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Research Article

Synthesis and Antibacterial Activity of Grafted Poly(Vinyl Chloride) Polymer against Gram-Positive and Gram-Negative Bacteria

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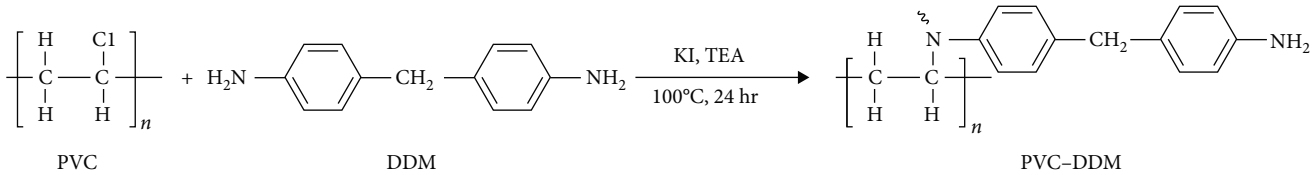
Infectious diseases caused by microorganisms have gained worldwide attention in recent years. According to data compiled by the World Health Organization, the number of deaths resulting from infectious diseases is on the rise. In light of these dangers, the study of antibacterial materials has become increasingly vital. In this research, an antibacterial polymer was developed using poly (vinyl chloride) (PVC) and 4,4-diamminodiphenylmethane (DDM). The produced polymer's chemical structure and thermal properties were investigated using Fourier-transform infrared spectroscopy, nuclear magnetic resonance, and thermo-gravimetric analysis. The antibacterial activity of the resulting PVC-g-DDM polymer was effective in killing both Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli*. The antimicrobial efficacy was tested using a spread plate method, demonstrating its potential utility in a variety of applications like biomedical, coatings, water purification systems, and others. Antimicrobial resistance is increasing, especially among bacteria that have acquired resistance to multiple therapeutics. To fully optimize and explore the polymer's potential and its usage, more research is needed.

1. Introduction

In view of the ongoing pandemic catastrophe, there is an immediate requirement to address the issue of the emergence and spread of developing diseases into the environment, which results in a variety of different types of contamination. Surface microbial contamination is one of them, and it is a primary duty in the areas of consumer protection, human health, and food safety all over the world [1, 2]. During the phase of microbial surface attachment, the severity of infections is at its peak, and growth takes place in a biofilm that has self-formed itself [2]. This biofilm is considered a source of infection and denotes a pool of bacteria. In this regard, the surface engineering of materials with antibacterial properties and their mode of action is considered to be one of the possible ways to increase biocompatibility and, as a result, reduce the danger of microbial contamination and avoid biofilm infection by modifying surfaces and the properties of materials [3–8]. The production and development of biomaterials that are capable of retarding microbial colonization and reducing the spread of pathogenic bacteria has generated a lot of interest in the functionalization of polymers with antimicrobial compounds [9, 10].

Antimicrobial polymers encompass a diverse class of materials, which can be categorized based on their mode of action, including contact-killing, release-based, and surface modification strategies. Contact-killing polymers directly interact with microbial cells, disrupting their structural integrity, and inducing cell death. Release-based polymers, on the other hand, gradually release antimicrobial agents over time, ensuring a sustained antimicrobial effect [11–15]. Biocide-releasing polymers are an effective category of antimicrobial polymers. These antimicrobial polymers involve polymers that are preloaded with biocide molecules. Surface modification polymers involve



Scheme 1: Chemical route to synthesize PVC-g-DDM polymer.

functionalizing material surfaces with antimicrobial compounds, creating an inhospitable environment for microorganisms. These versatile approaches offer numerous opportunities to tailor the properties of antimicrobial polymers to suit specific applications, such as medical devices [9, 16, 17], coatings [18–20], textiles [21–23], and packaging materials [24].

The field of antimicrobial coatings has witnessed rapid growth and extensive research as an integral approach to preventing the transmission of pathogenic microorganisms and mitigating the challenges associated with antimicrobial-contaminated surfaces. It serves as an effective strategy in controlling biofilms as well [25–30]. The mechanism of action of these coatings involves hindering microbial growth upon contact with the treated surface. This can be attributed to various factors, such as electrostatic interactions between the negatively charged bacteria and positively charged polymeric chains, disrupting the microbial cell membrane [31, 32]. Additionally, the adsorption of polymers onto the surface of bacteria can cause the leakage of cytoplasmic constituents, ultimately resulting in cell death. These mechanisms collectively contribute to the antimicrobial efficacy of the coatings, rendering them invaluable in combating microbial infections, and reducing the risk of surface-associated transmission [11–15, 26]. Compounds like PVC [33], chitosan [34], cellulose [35], and polyethylene glycol (PEG) [1], through skillful modification, acquire extraordinary antimicrobial properties that make them invaluable in a wide range of applications.

