Zinc Phthalocyanine-Functionalized Polyvinyl Chloride Surfaces for Singlet Oxygen-Mediated Antibacterial and Antiviral Activity

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Abstract

Functional polymer surfaces that combine antimicrobial activity with retained processability and material integrity are of growing interest for healthcare and high-contact applications. This study reports a photodynamically active polyvinyl chloride (PVC) system functionalized with a methacrylate-modified zinc phthalocyanine photosensitizer (ZnPTC-HEMA) and zinc pyrithione (ZPT), prepared by industrially relevant melt-processing a compression-molding methods. The resulting material platform was used to establish relationships between composition, structure, photoactivity, antimicrobial performance, and polymer stability. Quantitative analysis revealed efficient singlet oxygen generation even at low ZnPTC-HEMA loadings, with activity approaching saturation at higher concentrations. Under visible-light irradiation, the modified PVC surfaces exhibited pronounced antibacterial activity against *Staphylococcus aureus* and achieved more than a 5-log reduction of the enveloped bacteriophage Φ6, while the non-enveloped phage ΦX174 remained unaffected. The addition of ZPT broadened antibacterial efficacy, including under dark conditions. Morphological, spectroscopic, thermal, and mechanical analyses confirmed homogeneous additive incorporation, preservation of the PVC chemical structure, and retention of material integrity at low-to-moderate additive loadings. Migration studies further showed no detectable release of ZnPTC-HEMA after prolonged aqueous exposure. These results demonstrate that phthalocyanine-functionalized PVC provides a scalable platform for light-responsive antimicrobial polymer materials in which photoactive function can be introduced without compromising key processing and performance characteristics.

1. Introduction

Despite substantial advances in prevention and treatment, seasonal influenza remains a major public-health burden, accounting for nearly 30% of the infectious disease share in Europe,

while recurrent pandemics continue to underscore the vulnerability of modern societies to respiratory viral outbreaks.[1,2] Although influenza is generally less virulent than pandemic respiratory infections, it frequently predisposes patients to secondary bacterial pneumonia, most commonly caused by *Staphylococcus aureus*, *Streptococcus pneumoniae* and *Streptococcus pyogenes*, thereby substantially increasing morbidity and mortality.[1,3] In parallel, the recent coronavirus disease 2019 (COVID-19) pandemic, caused by severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2), further highlighted the urgent need for material-based strategies capable of reducing pathogen transmission at surfaces and interfaces.[4] Consequently, the development of antiviral and antibacterial functional materials for healthcare and daily-use applications has become an important research priority.[5]

The use of polymers in medical devices has risen sharply in recent decades. However, their widespread use is accompanied by a persistent risk of bacterial colonization, leading to biofilm formation. This limitation is particularly relevant for indwelling and short-term devices, including endotracheal tubes, catheters, and other polymer-based components that can support the adhesion and proliferation of both Gram-positive and Gram-negative bacteria, such as *Pseudomonas aeruginosa* and *Staphylococcus aureus.*[6] Among these materials, polyvinyl chloride (PVC) remains one of the most extensively used polymers in healthcare because of its low cost, transparency, flexibility, and excellent processability. Its compatibility with industrial manufacturing techniques such as extrusion, thermoforming, and blow molding has secured its continued use in tubing, blood bags, catheters, and intravenous therapy containers. Thus, despite increasing interest in alternative polymers, PVC continues to offer highly relevant and industrially scalable platform for the development of advanced antimicrobial medical materials.[6,7]

A key limitation of PVC is its hydrophobic surface character, which promotes microbial adhesion and contributes to hospital-acquired infection risk. Addressing this drawback has

therefore become an important objective in polymer and interface engineering, with current strategies focusing on surface modification or incorporation of functional additives. Recent advances highlight the potential of inorganic nanoparticles including TiO_2, ZnO, and gold, to impart robust antimicrobial properties, thereby reaffirming PVC's relevance as a platform for innovation in next-generation medical materials.[6] However, the search for alternative light-responsive additives with strong photoinduced antimicrobial activity, high stability, and compatibility with polymer processing remains ongoing.

Phthalocyanines (PTCs) represent a promising yet underexplored class of antimicrobial photoactive compounds for polymer applications. These aromatic compounds consist of four isoindoline units connected by azomethine bridges, with the ability to incorporate metal ions in their central cavity, which modulates their photoactivity.[8] PTCs are well known as photosensitizers because of their intense absorption in the near-infrared region (about 700 nm), enabling deep penetration. They are also distinguished by their exceptional singlet oxygen generation efficiency even at low concentrations, remarkable photostability, and structural versatility that allows facile chemical modification.[9,10] The photophysical properties of PTCs are greatly influenced by the presence and nature of the central metal ion. Metals with doubly occupied orbitals (i.e., paired electrons) and diamagnetic ions (which are repelled by magnetic fields), such as Zn^{2+}, Al^{3+}, and Ga^{3+}, provide PTC complexes with high triplet yields, long lifetimes, and associated strong photodynamic activity.[11] Zinc phthalocyanines (ZnPTC) in particular are among the most extensively studied derivatives because they combine favorable photodynamic properties with relatively accessible synthesis and structural tunability.[12]

Several reports support the antimicrobial potential of phthalocyanine-based system. Grammatikova et al. (2019) demonstrated strong antibacterial activity of cellulosic material

impregnated with ZnPTC,[13] while Efimov et al. (2024) reported significant antiviral photodynamic effect in textiles impregnated with LASU phthalocyanine.[14] Fang et al. (2026) further showed that hybrid fibrous membranes composed of zinc phthalocyanine-polycaprolactone/gelatin achieved 99% antibacterial efficacy against *E. coli* and *S. aureus*.[15] More broadly, PTCs have also been investigated as visible-light-active photocatalysts for self-cleaning and environmental decontamination applications.[8,16] Nevertheless, their integration into melt-processable commodity polymers, especially PVC, remains insufficiently explored, and studies that simultaneously address antimicrobial performance and the resulting effects on polymer properties are still scarce.

Evaluation of new antimicrobial materials increasingly require both antibacterial and antiviral assessment. However, experiments involving human pathogenic viruses are often expensive, technically demanding, and constrained by biosafety requirements. In this regard, bacteriophages offer practical and informative viral surrogates because they are safe to handle, readily propagated to high titers, and supported by established purification and quantification protocols. Importantly, selected bacteriophages share key structural and physicochemical characteristics with eukaryotic viruses, including morphology, envelope presence or absence, capsid dimensions, genome material and disinfectant resistance.[17,18] Serrano-Aroca (2022) identified bacteriophage Φ6 as a suitable surrogate for SARS-CoV-2 and other enveloped viruses, including influenza and Ebola,[19] and additional studies by Dey et al. (2021) and Franke et al. (2021) further support the use of phage Φ6 as a safe model for highly pathogenic enveloped viruses in diverse biotechnological contexts.[20–22] By contrast, bacteriophage ΦX174 has been widely employed as a surrogate for non-enveloped viruses, including enteric viruses, hepatitis A virus and poliovirus, in the studies of airborne transmission, filtration, and water purification.[18,23,24] Guo et al. (2018) also used ΦX174 to

investigate plasma-assisted inactivation, highlighting the central role of singlet oxygen in viral inactivation pathways.[25]

On the basis of this framework, the present study employed two tailless phages in antiviral assays: the enveloped *Pseudomonas* phage Φ6 (*Cystoviridae* family) as a surrogate for enveloped human viruses, and the non-enveloped coliphage ΦX174 (*Microviridae* family) as a model for non-enveloped viruses.[18] This study aimed to develop and comprehensively evaluate a PVC-based polymer system with light-activated antimicrobial functionality enabled by phthalocyanine incorporation. The material was assessed for antibacterial activity against representative Gram-positive and Gram-negative bacteria and for antiviral performance against Φ6 and ΦX174 as model enveloped and non-enveloped viruses, respectively. In addition to antimicrobial efficacy, we examined the effect of the active additive on key material parameters relevant to practical implementation, including additive dispersion, migration resistance, thermal stability, and mechanical performance. Although antiviral polymers and bacteriophage-based antiviral testing have each been reported previously,[4] to the best of our knowledge, this is the first study to integrate a zinc phthalocyanine photosensitizer into a melt-processed PVC matrix and systematically relate singlet oxygen generation and antimicrobial performance to polymer morphology, stability, and mechanical behavior.

2. Materials and Methods

2.1 Materials

PVC RB3 polymer matrix was purchased from ModenPlast Medical Srl (Ubersetto di fiorino, Italy). The zinc 2-[3-(phthtalocyaninsulphonamido)propoxy]ethylmetacrylate (ZnPTC-HEMA) was synthesized in the Centre of Organic Chemistry (Rybitví, Czech Republic). Zinc Pyrithione (ZPT) was supported by Alchimica (Prague, Czech Republic). All other chemicals were purchased from Merck (Prague, Czech Republic).

