a potent tool for producing advanced coatings with antibacterial properties not possible through traditional solution-based processes. The functional surfaces for various applications, including medical devices and water treatment membranes, can be created through iCVD, PECVD, and CVD deposition of parylene due to substrate independence, conformal

coverage and precise chemical control.

The variety of vapour deposition techniques has led to the development of complex coatings with specific antimicrobial action mechanisms. Zwitterionic and hydrophilic polymers are effective at resisting fouling through hydration barriers, but QAC-based coatings and immobilised antimicrobial peptides are potent and contact-killing. Copolymers having amphiphilic characteristics can be used to improve the tough three-phase interface.

The state-of-the-art approach is now the utilisation of multifunctionality approaches comprising complementary mechanisms that are made possible by the powerful compositional control of vapour deposition, including graded, layered or molecularly integrated implementation. The efficacy can be further improved with synergetic physical and biological effects due to chemical functionality with topography. We have made a lot of progress, but there are still challenges to expanding accessible chemistries and improving the environment. In the future, advancements will probably include integration with new technologies. For example, systems that respond to stimuli or engineered living materials could be included, as well as digital manufacturing approaches. As performance assessment techniques become standardized and understanding of biological-material interactions becomes widely accepted, it is expected that vapour-deposited antibacterial coatings will play an ever-greater role in mitigating microbial contamination in healthcare, industrial, and environmental applications. Due to its excellent potential, vapour-phase polymerisation is considered a key enabling technology for next-generation antimicrobial surfaces.

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