Poly(vinyl chloride) (PVC) is a commercial thermoplastic polymer that is also one of the most used medical surface materials. PVC is being researched as a potential antibacterial material modification that could lessen the likelihood of industrial illnesses and cross-contamination [36, 37]. PVC is a versatile synthetic polymer widely used in various industries due to its favorable physical properties and cost-effectiveness [38–42]. Its exceptional versatility enables its application in multiple industries, including biomedical devices, tubing, bottles, packaging formats, coatings [43], plastisols, and films. One notable attribute of PVC is its inherent antimicrobial property, making it a preferred material for critical applications that require the prevention of microbial growth and transmission. Target compounds that can modify microbial cell walls and disrupt the cytoplasmic membrane via creating a complex with the lipid bilayer can be synthesized, however, from polymers that have been changed with an active organic and/or inorganic admixture [44]. Villanueva et al. [39] conducted a groundbreaking study where they successfully synthesized an antimicrobial polymer based on guanidine. Their innovative approach involved grafting PVC onto poly hexamethylenediamine guanidine hydrochloride (PHMG) to create this remarkable compound [39]. Palencia et al. [45] synthesized antibacterial cationic PVC by quaternization of amino groups using dimethylamine and 1-bromoethane, respectively. Feit et al. [46] incorporated S-nitroso-*N*-acetylpenicillamine (SNAP) into PVC tubing using a solvent-swelling-impregnation method to create an antimicrobial medical device interface. These achievements represent a significant advancement in the field of antimicrobial materials, offering promising applications in combating harmful microbes.

In the current article, the reaction between PVC and 4,4-diaminodiphenyl methane (DDM) was carried out, showing significant antibacterial efficacy against Gram-positive (*Staphylococcus aureus*) and Gram-negative bacteria (*Escherichia coli*). The coating was applied to a glass slide by mixing the polymer sample with paint, and the SEM structure was analyzed. The synthesis of the PVC–DDM polymer is of crucial importance due to its potential in addressing common microbiological challenges. PVC-based antimicrobial polymers have garnered attention for their ability to impede bacterial growth, offering hope for resolving various issues, including antibiotic resistance, food and water pollution, and infectious disease outbreaks. The intentional and significant use of 4,4′-diamminodiphenylmethane (DDM) as a component in this polymer synthesis is attributed to its well-known antibacterial qualities. DDM plays a key role in effectively limiting the growth of microorganisms, particularly targeting Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli*. The unique combination of PVC and DDM in this synthesis leads to a polymer with enhanced antibacterial efficiency, especially effective against a broad spectrum of bacteria. This polymer demonstrates promise for a variety of applications.

2. Experimental

2.1. Materials and Methods. Poly(vinyl chloride) (PVC, average M_w ~ 62,000, Sigma–Aldrich, purity: ≥99%) and 4,4-diamminodiphenylmethane (DDM, 97%, Sigma–Aldrich) were used without further purification. The solvents, tetrahydrofuran (THF), triethylamine (TEA, purity: ≥99%), and potassium iodide (KI, purity: ≥99.5%), were purchased from Sigma–Aldrich and used as received.

2.2. Preparation of PVC-g-DDM Polymer. The preparation of the PVC-g-DDM polymer (Scheme 1) is a meticulous process that begins with the precise weighing and dissolution of 0.645 g (0.01 moles) of PVC and 1.98 g (0.01 moles) of 4,4-diamminodiphenylmethane (DDM) in an appropriate amount of tetrahydrofuran (THF), resulting in the creation of a homogeneous solution. An essential step in this process is the gradual

addition of 0.5 mL of potassium iodide (KI) and 1 mL of triethylamine (TEA) drop by drop to the solution. KI likely functions as an initiator, while TEA acts as an acid scavenger, facilitating the subsequent polymerization process. The reaction is allowed to proceed for 24 hr under reflux conditions at 100°C, providing the ideal environment for copolymer formation. After the reaction, the solid PVC–DDM copolymer is separated from the liquid phase by precipitating the solution in water and then filtering it using Whatman filter paper. A thorough washing with THF is performed to eliminate any remaining unreacted compounds or byproducts. Finally, the resulting PVC–DDM copolymer, with its pale-yellowish color, is obtained after drying at room temperature.

3. Characterization

3.1. Chemical Structure Studies. The structural properties of the polymer were studied using Fourier-transform infrared spectroscopy (FTIR), proton, and carbon-13 nuclear magnetic resonance (NMR) spectroscopy (^{1}H-NMR and ^{13}C-NMR). Shimadzu-8400S FTIR spectrophotometer was used to capture the FTIR spectra ranging from 400 to 4,000 cm^{-1}. Bruker Avance 400 spectrometer was used to record the ^{1}H-NMR and ^{13}C-NMR spectrum (400 MHz).