Preparation of ZnPTC-HEMA

ZnPTC-HEMA was prepared by a three-step process (Figure 1). To begin, 304 mL of chlorosulphonic acid was placed in a 1.5 L flask and cooled to 0 – 5 °C in an ice bath. Then, 100 g (173 mmol) of ZnPTC was added in portions, allowing the temperature to rise to 20 °C. The mixture was stirred at this temperature for 30 minutes, then heated to 120 °C for 1 hour. After cooling to 100 °C, 64 mL of thionyl chloride ($SOCl_2$) was added dropwise, and the mixture was maintained at 100 °C for an additional hour. The reaction mixture was then cooled to 20 °C and poured onto a water-ice mixture. The resulting precipitate was collected by filtration, and the filter cake was washed repeatedly with cold water until no sulfate or chloride ions were detected. The resulting paste of phthalocyanine sulfochloride (Pc-SO_2Cl, 603 g) was stored in a refrigerator.

The paste was analyzed for hydrolyzable chlorine and dry matter content (dried at 80 °C). The dry matter was found to be 20.3%, and the hydrolyzable chlorine content (calculated based on dry mass) was 8.9% (the theoretical value for the bis-substituted derivative is 9.14%).

Next, 593 g of the frozen Pc-SO_2Cl was thoroughly dispersed in 543 mL of cold water, followed by the addition of 39 mL of allylamine (521 mmol). The reaction mixture was heated to 40 °C and stirred for 5 hours, then cooled to room temperature and filtered. The filter cake was washed thoroughly with water to remove excess amine and dried at 50 °C, yielding 100 g (80%) of blue ZnPTC-AA.

Subsequently, 100 g of ZnPTC-AA was vigorously dispersed in 450 mL of cold water. Hydroxyethyl methacrylate (19.8 mL, 163 mmol) was then added under stirring. The pH of the reaction mixture (~7) was adjusted to 11 using 4 M NaOH, after which it was heated at 60 °C for 1.5 hours. The mixture was cooled to approximately 25 °C and filtered. The filter

cake was washed with 100 mL of water and dried at 50 °C to afford 92 g (76%) of blue ZnPTC-HEMA.

^{1}H and ^{13}C NMR spectroscopy of the final product was performed in DMSO. The spectra were complex due to the presence of multiple isomers with varying degrees of substitution. Nevertheless, several characteristic signals confirmed the molecular structure. In the ^{1}H NMR spectrum, two distinct signals corresponding to the methylene group were observed at 5.7 and 6.3 ppm, along with a singlet at 11.0 ppm for the NH group and a methyl signal at 1.9 ppm. The ^{13}C NMR spectrum confirmed the presence of the ester carbon of the methacrylate group at 166.7 ppm, as well as eight aliphatic carbon signals, including the terminal methyl at 18.0 ppm.

2,5-Bis(2-ethylhexyl)-3,6-diphenyl-1H,2H,4H,5H-pyrrolo[3,4-c]pyrrole-1,4-dione (DPP) was synthesized following a modified procedure based on Pop et al. (2019), in which K_2CO_3/DMF was employed instead of Cs_2CO_3/CH_3CN.[26]

3,6-Diphenyl-1,4-diketopyrrolo[3,4-c]pyrrole (5.00 g, 17.34 mmol) was suspended in anhydrous DMF (150 mL) under a nitrogen atmosphere. Finely powdered K_2CO_3 (9.60 g, 69.37 mmol) was added, and the resulting heterogeneous mixture was stirred at 125 °C for 1 h. 2-Ethylhexyl bromide (13.4 g, 69.37 mmol) was then added dropwise over 3 h, and the reaction mixture was maintained at 125 °C for an additional 20 h.

After cooling to room temperature, the reaction mixture was poured into excess water to induce precipitation. The resulting solid was collected by vacuum filtration, washed thoroughly with water, and dried under reduced pressure. Purification by recrystallization from hot methanol afforded the target compound as a red solid (1.6 g, 18% yield).

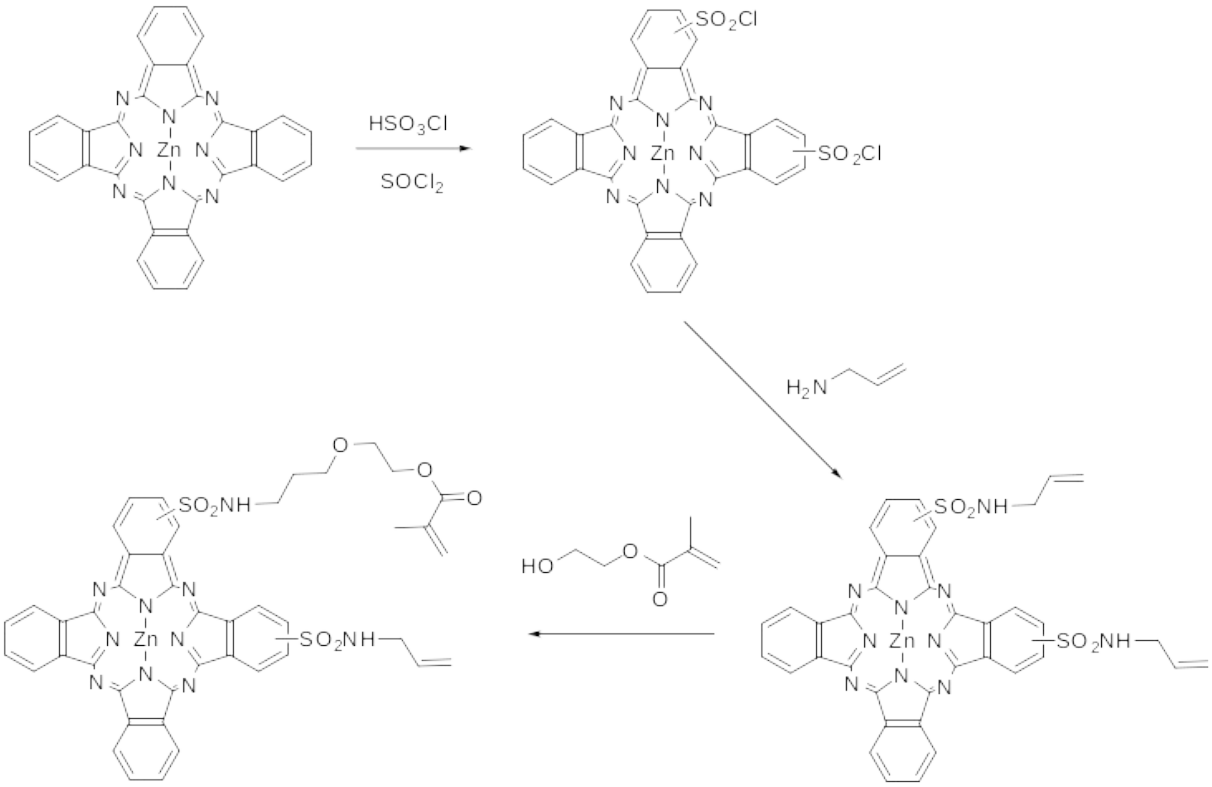

Figure 1. Synthetic route yielding ZnPc-HEMA.

Sample preparation

Firstly, the PVC compound RB3 polymer masterbatch, plasticized with di-2-ethylhexyl phthalate (DEHP) and ZPT, was processed using a Brabender Plastrograph (Brabender GmbH & Co. KG, Duisburg, Germany) at 50 RPM for 3 minutes at 150 °C and then set aside for further steps. Secondly, the PVC mixture with the ZnPTC-HEMA additive was melt-compounded under identical conditions for 6 minutes to achieve a homogenized blend.

A calculated amount of this masterbatch and the PVC-ZnPTC-HEMA blend were then reprocessed using an Xplore MC15 micro-compounder (Xplore Instruments BV, Sittard, The Netherlands) at 150 °C and 100 RPM for 5 minutes. The final composition of the samples is listed in Table 1. For comparison, a reference PVC sample was prepared under the same conditions and with the same instruments.

The final processing step involved compression moulding with a FONTIJNE LabEcon 300 hydraulic press (Fontijne Presses b.v., Rotterdam, The Netherlands) at 150 °C, with an 8-minute tempering period, followed by 3 minutes of pressing at 200 kN and 3 minutes of cooling at 400 kN using a Metallkraft WPP 50 M press (Stürmer Maschinen GmbH, Hallstadt, Germany).

Table 1. Quantification of singlet oxygen with varying concentrations of ZnPTC-HEMA

Sample name	Component (wt %)		
	PVC	ZnPTC-HEMA	ZPT
PVC-0	100	-	-
PVC-0.1	99.9	0.1	-
PVC-0.2	99.8	0.2	-
PVC-0.5	99.5	0.5	-
PVC-1	99.0	1.0	-
PVC-3	97.0	3.0	-
PVC-0-ZPT	100	-	0.005
PVC-0.1-ZPT	99.9	0.1	0.005
PVC-0.2-ZPT	99.8	0.2	0.005
PVC-0.5-ZPT	99.5	0.5	0.005
PVC-1-ZPT	99.0	1.0	0.005
PVC-3-ZPT	97.0	3.0	0.005

2.2 Morphology analysis

FEI NanoSEM 450 (FEI Company, The Netherlands) was used to analyse the morphology of PVC samples´ fracture in order to evaluate the degree of homogeneity. The microscope was

operated in vacuum mode at an acceleration volage of 5 kV. The samples were beforehand sputtered with gold and palladium for 30 s.