3.2. Thermal Studies. The thermal properties of the synthesized polymer were studied using TA Instruments SDT-Q600 at CSIR Pune. Thermogravimetric analysis (TGA) thermograms were obtained at a heating rate of 5°C/min over a 25−800°C temperature range using aluminum pans at a static nitrogen atmosphere.

3.3. Scanning Electron Microscopy (SEM). To prepare the coating substrate, glass slides were first cleaned by sonication in distilled water, acetone, and ethanol for 15 min each, and then air-dried. A polymer solution was made by dissolving 10 mg of polymer in 1 mL of DMSO, which was then mixed with paint in an equimolar ratio and then coated on glass slides. The surface morphology of the painted glass slide was observed using a scanning electron microscope (SEM) with a ZEISS EVO MA18 instrument at 10 kV operating voltage. The SEM images were captured and analyzed.

3.4. Antibacterial Testing. The synthesized polymer was tested for its antibacterial activity against Gram-negative *E. coli* (MTCC 1687) and Gram-positive *S. aureus* (MTCC 3160). The bacterial strains used in this study were obtained from the Manipal Institute of Technology, Manipal, Udupi, Karnataka. The antibacterial testing was conducted using the spread plate method, and the reduction in colonies was observed.

The 100 μL of bacterial culture was obtained from storage and introduced into freshly prepared nutrient broth specific to each culture. The mixture was then incubated in an incubator shaker at a temperature of 31.1°C for a duration of 12 hr, with an agitation speed of 120 rpm. This process was carried out to facilitate the evaluation of the antibacterial activity of a synthesized polymer. Subsequently, autoclaved nutrient agar medium was poured into Petri plates and left undisturbed for ∼20 min in a laminar airflow chamber to allow for solidification. After the incubation period, the 12-hr-old bacterial culture was retrieved and appropriately diluted by the 0.5 McFarland standard. Using sterile cotton earbuds, the diluted cultures were evenly spread across the surface of the agar Petri plates. The 50 mg/mL of polymer sample was dissolved in DMSO and then placed on the Petri plates and incubated at 37°C for 24 hr.

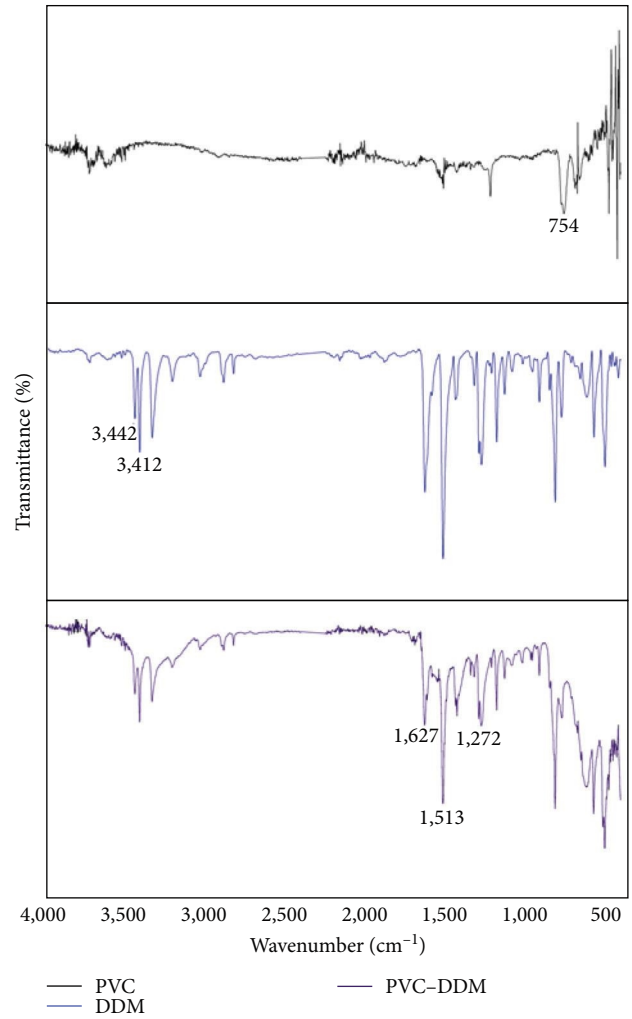


Figure 1: FTIR spectra of PVC, DDM, and PVC–DDM polymer.

4. Results and Discussion

4.1. Chemical Structure Studies

4.1.1. Fourier Transform Infrared (FTIR) Analysis. Figure 1 presents the results of the FTIR analysis conducted on PVC, DDM, and the PVC-g-DDM polymer samples. The FTIR spectrum of PVC exhibited a distinct peak at 754 cm^{-1}, attributed to C—Cl stretching, a characteristic feature of PVC due to its chlorine content. In contrast, the FTIR spectrum of the synthesized polymer displayed a reduced prominence of the C—Cl stretching peak, suggesting that chemical reactions occurred during polymerization, involving the chlorine atoms from PVC and the amine groups. This implies the formation of covalent bonds between PVC and

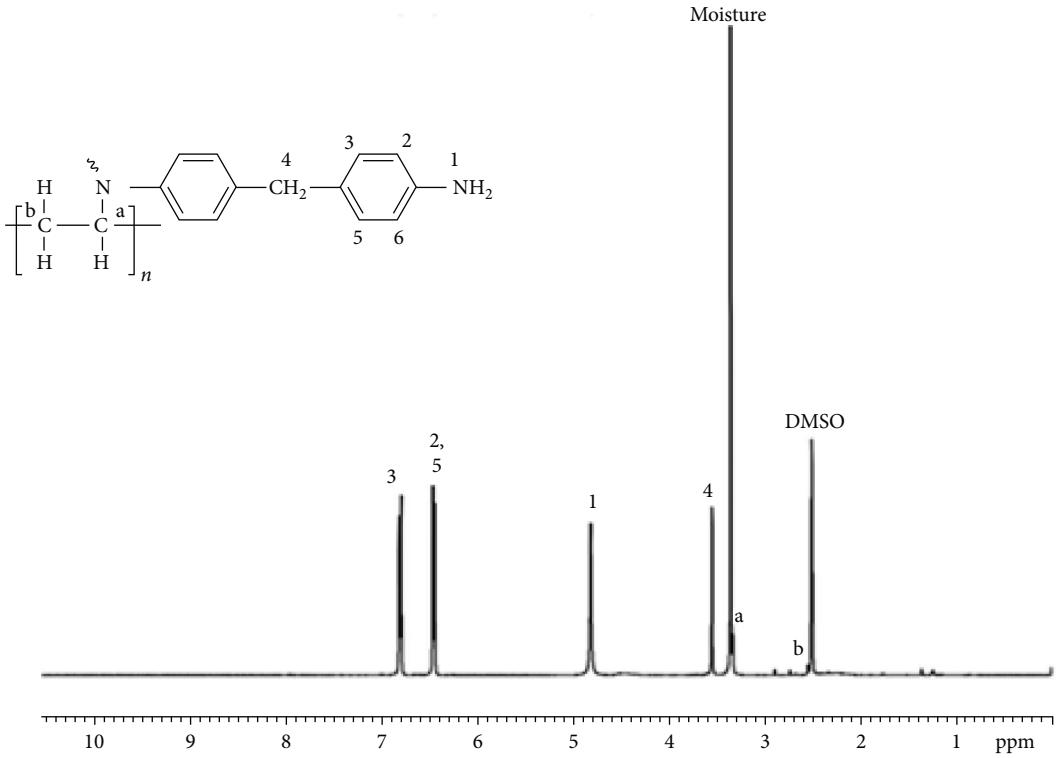


Figure 2: ^{1}H-NMR spectrum of PVC–DDM polymer.

DDM, resulting in the polymer (PVC-g-DDM). The FTIR spectrum also revealed a peak at 1,272 cm^{-1}, associated with the aromatic C—N stretching vibration, confirming the incorporation of components in the copolymer. Additionally, the C═C peak of DDM appeared at 1,513 cm^{-1}, indicating the presence of DDM in the polymer. The spectrum showed bands at 3,500–3,400 cm^{-1} corresponding to asymmetric and symmetric N—H stretching, with another peak at 1,627 cm^{-1} attributed to N—H bending [47]. These observations collectively support the successful formation of the polymer. In summary, FTIR analysis provided valuable insights into the chemical transformations during polymerization, indicating the covalent bonding between PVC and DDM in the preparation of the PVC-g-DDM polymer.

4.1.2. Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR). The ^{1}H-NMR analysis of the PVC-g-DDM sample, depicted in Figure 2 and conducted on a δ scale in deuterated-dimethyl sulfoxide (*d*-DMSO), provides a comprehensive molecular profile. The presence of a consistent reference peak at 2.5 ppm ensures precise chemical shift measurements. Notably, the distinct chemical shift at 4.8 ppm confirms the presence of N—H protons, unequivocally establishing the incorporation of an amine functional group within the polymer structure, a finding of significant scientific importance due to its potential impact on reactivity and molecular interactions. Further examination of the spectrum reveals chemical shifts between 6.4 and 7.0 ppm, corresponding to the aromatic protons (CH^2, CH^3, and CH^5) of DDM, validating its successful integration into the polymer matrix. Additionally, the presence of the methyl proton ($CH_2{}^4$) of DDM in between two benzene rings, evident at 3.5 ppm, substantiates the effective synthesis of the PVC–DDM copolymer and offers insights into the molecular arrangement. The spectrum also confirms the presence of PVC through the CH^a proton peak at 3.4 ppm, with a smaller peak at 2.5 ppm indicating the $CH_2{}^b$ proton of PVC, providing valuable information about the polymer's local chemical environment and intermolecular interactions. This ^{1}H-NMR analysis stands as a rigorous scientific method for characterizing the grafted polymer, aiding in the understanding of its composition and potential applications.