2.3 Chemical structure analysis - Fourier transform infrared spectroscopy (ATR-FTIR)

Infrared spectra were recorded using a Nicolet iS5 FTIR spectrometer (Thermo Fisher Scientific, USA) equipped with a diamond ATR crystal. Spectra were collected over the range 4000–400 cm^{-1} at a resolution of 4 cm^{-1}, averaging 64 scans per sample.

2.4 Colorimetric analysis

The colorimetric properties of the PVC samples were analyzed using a UltraScan VIS spectrophotometer (Hunter Lab, USA). The primary analysis utilized the D65/10° spectrum, which simulates daylight at 6500 K, with a viewing angle consistent with the D/8 geometry of the HunterLab Ultrascan instrument.

2.5 Thermal properties

The thermal stability and thus the suitability of additives for thermoplastic processing were confirmed using thermogravimetric analysis (TGA). Samples for thermogravimetry measurement were prepared at 8 mg in weight and investigated on a TA Q500 thermogravimetric analyser (TA Instruments, Wilmington, DE, USA) by a TA Universal Analyzer 2000 version 4.5A (TA Instruments − Waters LLC, Wilmington, DE, USA). The instrument was set to a heating rate of 10 °C/min from 25 to 800 °C under a nitrogen atmosphere. Data of initial degradation temperature (T_i), the peak degradation temperature with maximum weight loss rate (T_p), and thermal degradation weight loss of both antimicrobials were collected.

2.6 Singlet Oxygen Quantification

Singlet oxygen production generation was quantified using the 1,3-diphenylisobenzofuran (DPIBF) method in hexan. DPIBF selectively reacts with intermediate singlet oxygen $^1O_2$ to form an unstable peroxide that decomposes into the colourless product 1,2-dibenzoylbenzene, enabling specific detection without interference from other reactive oxygen species. Hexane was selected as the solvent because it dissolves DPIBF while leaving PVC and ZnPTC-HEMA insoluble, and it provides a higher molar oxygen solubility compared to water.

Polymer samples were cut into 8 × 8 mm squares, accurately weighed, and placed at the bottom of a spectrophotometer cuvette. Subsequently, 2 mL of hexane and DPIBF ($c \approx 2$ g/L) were added to reach absorbance $\lambda = 417$ nm in the range 0.7–0.8. The samples were irradiated with a 661 nm laser (40 mW, focused beam), and the decrease in absorbance at 417 nm was monitored to follow the reaction kinetics. The rate constant $\boldsymbol{k}$ (J^{-1}), proportional to $^1O_2$ generation, was determined from the absorbance decay as a function of incident light energy. From these slopes, the indicator half-life values (τ 1/2, s) were calculated for each sample.[27]

2.7 Antimicrobial assays

Antibacterial efficacy

The antibacterial efficacy of the investigated samples was evaluated under laboratory conditions using standardized test microorganisms and procedures, as detailed below. Before antibacterial testing, samples and polypropylene foils were disinfected by rinsing with 70% denatured ethanol. For the determination two bacterial strains were used, Gram-negative *Escherichia coli* CCM 4517 and Gram-positive *Staphylococcus aureus* CCM 4516 purchased from the Czech Collection of Microorganisms (Brno, Czech Republic). These bacteria were selected as model microorganisms because they represent environmentally relevant species. The antibacterial testing was performed according to ISO 22196 with modifications. Bacterial suspensions (*Escherichia coli* $3{,}4 \cdot 10^5$ CFU/mL; *Staphylococcus aureus* $1{,}2 \cdot 10^5$ CFU/mL) were

prepared in 500x diluted Nutrient broth (HiMedia laboratories, India). The bacterial suspension was dispensed on the sample surface (dimensions 25×25 mm) in the volume 100 µL and the sample was covered with the polypropylene foil (dimensions 20×20 mm). Samples with foils were cultivated at 35 °C and ≥90% relative humidity for 18 hours. The samples for illumination were incubated in a polymethylmethacrylate incubator with transparent walls and illuminated from a distance of 200 cm by an artificial daylight source (LED source: blue primary emitter 450 nm; Illumination intensity = 1250 lx). After the incubation time, polypropylene foil was removed and each sample was completely washed by SCDLP broth (HiMedia laboratories, India), which was subsequently collected. The viable bacteria count was determined by the pour plate culture method (PCA, HiMedia laboratories, India). After the incubation, the number of bacteria colonies in the Petri dishes was determined.

The antibacterial activity (R) was calculated using Equation (1):

$$R = \log N_{blank} - \log N_{sample}, \quad (1)$$

where $\log N_{blank}$ and $\log N_{sample}$ are the logarithms of viable bacteria number in the reference and modified sample, respectively. All experiments were conducted in triplicate, with a minimum of two independent determinations for each parameter.

Statistical significance was evaluated by applying one-way ANOVA ($P < 0.05$); (OriginPro 2024, OriginLab Corporation, Massachusetts, USA); experimental data are reported as the mean values of three replicates ± standard deviation.

Antiviral efficacy

In this work, bacteriophages Pseudomonas phage Φ6 DSM 21518, Escherichia phage ΦX174 DSM 4497 and their host cultures *Pseudomonas syringae* DSM 21518 and *Escherichia*

coli DSM 13127 were sourced from Leibniz Institute DSMZ-German collection of Microorganisms and Cell Culture GmbH (Braunschweig, Germany). The received microorganisms were cultured following the manufacturer's instructions. Stock cultures of *P. syringae* and *E. coli* were stored at -70°C, whilst the Φ6 and ΦX174 bacteriophages were stored in refrigerator at 4°C.

The antiviral activity of the samples was compared to neat PVC without active substances in a polymer matrix and were performed according to a modified ISO 22196:2021 standard. A phage lysate with an initial viral particle concentration of approximately 10^9 PFU/mL, prepared according to the supplier's instructions, was diluted 500-fold in nutrient broth (HiMedia Laboratories, India) to obtain viral suspensions with final concentrations of Φ6 (1.8×10^6 PFU/mL) and ΦX174 (7.7×10^6 PFU/mL). Samples were incubated with the respective viral suspensions for 18 h. Incubation was carried out according to the preferences of the host culture: 25 °C for phage Φ6 and 35 °C for ΦX174 and relative humidity ≥90%. After rinsing the samples, phage was assayed by the double layer method, when phage suspension (0.1 mL) was mixed with 0.1 mL host culture (OD = 0.3) and 3 mL top agar and poured on to surface of a bottom agar plate. Sterilization of the samples, methodology, sample dimensions and calculation of antiviral activity were the same as for bacteria.

2.8 Migration study

Migration testing was carried out according to ČSN EN 1186 (Migration from plastics into food simulants). Prior to testing, PVC foils containing phthalocyanines were rinsed with demineralized water and dried on filter paper. Samples were immersed in distilled water, maintaining a contact ratio of 1 dm^2/100 mL. Incubation was performed at 40 °C for 10 days (240 h) in the dark with mild agitation (110 rpm), representing standard migration conditions for long-term room temperature contact. Control samples (pure water and PVC without

phthalocyanine) were prepared in parallel. The same prepared samples were also subjected to UV-Vis and EDX-XRF analysis, respectively.

UV-Vis analysis

Measurements were carried out on a Tecan Infinite 200 PRO (Tecan, Austria). Absorption spectra of the calibration series (0.01–5.0 µg/mL) were recorded in the range of 300–800 nm. The absorption maximum was determined at 628 nm, which was subsequently used for quantitative measurements. The limit of detection for this method was 0.24 µg of PTC per mL.

EDX-XRF analysis

The content of elements in the sample water extracts was determined by EDX-XRF method (Energy ray dispersion spectroscopy - X ray fluorescence), which is based on elemental analysis of X-ray diffraction (energy) materials. The amount of element analyzed was evaluated in weight percent (wt %).

Samples in special cups were placed (3 g) inside the instrument at the appropriate sample to autosampler. The content of the elements was determined using an Energy Dispersive X-ray Spectrometer (Thermo Scientific, ARL Quant X). The samples were analyzed in a special selected method: Any sample Air in Quant Unite program. The limit of detection is until: 0.1 – 0.5 wt %, and the limit of quantification is until: 0,1 wt %.

3. Results and Discussion

3.1 Morphology analysis

The morphology of the prepared PVC samples was investigated by SEM. Representative surface micrographs of cryo-sectioned moulded foils are shown in Figure 2. Discrete

particulate features were observed within a narrow size range across all samples, including neat PVC (Figure 2A), despite the absence of intentionally added additives. Their ubiquitous presence strongly suggests that these particulates originate from processing additives incorporated by the PVC granulate manufacturer to enhance material performance, as previously reported.[28,29]

In comparison with neat PVC (Figure 2A), the PVC sample containing ZPT (0.005 wt %; Figure 3G) exhibits a homogeneous morphology with no discernible ZPT particles, indicating good compatibility and dispersion of ZPT within the PVC matrix. Similarly, samples containing Zn-PTC-HEMA at lower loadings (Figure 2B–E and Figure 2H–K) display smooth fracture surfaces and a uniform distribution of PTC, with no evidence of particle agglomeration.