4.1.3. Carbon-13 Nuclear Magnetic Resonance Spectroscopy (^{13}C-NMR). The ^{13}C-NMR spectrum presented in Figure 3 stands as a comprehensive data source that intricately elucidates the structural composition of the PVC-g-DDM polymer. Within this spectrum, precise chemical shift data for various carbon atoms within the polymer offer essential insights into its composition. Notably, the secondary carbon atom ($CH_2{}^5$) within DDM is discerned at a chemical shift of ~129.8 ppm, indicating its unique chemical environment. Furthermore, the quaternary carbon atom (C^4) positioned within DDM's benzene ring, near the amine functional group, prominently displays a chemical shift at 152.38 ppm, while the quaternary carbon atom (C^1) linked to the methylene group registers at 112.59 ppm. These precise chemical

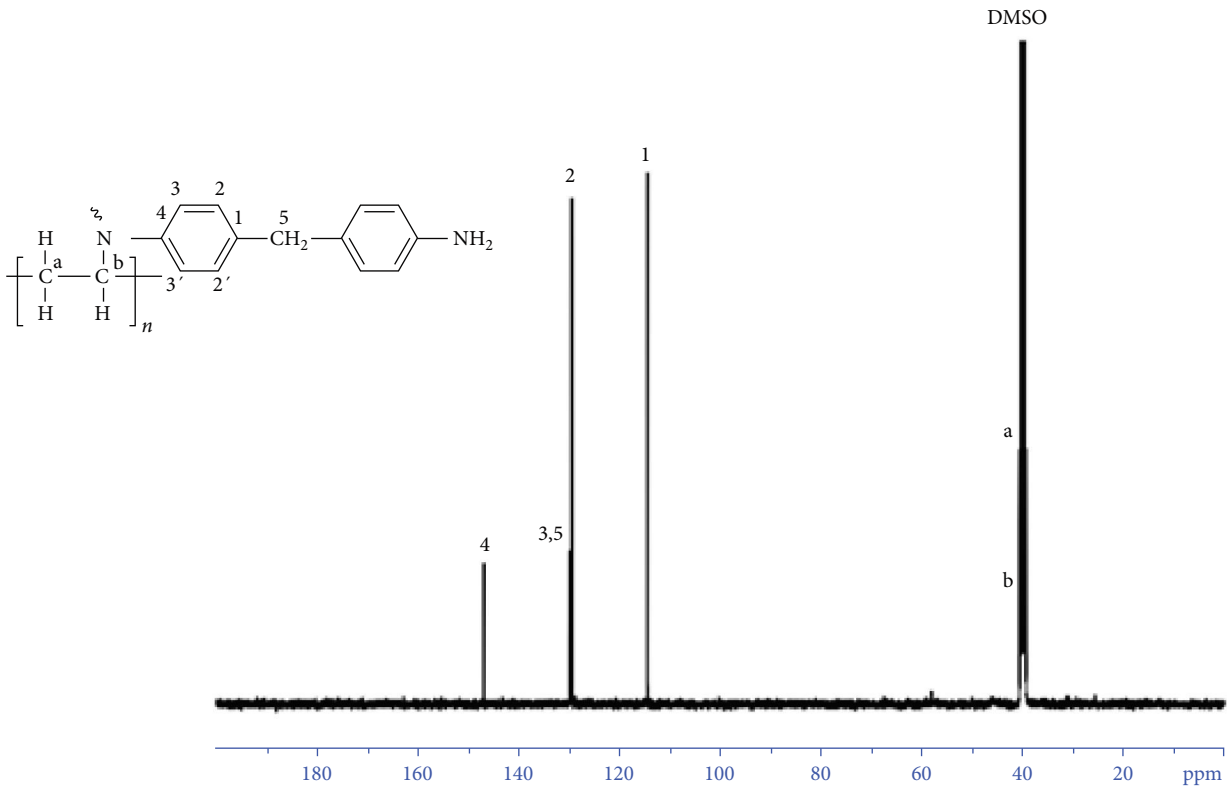


Figure 3: ^{13}C-NMR spectrum of PVC–DDM polymer.

shifts provide critical information about the local chemical environments of these carbon atoms and their respective roles within the polymer's structural framework. The spectrum also reaffirms the structural integrity of DDM's benzene ring, highlighting the chemical shifts of tertiary aromatic carbon atoms ($CH^{2,2'}$) at 129.38 ppm and ($CH^{3,3'}$) at 129.86 ppm. Additionally, it identifies the quaternary carbon atom (C^b) affiliated with PVC's amine moiety at 40.59 ppm and the adjacent carbon atom (C^a) at 40.18 ppm. This dataset serves as an indispensable resource for comprehending the molecular architecture of the grafted polymer and its potential applications across diverse academic and industrial contexts.

4.2. Thermogravimetric Analysis (TGA). The thermal behavior of the synthesized PVC-g-DDM polymer has been comprehensively examined through TGA, yielding profound insights. Figure 4 illustrates the TGA curve, revealing a multifaceted degradation profile characterized by distinct degradation events occurring at 171, 235, and 371°C. These discrete temperature thresholds correspond to various stages of thermal decomposition, signifying molecular transformations within the polymer leading to weight loss. Of particular significance is the striking exothermic peak observed at 431°C, indicative of an abrupt and highly exothermic reaction transpiring within the copolymer during its decomposition. Such exothermic peaks are typically associated with intricate chemical reactions, potentially involving cross-

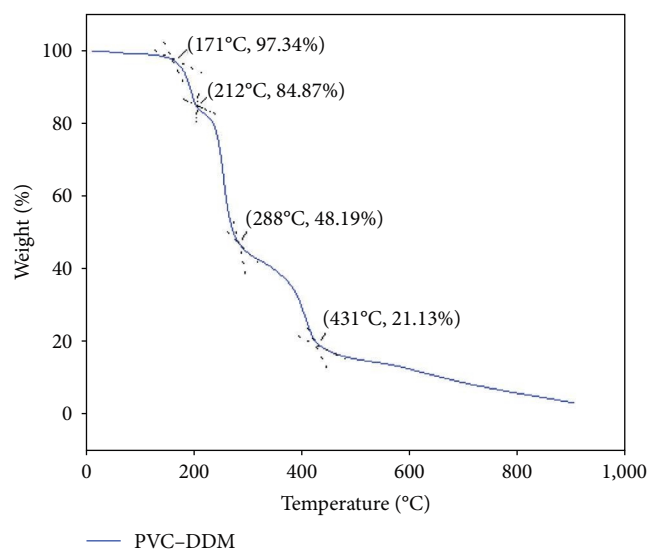


Figure 4: Thermogravimetric analysis of PVC–DDM polymer.

linking processes, the cleavage of specific chemical bonds, or the formation of more stable compounds within the polymer matrix. Notably, following this exothermic event, the TGA curve stabilizes, denoting the conclusion of weight loss and the completion of the polymer's decomposition process. These TGA results offer invaluable insights into the PVC-g-DDM polymer's complex molecular structure,

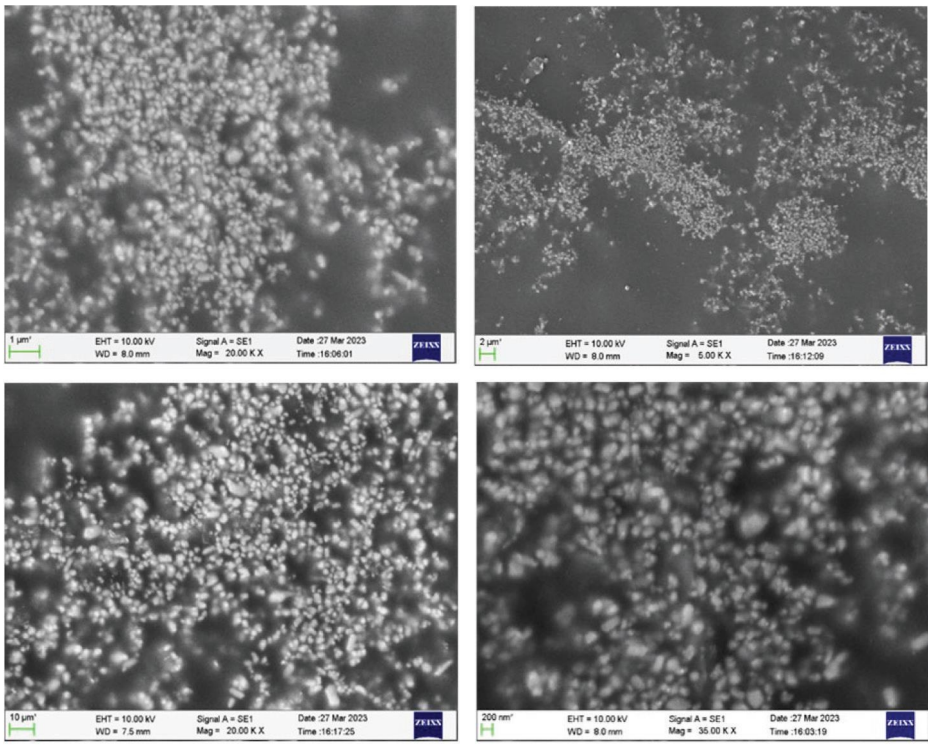


Figure 5: SEM images of painted glass slides at different magnifications.

its potential for diverse chemical transformations across varying temperature conditions, and its overall thermal stability—critical factors for evaluating its applicability in specific industrial or research contexts.