In contrast, samples containing 3 wt % Zn-PTC-HEMA, both without and with ZPT (Figure 2F and Figure 2L, respectively), show a homogeneous matrix populated by a markedly higher number of particulate features. Notably, sample L exhibits a significantly roughened fracture surface. This morphology is indicative of an excessive loading of the phthalocyanine additive, leading to microstructural heterogeneity. The observed surface roughness correlates well with the deterioration in mechanical properties discussed in the following section. Similar effects associated with high PTCs loadings in polymer matrices have been reported elsewhere.[30]

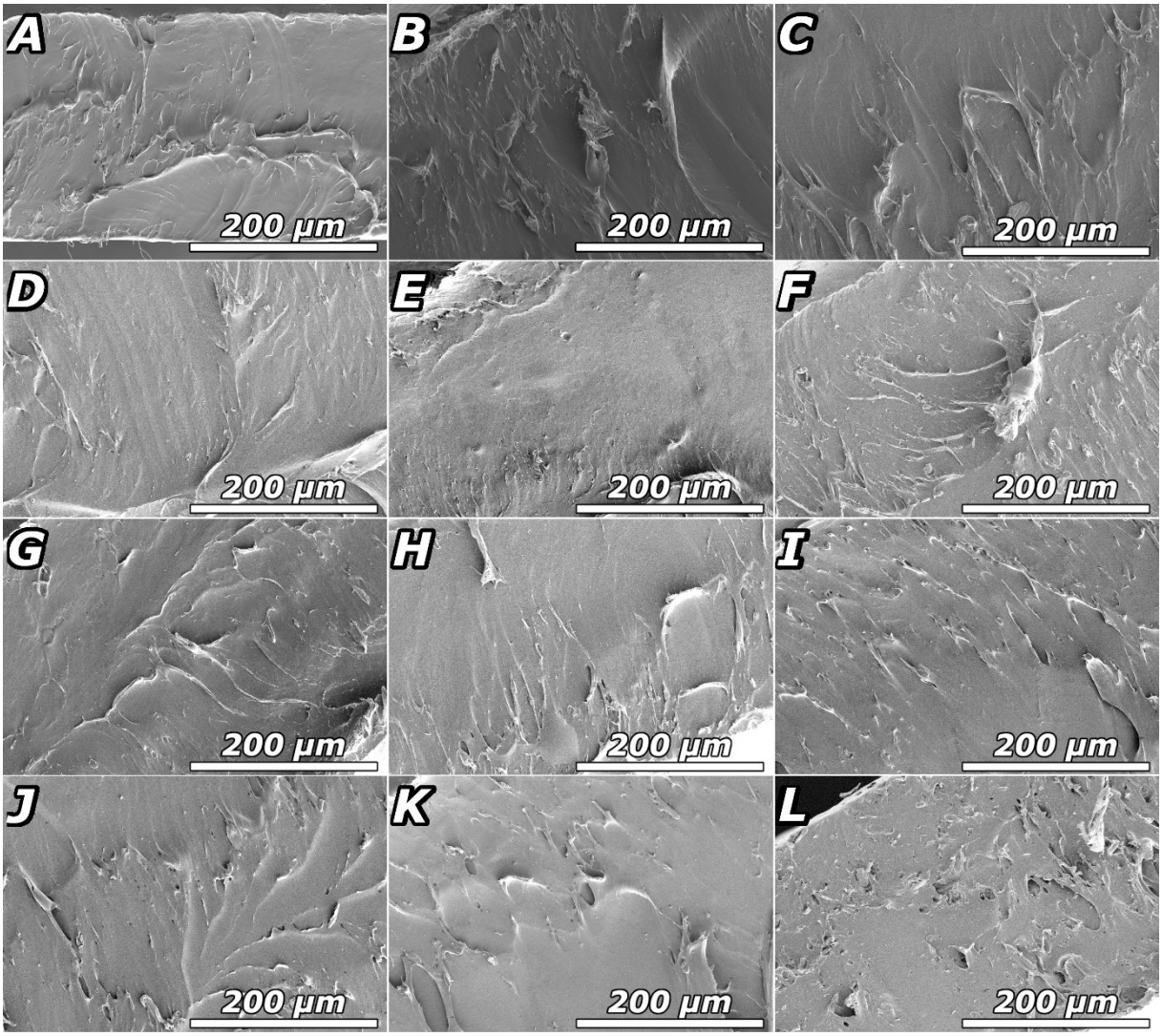

Figure 2. SEM images of A) PVC-0, B) PVC-0.1, C) PVC-0.2, D) PVC-0.5, E) PVC-1, F) PVC-3, G) PVC-0-ZPT, H) PVC-0.1-ZPT, I) PVC-0.2-ZPT, J) PVC-0.5-ZPT, K) PVC-1-ZPT, L) PVC- 3-ZPT.

3.1 Chemical structure analysis - Fourier transform infrared spectroscopy (ATR-FTIR)

The FTIR spectrum of neat PVC exhibits characteristic absorption bands associated with specific functional groups in the repeating $–CH_2–CHCl–$ units (Figure 3). Strong bands at 2970–2850 cm^{-1} correspond to C–H stretching vibrations of the methylene ($–CH_2–$) groups, typical of aliphatic polymers and indicative of the saturated polymer backbone. The prominent band at 1425 cm^{-1} arises from CH_2 scissoring vibrations and is a key diagnostic

feature of PVC. Additional bands in the 1330–1250 cm^{-1} region are assigned to CH_2 wagging and rocking modes, while those at 1095–1020 cm^{-1} correspond to C–C stretching vibrations along the polymer chain. A distinctive set of absorptions between 960 and 610 cm^{-1} is attributed to C–Cl stretching vibrations, which are characteristic of PVC and confirm the presence of chlorine in the macromolecular structure.

Bands near 1730 cm^{-1} (C=O stretching) and 1650 cm^{-1} (C=C stretching), which would indicate oxidation or dehydrochlorination, are absent, confirming that the material is chemically unaltered PVC. Overall, the obtained FTIR spectrum agrees well with reference data[31,32] and displays all diagnostic features of unmodified PVC, including pronounced C–H, CH_2, and C–Cl absorptions. The FTIR spectra of PVC formulations containing additives closely resemble that of neat PVC (PVC-0). However, a distinct weak band at ~1538 cm^{-1} appears exclusively in the modified samples and is absent in neat PVC. This band is attributed to coordination-sensitive ring vibrations of ZPT and confirms its successful incorporation in the polymer matrix. Its position (≈1536–1538 cm^{-1}) corresponds to ligand ring vibrations sensitive to metal coordination, supporting the presence of Zn–pyrithione in a chelated form.[33]

FTIR spectroscopy shows that, even at the highest loadings of ZnPTC-HEMA and ZPT, the characteristic bands of PVC remain unchanged in position and relative intensity (Figure 3). This indicates that incorporation of these additives does not alter the chemical environment of the PVC chains, implying the absence of chain rearrangement, disruption of the polymer backbone, or formation of new interactions that would modify the matrix structure.

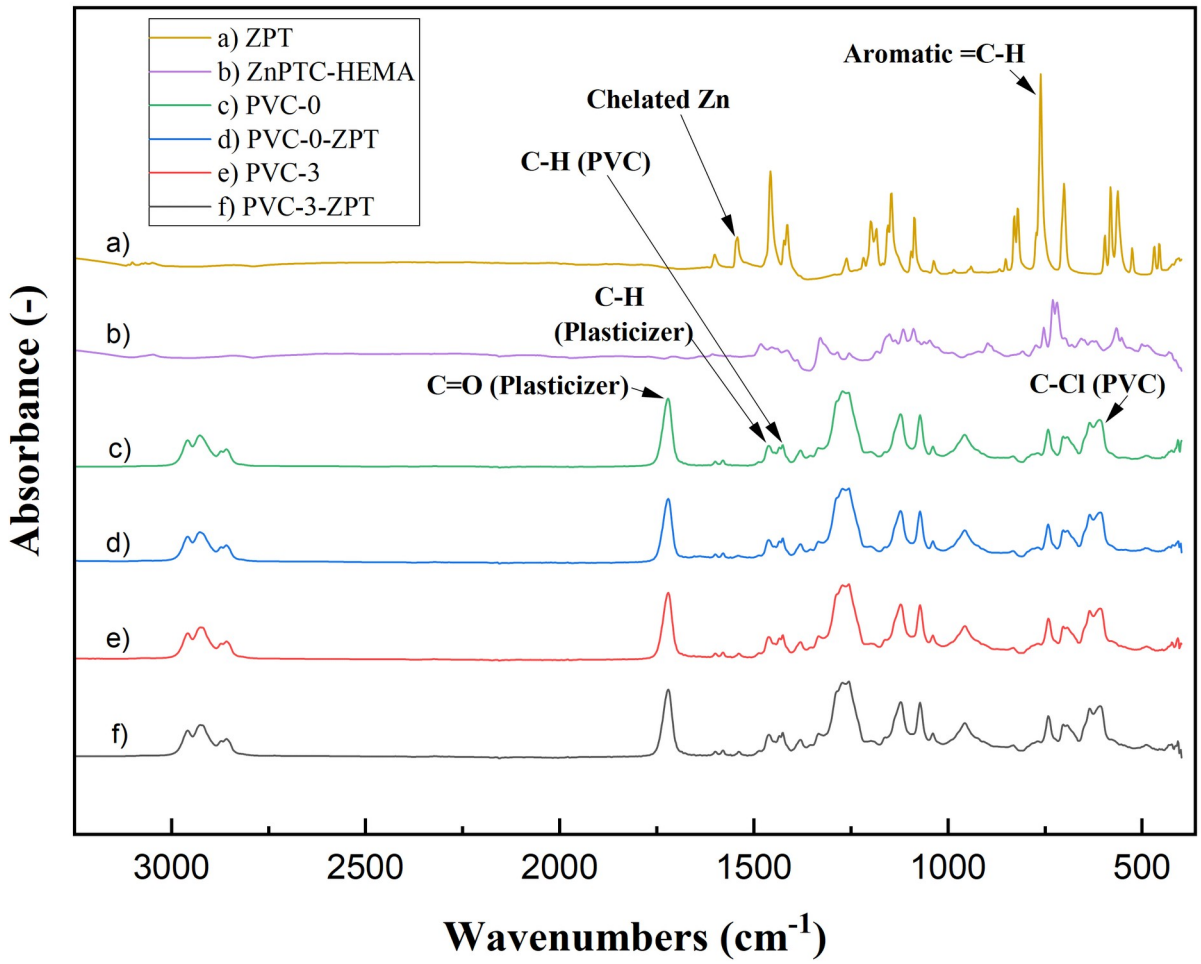

Figure 3. FTIR spectra for pure ZnPTC-HEMA; a) pure ZPT, b) ZnPTC-HEMA, c) PVC-0, d) PVC-0-ZPT, e) PVC- 3 and f) PVC- 3-ZPT. In accordance with Deleanu et al. (2024).[34]

3.2 Colorimetric study

The transmission spectra (Figure 4) of neat PVC (PVC-0) and PVC compounds containing ZnPTC-HEMA at different loadings (0.1–3.0 wt %), with and without the presence of ZPT (0.005 wt %), reveal distinct modifications in optical behavior that are strongly dependent on the concentration of ZnPTC-HEMA (Figure 4).

Neat PVC exhibits a baseline spectrum typical of an unmodified polymer matrix, with relatively high transmission across the visible region and minimal absorption features.[35] Upon

incorporation of **ZnPTC-HEMA at low concentrations (0.1–0.2 wt %)**, a slight decrease in transmission is observed, indicating the introduction of weak absorptive species into the polymer matrix. The effect is slightly more pronounced with the simultaneous introduction of ZPT.

At concentrations of 0.5–1.0 wt % ZnPTC-HEMA, the spectra reveal a pronounced reduction in transmittance, most notably within the UV region. This trend is attributable to the increased absorbance associated with the higher density of ZnPTC-HEMA chromophore units. Co-addition of ZPT induces a further, albeit modest, decrease in transmittance; however, the relative influence of ZPT diminishes progressively with increasing ZnPTC-HEMA concentration.

At the highest concentration examined (3.0 wt % ZnPTC-HEMA; samples PVC-3 and PVC-3-ZPT), the spectra exhibit the lowest overall transmittance, characterized by substantial attenuation across both the UV and visible regions. Under these conditions, the presence of ZPT does not produce a significant additional suppression of transmittance, indicating that optical shielding is dominated by the ZnPTC-HEMA component at this concentration.

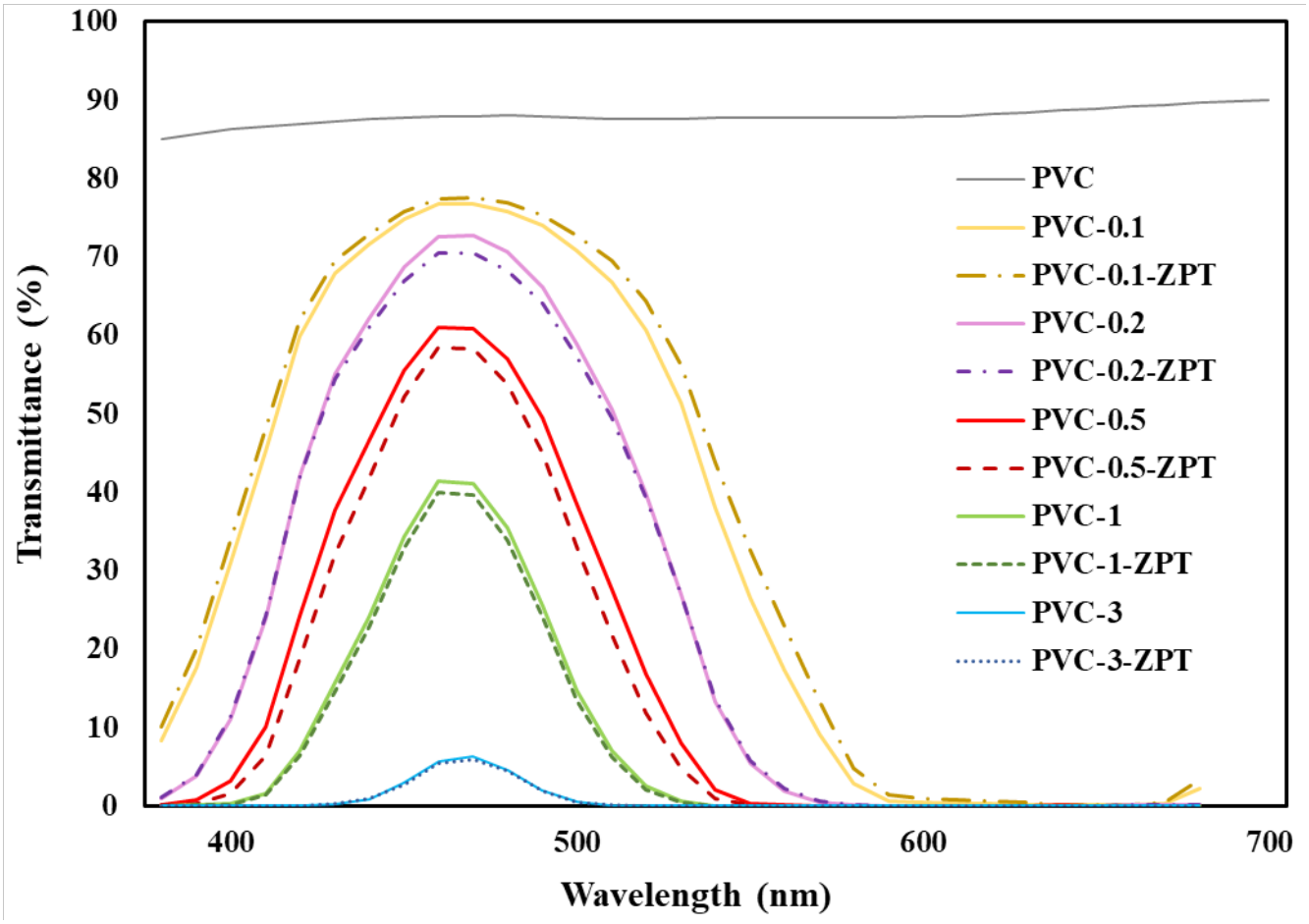

Figure 4. Transmission spectra of PVC-0; PVC-0.1; PVC-0.1- ZPT; PVC-0.2; PVC-0.2-ZPT; PVC-0.5; PVC-0.5-ZPT; PVC-1; PVC-1-ZPT; PVC-3; PVC-3-ZPT.

The visual appearance of the samples (Figure 5) is fully consistent with the spectroscopic data. Increasing ZnPTC-HEMA concentration leads to a progressive darkening and loss of transparency, while samples with and without ZPT at the same ZnPTC-HEMA loading are visually indistinguishable or show only negligible differences. Together, these results demonstrate that the colorimetric and optical properties of the compounds are controlled almost exclusively by ZnPTC-HEMA content. The addition of ZPT at 0.005 wt % does not significantly affect the transmission behavior, confirming that ZPT can be incorporated without compromising the optical characteristics of the PVC/ZnPTC-HEMA compound.