4.3. Morphological Characteristic. Employing a SEM, a powerful tool renowned for its ability to scrutinize materials at an exceptional level of detail, a thorough investigation into the surface morphology of the synthesized PVC-g-DDM polymer was meticulously executed and shown in Figure 5. The process commenced by dissolving 10 mg of PVC-g-DDM in dimethyl sulfoxide (DMSO) followed by blending it with commercially available paint, precisely measured in an equimolar ratio of 1 : 1, to craft the SEM specimen. This precisely calculated amalgamation underwent a thorough agitation process for ∼10 min, ensuring a homogeneous mixture. Following this detailed procedure, the resulting composite was deposited onto glass slides. Subsequently, these glass slides, now bearing the coated specimen, were subjected to a rigorously controlled air-drying regimen, sustained at room temperature for a duration of 1 week.

The outcomes of this comprehensive surface analysis yielded profoundly instructive insights. They unveiled a seemingly stochastic dispersion pattern of particles across the coating, illustrating remarkable uniformity. This dispersion signified that the particles were consistently distributed across the surface, effectively impeding any concentration in localized regions. The significance of maintaining such uniformity reverberates across multiple facets: it not only elevates the visual appeal of the coating but also ensures unwavering performance characteristics that span the entirety of the coated surface. Moreover, this uniform dispersion substantially enhances the mechanical flexibility of the coating, markedly reducing the susceptibility to structural vulnerabilities such as cracking or flaking, which are frequently associated with irregular particle concentration. Hence, our SEM-facilitated surface morphology investigation furnishes not only an understanding of the structural attributes that define the PVC-g-DDM polymer but also spotlights its extensive potential across diverse applications, where surface characteristics play pivotal roles in defining and sustaining performance and durability.

4.4. Antibacterial Tests. The synthesized polymer based on PVC showed a considerable reduction in microbial growth when tested against both the Gram-negative bacterium *E. coli* and the Gram-positive bacterium *S. aureus*, as presented in Figure 6, which is a graphic illustration of the phenomenon. In order to conduct this experiment, a precise measurement of 20 μL of the prepared polymer solution was put into Petri plates with great care. When compared to the control groups, the researchers found that the polymer was significantly more effective in preventing the formation of microbial colonies. Both *Staphylococcus aureus* (15 ± 1.0 mm) and *Escherichia coli* (19 ± 0.5 mm) were seen to have an inhibitory zone surrounding the sample. When we applied DMSO as a control, there was certainly no bacterial inhibition zone present.

To unravel the involved mechanism behind this polymer's exceptional antibacterial potency, it is important to explore the complex interplay between its amine functionality and the presence of unreacted chlorine atoms when in contact with bacterial cells. Bacterial cell membranes, characterized by their negative