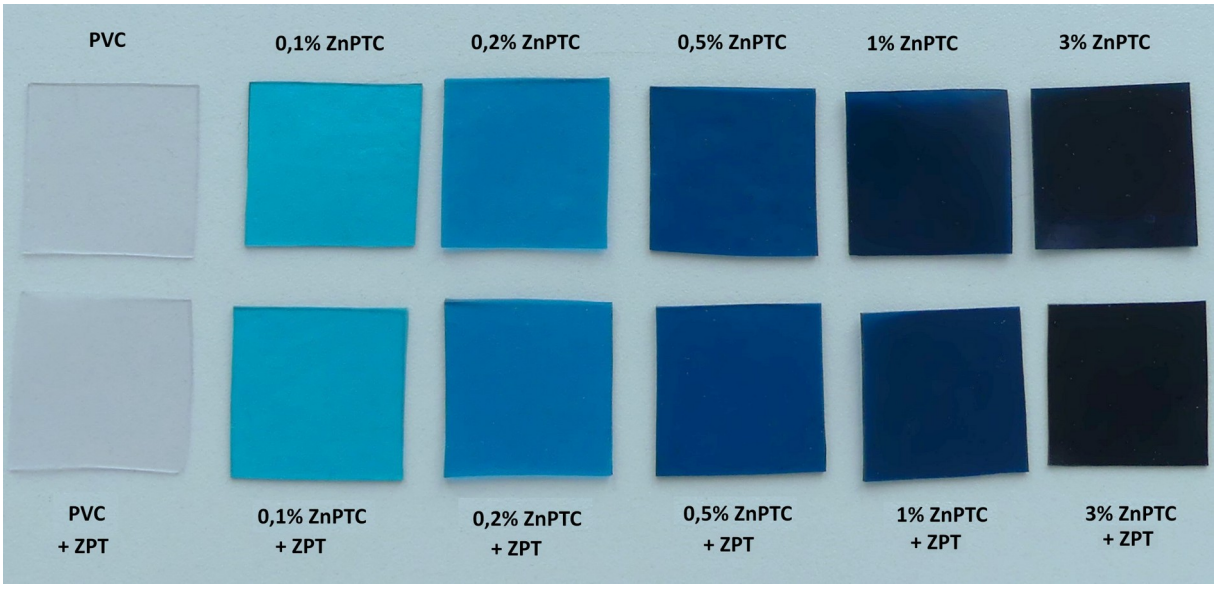

Figure 5. PVC samples with increasing ZnPTC-HEMA; PVC-0, PVC-0.1, PVC-0.2, PVC-0.5, PVC-1, PVC-3; (top) and with the addition of ZPT (0.005 wt %); PVC-0.1-ZPT, PVC-0.2-ZPT, PVC-0.5-ZPT, PVC-1-ZPT, PVC- 3-ZPT (bottom).

3.2 Thermal properties

The applicability of antimicrobial agents incorporated into polymers is determined not only by their compatibility with the polymer matrix but also by their thermal stability. PVC undergoes thermal degradation in distinct stages. The initial degradation phase occurs between 25 °C and 350 °C and is primarily associated with dehydrochlorination and the volatilization of plasticizers, such as di(2-ethylhexyl) phthalate (DEHP).[36] This stage exhibited two distinct degradation events, with peak maxima at 255 °C and 280 °C. During this phase, a weight loss of approximately 72.4 wt % was observed, with the maximum degradation rate occurring at 280 °C (Table 2), as indicated by the peak temperature (Tp) on the DTG curve. This is in accordance with other studies of thermal behavior of PVC.[37,38]

The second degradation stage occurred between 350 °C and 600 °C and is likely associated with the breakdown of conjugated polyenes into benzene and alkylated benzenes, as well as the thermal cracking of the polymer backbone. Finally, at temperatures above 600 °C, the last

degradation stage takes place, which can be attributed to the decomposition of byproducts, such as hydrocarbon residues, formed during the earlier degradation processes.[38–40]

The incorporation of the antimicrobial agents ZPT and ZnPTC-HEMA had only a minor effect on the thermal degradation behavior of PVC. Unlike neat PVC (PVC-0), the compound material (PVC-3-ZPT) exhibited a single broad degradation step in the temperature range of 25 °C to 350 °C, with a peak maximum at 280 °C, which is characteristic of PVC with no significant difference in weight loss. The influence of the antimicrobial agents became more apparent in the subsequent degradation stages. Although these stages occurred within the same temperature ranges as for neat PVC, they exhibited varying weight changes. Specifically, the second degradation step showed reduced weight loss in the presence of ZPT, while the addition of ZnPTC-HEMA resulted in increased weight loss during the final degradation stage. To support these observations, TGA of the pure antimicrobial agents was also conducted to better understand their individual thermal degradation behaviors. Overall, the total weight loss was approximately 92.41 wt % for neat PVC (PVC-0) and 88.41 wt % for the PVC/ZPT/ZnPTC-HEMA compound (PVC-3-ZPT).

Table 2. Thermal characterization analysis of antimicrobial additives and PVC

Samples	**T_i (°C)**	**T_p (°C)**	**Temperature range (°C) Weight loss (wt %)**		
			25-350	**350-600**	**600-800**
PVC-0	197	280	72.38	19.23	0.80
PVC- 3-ZPT	200	278	71.11	15.81	1.49
			25-150	**150-420**	**420-800**
ZnPTC-HEMA		322	3.70	23.07	37.2
			25-420	**420-600**	**600-800**

ZPT	265	282	49.04	5.53	5.31

the initial decomposition (onset) temperature (T_i), the peak maximum on DTG curve T_p

For the pure ZPT, the degradation initiation temperature was observed at approximately 265 °C, with the first peak maximum occurring at 282 °C (Table 2). The overall thermal decomposition can be divided into three distinct degradation stages. The first stage, associated with the decomposition of the ZPT complex, occurred within the temperature range of 25 °C to 420 °C. This stage exhibited two distinct degradation events, with peak maxima at 282 °C and 330 °C, which are consistent with values reported in the literature.[41] These peaks are attributed to the solid-state dimeric structure of ZPT.

The second degradation stage, characterized by a weight loss of 5.53 wt %, occurred between 420 °C and 600 °C and is likely associated with the degradation of specific components of the ZPT complex. The final degradation stage, observed at temperatures above 600 °C, is attributed to the decomposition of residual byproducts.

Additionally, ZPT exhibits a melting point of approximately 240 °C, which facilitates its incorporation into a range of thermoplastics and elastomers. Notably, previous studies have shown that the addition of ZPT does not compromise the thermal stability of high-density polyethylene (HDPE) foils, indicating that ZPT can be effectively used in polymer matrices without significantly affecting their thermal properties.[42]

The thermal stability of the pure ZnPTC-HEMA dye was also evaluated using the TGA. The TGA curve revealed multiple decomposition steps. The initial weight loss of 3.70 wt % was observed from room temperature up to 150 °C (Table 2), corresponding to the evaporation of adsorbed moisture.

The degradation behavior of this newly synthesized material was complex and analyzed in terms of the decomposition of its constituent components. Specifically, the PTC segment

degraded in two distinct temperature intervals, with degradation of the HEMA component occurring between these stages. The soft HEMA segments degraded in the temperature range of 200 °C to 420 °C, with a maximum degradation rate at 322 °C. Additionally, the initial degradation of the PTC component began earlier, between 150 °C and 200 °C, and was attributed to the breakdown of the phthalocyanine ring.

At elevated temperatures above 420 °C, the degradation of both the PTC component and the hard HEMA segments continued, with overlapping processes that prevented the clear distinction of individual degradation steps. For instance, the hard HEMA segments were expected to degrade within the range of 327 °C to 670 °C, while the residual PTC component decomposed between 450 °C and 700 °C. Despite the complexity, the overall decomposition behavior observed in this study is consistent with previously reported findings.[43–45]

3.3 Mechanical properties

The mechanical properties of neat PVC (PVC-0) and PVC compounds containing 0.1 and 3 wt % ZnPTC-HEMA, prepared with and without ZPT, are summarized in Table 3. The Young's modulus of PVC-0 (10.2 ± 0.8 MPa) is not affected by the incorporation of a low loading of ZnPTC-HEMA (0.1 wt %) nor by the presence of ZPT. In contrast, increasing the ZnPTC-HEMA content to 3 wt % (PVC-3) leads to a measurable stiffening of the material, with the modulus rising to 12.6 ± 1.7 MPa in the absence of ZPT and to 13.0 ± 1.9 MPa when ZPT is present (PVC-3-ZPT). Statistical analysis using a two-sample Student's *t*-test (α = 0.05, 95% confidence level), performed relative to neat PVC, confirms that this increase is statistically significant only at the highest phthalocyanine loading (3 wt %), irrespective of ZPT addition. This trend is consistent with the morphological features observed in the SEM micrographs, which indicate a more rigid microstructure at higher additive contents.

The tensile strength (stress at break) of all samples falls within a narrow range of 7.5 ± 1.4 to 9.9 ± 1.8 MPa, while the strain at break varies between 174.4 ± 34.8% and 196.6 ± 26.2% (Table 3). No statistically significant differences in either tensile strength or elongation at break are observed compared to neat PVC (PVC-0). These results indicate that, within the investigated concentration range, ZnPTC-HEMA does not detrimentally affect the ductility or ultimate strength of the PVC matrix.