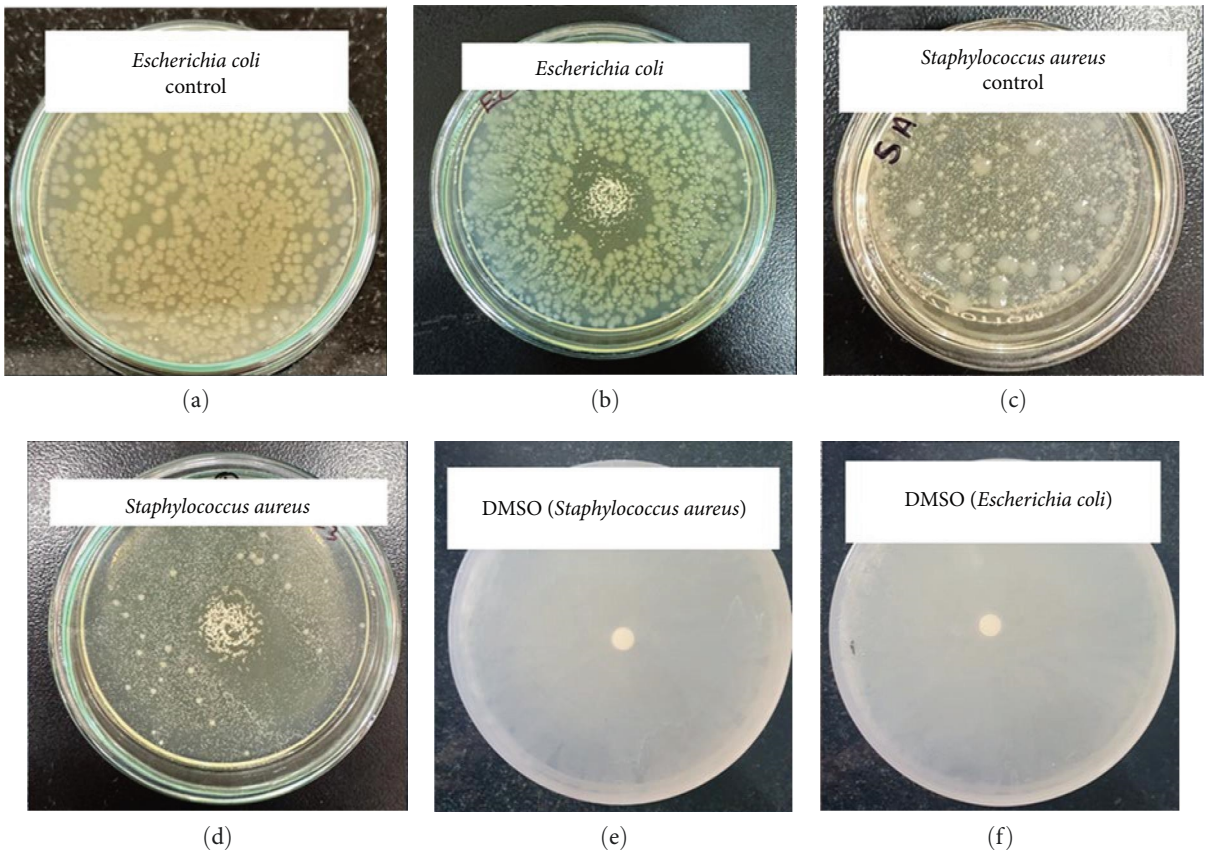


Figure 6: The inhibition exhibited by the polymer in comparison to the control against (a–d) *S. aureus* and *E. coli*, whereas (e and f) represents DMSO reference.

charge, interact with the polymer's amine groups, which are typically positively charged under physiological conditions, initiating a cascade of events that compromises the structural integrity of the cell membrane. This interaction renders the cell membrane increasingly permeable to external influences. Simultaneously, latent chlorine atoms within the polymer gradually release chlorine ions (Cl^-), well-known for their potent antibacterial properties. These chlorine ions penetrate the compromised cell membrane, increasing the charge on bacterial cells. This combined effect precipitates membrane dysfunction, disrupting vital cellular functions, leading to the leakage of critical intracellular components, and ending in the lysis and demise of microbial cells. The keystone of the polymer's enhanced antibacterial efficacy against both *E. coli* and *S. aureus* lies in the precisely composed synergy between amine functionality and chlorine release, underscoring its potential as a daunting antibacterial agent with promising applications in the biomedical and materials science domains, where the imperative of effective microbial control prevails [48, 49].

5. Conclusion and Future Prospects

The current investigation reveals the following conclusions:

(1) The obtained PVC-g-DDM polymer was confirmed by FTIR analysis, which showed a significant reduction in C—Cl and —NH stretching peaks at 754 and 3,412 cm^{-1}, respectively. Further, the polymer structure was confirmed by ^{1}H-NMR and ^{13}C-NMR with peaks at 3.4 ppm (CH^a) and 2.5 ppm ($CH_2{}^b$) for PVC; peaks at 4.8 ppm for N—H protons and 6.4–7.0 ppm for aromatic protons of DDM and peaks at 129.8 ppm ($CH_2{}^5$), 152.38 ppm (C^4), and 112.59 ppm (C^1) for carbon atoms.

(2) TGA results revealed that the synthesized polymer exhibited high thermal stability with minimal weight loss observed up to 235°C.

(3) The SEM images of the polymer in paints have provided valuable insights into the microstructure, distribution, and interface characteristics of the polymer particles within the paint matrix.

(4) Significant antibacterial activity was shown by the obtained PVC-g-DDM polymer against Gram-negative *E. coli* and Gram-positive *S. aureus*. This may be due to the combined effects of the amine functionality and the release of chlorine ions, underscoring its potential as a daunting antibacterial agent with promising applications in the biomedical and materials science domains, where the imperative of effective microbial control prevails.

In light of potential obstacles and in order to maximize the practical applications of the PVC-g-DDM polymer, future

research should incorporate a number of strategic domains. Priority number one must be a focused investigation of structural modifications, with an emphasis on minimizing degradation and increasing the stability of the polymer. Simultaneously, endeavors ought to be focused on reducing potential leaching concerns, potentially by exploring alternative additives or implementing barrier coatings. It is imperative to comprehend the polymer's enduring efficacy under a variety of environmental circumstances, including fluctuations in temperature and exposure to distinct substances, in order to proficiently customize its applications. Furthermore, in order to ascertain its wider applicability, it is crucial to investigate the biocompatibility of PVC-g-DDM for potential biomedical applications and perform extended durability experiments in practical settings, specifically in paint coatings and water purification systems. In order to expedite the implementation of this research, it is crucial to conduct additional research on the optimization of synthesis techniques to achieve scalability and cost-efficiency. By thoroughly examining these complex elements, subsequent investigations can lay the foundation for the effective incorporation of PVC-g-DDM across various sectors and implementations. Collaboration among stakeholders, industry partners, and researchers will be crucial to advancing these research directions and realizing the polymer's maximum potential.

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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