Pronounced effects of phthalocyanines on polymer mechanical properties have been reported previously, for example for copper phthalocyanine incorporated into a polyurethane matrix; however, such effects were observed at substantially higher filler loadings (up to 30 wt %) (Youssef, Al-Turaif, and Wazzan 2015). In contrast, our findings are in line with reports describing negligible changes in mechanical performance upon the incorporation of moderate amounts of photocatalytic additives into PVC, such as 4.8 wt % reported by Yang et al. (2016). Overall, the present results demonstrate that low to moderate ZnPTC-HEMA loadings preserve the mechanical integrity of PVC, while higher loadings can induce a modest but statistically significant increase in stiffness without compromising tensile strength or elongation.

Table 3. Mechanical Properties of PVC and ZnPTC-HEMA Compounds with/without ZPT (0.005 wt %)

Samples	Young Modulus (MPa)	Strain at Break (%)	Stress at Break (MPa)
PVC-0	10.2 ± 0.8[a]	185.5 ± 35.0[a]	9.7 ± 1.9[a]
PVC-0.1	10.8 ± 0.6[a]	174.4 ± 34.8[a]	8.0 ± 1.4[a]
PVC- 3	12.6 ± 1.7[b]	196.6 ± 26.2[a]	9.9 ± 1.8[a]
PVC-0-ZPT	9.7 ± 0.7[a]	172.5 ± 22.4[a]	9.2 ± 1.8[a]

PVC-0.1-ZPT	10.8 ± 0.1[a]	196.5 ± 35.7[a]	7.5 ± 1.4[a]
PVC-3-ZPT	13.0 ± 1.9[b]	186.3 ± 36.3[a]	9.7 ± 1.9[a]

3.4 Singlet oxygen quantification

The quantitative analysis of singlet oxygen generation, summarized in the Table 3, demonstrates that incorporation of ZnPTC-HEMA into the PVC matrix markedly enhances singlet oxygen production relative to neat PVC. The pristine polymer exhibits a very low rate constant ($k = 0.0031\ J^{-1}$) and a correspondingly long half-time ($\tau_1/_2 \approx 5590$ s), confirming the negligible intrinsic photosensitizing activity of unmodified PVC under the applied experimental conditions.

Even at the lowest ZnPTC-HEMA loading of 0.1 wt % (PVC-0.1), a pronounced increase in singlet oxygen generation is observed, with k increasing by nearly an order of magnitude and $\tau_1/_2$ decreasing to approximately 600 s. This sharp transition indicates that ZnPTC-HEMA acts as a highly efficient photosensitizer within the polymer matrix and that only minimal additive concentrations are required to activate effective photodynamic behavior. As the ZnPTC-HEMA content increases from 0.1 to 1 wt % (PVC-1 to PVC-1), a monotonic increase in k is accompanied by a progressive reduction in $\tau_1/_2$, reflecting accelerated singlet oxygen production. The most substantial gains occur up to approximately 0.5–1 wt % (PVC-0.5 to PVC-1), beyond which further increases in additive content yield only marginal improvements.

At higher loadings (1–3 wt %), the system approaches a plateau regime, with k values converging to ~$0.05\ J^{-1}$ and $\tau_1/_2$ stabilizing in the range of 317–333 s. This saturation behavior suggests that singlet oxygen generation becomes limited by factors other than photosensitizer

concentration, such as light absorption efficiency, excited-state quenching, or oxygen diffusion within the polymer matrix.

The addition of ZPT at 0.005 wt % (Table 4) leads to a modest reduction in singlet oxygen generation across all ZnPTC-HEMA concentrations. This effect is reflected in slightly lower k values and correspondingly higher $\tau_1/_2$ values relative to the ZPT-free systems. Importantly, the preservation of high singlet oxygen production in the presence of ZPT indicates that the two antimicrobial strategies, single oxygen production and conventional biocidal action, can coexist without strong antagonistic interactions. This observation is consistent with the antimicrobial assay results, which show sustained efficacy even in formulations containing both additives. From an application perspective, these findings support the feasibility of designing multifunctional PVC materials in which ZnPTC-HEMA provides robust photodynamic activity at relatively low loadings, while ZPT contributes complementary antimicrobial protection without significantly impairing ROS generation.

All samples were analyzed in triplicate. The relative standard deviation (RSD) for replicate measurements was below 10% for each sample, demonstrating good repeatability of the analytical procedure. Accordingly, the measured values were deemed sufficiently reliable for subsequent evaluation of photoactivity.

Overall, the singlet oxygen quantification data highlight an optimal ZnPTC-HEMA concentration window around 0.5–1 wt %, where high photodynamic efficiency is achieved without unnecessary additive excess. This balance is particularly relevant for practical implementation, as it aligns enhanced antimicrobial performance with material stability and processability requirements expected for advanced polymeric antimicrobial surfaces.

Table 4. Singlet oxygen production as a function of ZnPTC-HEMA concentration with/without fixed ZPT loading (0.005 wt %)

Sample	ZnPTC-HEMA (wt %)	ZPT (wt %)	k (J^{-1})	$\tau_{1/2}$ (s)
PVC-0	-	-	0.0031	5590
PVC-0.1	0.1	-	0.0287	604
PVC-0.2	0.2	-	0.0373	465
PVC-0.5	0.5	-	0.0492	352
PVC-1	1.0	-	0.0521	333
PVC-3	3.0	-	0.0547	317
PVC-0.1-ZPT	0.1	0.005	0.0272	637
PVC-0.2-ZPT	0.2	0.005	0.0368	471
PVC-0.5-ZPT	0.5	0.005	0.0463	374
PVC-1-ZPT	1.0	0.005	0.0502	345
PVC-3-ZPT	3.0	0.005	0.0452	383

All samples were analyzed in triplicate. The relative standard deviation (RSD) for replicate measurements was below 10% for each sample.

3.5 Antimicrobial assays

Antibacterial efficacy

The study results demonstrated that PVC modified with phthalocyanine derivate ZnPTC-HEMA exhibits pronounced light-activated antimicrobial activity. Under illumination at 1000 lux, the material effectively suppressed the growth of Gram-positive *S. aureus* even at a loading of 0.1% (PVC-0.1), indicating a bactericidal response (Figure 6). In contrast, Gram-negative *E. coli* showed substantially lower susceptibility: only weak inhibition was observed at ZnPTC-HEMA concentrations up to 0.5% (R = 1.4 ± 0.2), while strong antimicrobial

activity (R = 3.8 ± 0.1) was achieved only at the highest loading tested (3%) under light exposure. Samples incubated in the dark exhibited only marginal activity (R = 1.6 ± 0.2), detectable solely against *S. aureus* at loadings ≥1%, indicating that the effect is primarily photoactivation-driven rather than due to passive toxicity of the material.

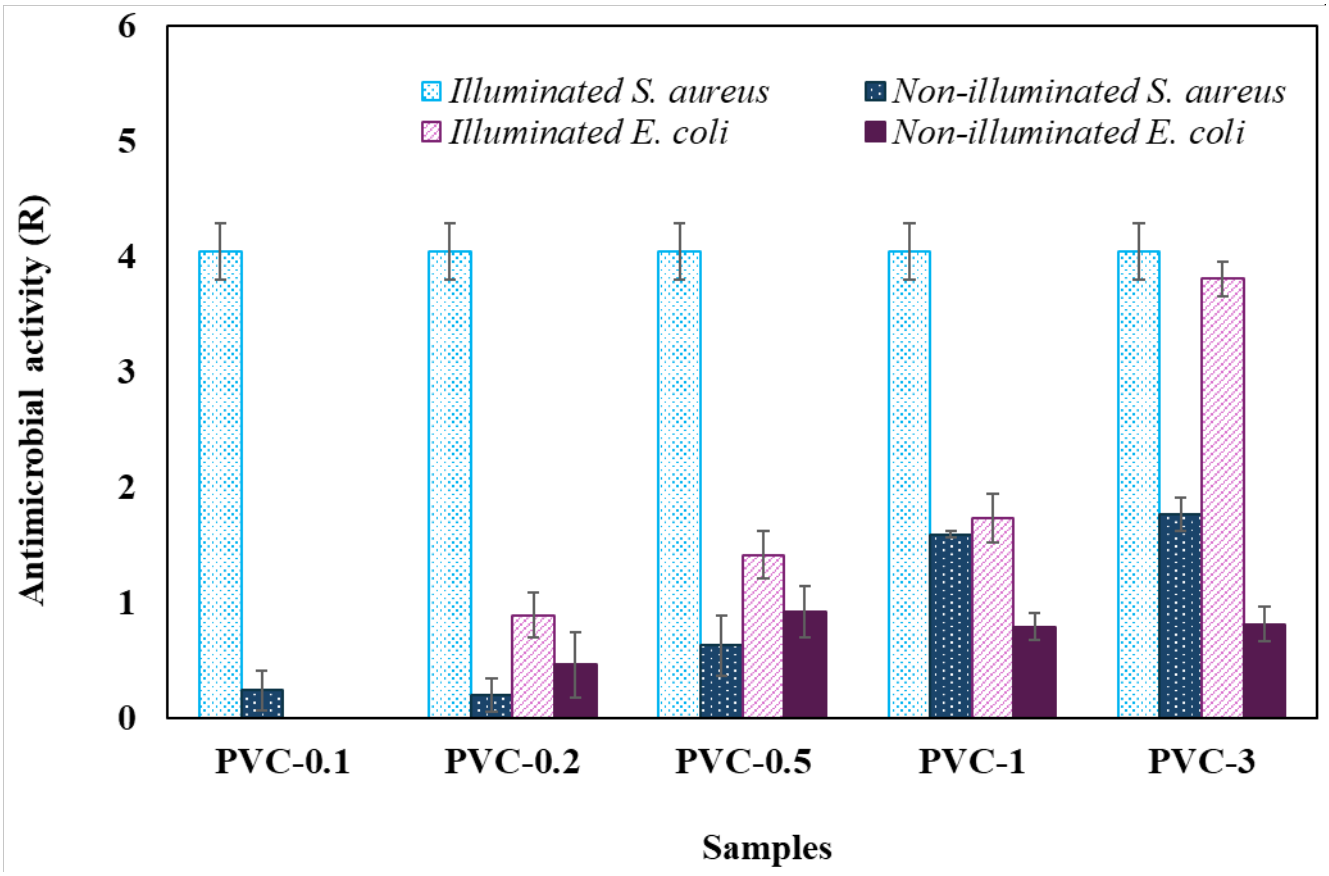

Figure 6. Antibacterial activity of illuminated/non-illuminated PVC samples with ZnPTC-HEMA concentration scale against *S. aureus* and *E. coli.*

The addition of ZPT (0.005 wt %) significantly (P > 0.05) enhanced the antimicrobial properties, even in non-illuminated samples (Figure 7). The figure shows that antimicrobial efficiency depends on the dye concentration. This enhancement was notable, as strong

antimicrobial activity (R > 3) against both monitored bacteria strains at only 0.5% ZnPTC-HEMA (PVC-0.5-ZPT), suggesting a synergistic enhancement of photodynamic activity.

The results of the antibacterial activity assessment, summarized in Figures 6 and 7, reveal higher efficacy against Gram-positive *S. aureus*. This observation aligns with findings reported in previous studies.[30,46] Grammatikova et al. (2019) demonstrated a strong antibacterial effect of phthalocyanine-stained paper against *S. aureus* after just 60 minutes of exposure to light at an intensity of 270 lux.[47] Similarly, Mapukata et al. (2021) also reported high antibacterial activity against *S. aureus* under illumination.[48]

The photodynamic mechanism of phthalocyanines is well established and involves light absorption followed by intersystem crossing to the triplet excited state and subsequent electron energy transfer to molecular oxygen. This process generates reactive oxygen species, including singlet oxygen, which exhibit potent antibacterial effects.[48] Some studies have shown that these species can penetrate the porous peptidoglycan layer of Gram-positive bacteria, making them more susceptible to photodynamic inactivation.[49–51]

In contrast, Gram-negative bacteria possess an additional outer lipopolysaccharide layer, which reduces their permeability to lipophilic small molecules and increases their resistance to both antibiotics and photodynamic treatments. However, the photosensitivity of Gram-negative bacteria can be enhanced by substances such as $CaCl_2$, EDTA, or polymyxin B, which alter outer membrane permeability. The underlying reasons for Gram-negative bacteria's resistance to photosensitization remain unclear but may involve the charge on the photosensitizer and its resulting subcellular distribution and localization within these organisms.[49,50] Additionally, weak antimicrobial activity against *E. coli* was also recently demonstrated for a polyhydroxybutyrate submicron fibber mat with 0.1 wt % zinc phthalocyanine derivative content.[51]

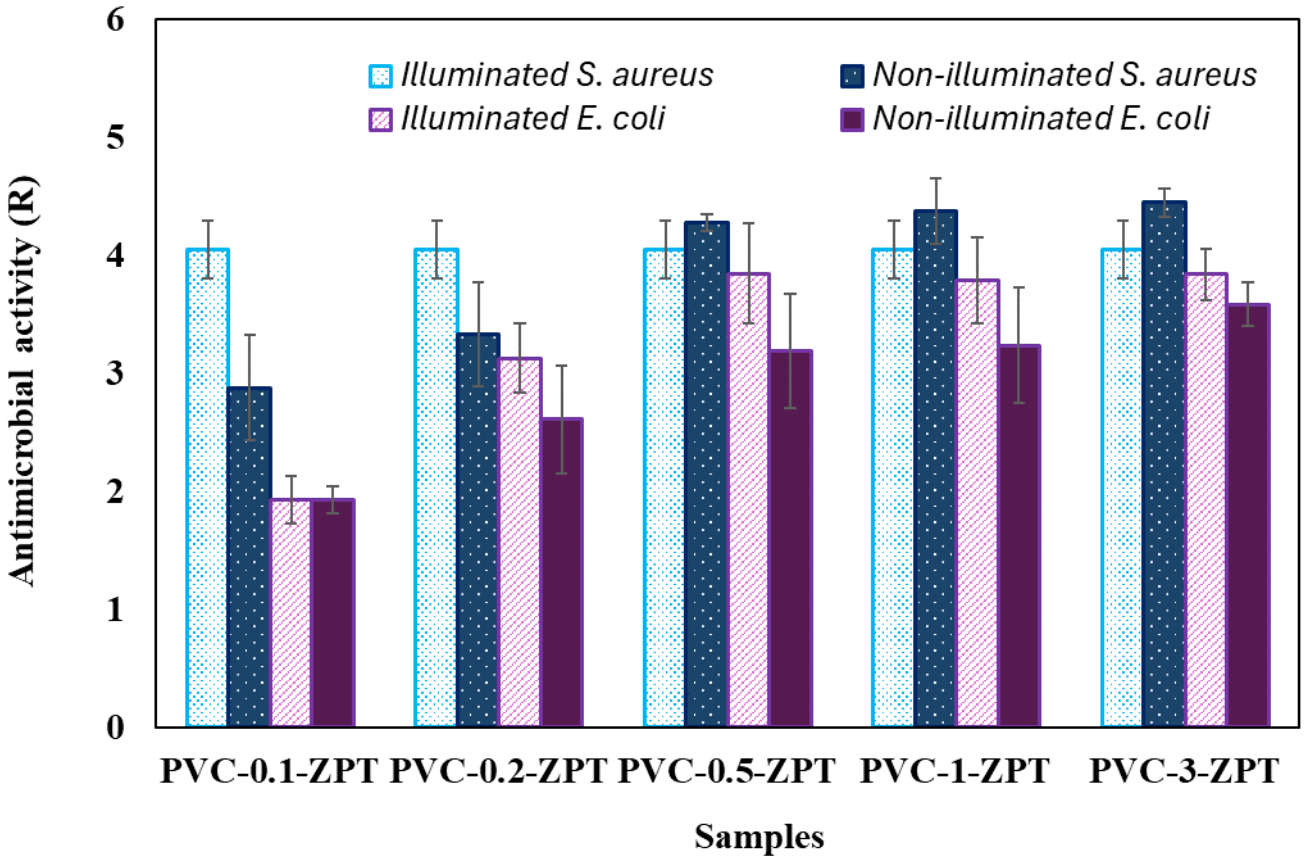

Figure 7. Antibacterial activity of of illuminated/non-illuminated PVC samples with ZnPTC-HEMA concentration scale and ZPT (0.005 wt %) against *S. aureus* and *E. coli*.

Antiviral efficacy

The antibacterial activity of the prepared samples was assessed following the ISO 22196:2021 standard, with protocol modifications to accommodate bacteriophage propagation requirements. Table 5 summarizes the antiviral performance of illuminated and non-illuminated PVC specimens incorporating increasing concentrations of ZnPTC-HEMA. Antiviral efficacy was assessed against the enveloped bacteriophage Φ6 and the non-enveloped bacteriophage ΦX174.

The results demonstrate that incorporation of 0.1 wt % ZnPTC-HEMA yields (PVC-0.1) a statistically significant ($P < 0.05$) microbicidal effect against Φ6 under light irradiation ($R = 5.1 \pm 0.2$). In contrast, no measurable antiviral activity was detected in samples maintained

under dark conditions. Furthermore, no reduction in infectivity was observed for ΦX174 under either illuminated or non-illuminated conditions, indicating that singlet oxygen generated upon irradiation selectively inactivates the enveloped bacteriophage Φ6 but does not affect the non-enveloped ΦX174.

Table 5. Antiviral activity of illuminated/non-illuminated PVC samples with ZnPTC-HEMA concentration scale

Sample →		**PVC-0.1**	**PVC-0.2**	**PVC-1**	**PVC-3**
Phage ↓	**ZnPTC-HEMA (wt %) →**	**0.1**	**0.2**	**1**	**3**
R Φ6	Illuminated	5.1±0.2	5.1±0.2	5.1±0.2	5.1±0.2
	Non-illuminated	0±0.0	0.1±0.0	0±0.0	0±0.0
R ΦX174	Illuminated	-	-	-	0.2±0.02
	Non-illuminated	-	-	-	0±0.0

The antiviral test results in Table 6 indicate, in contrast to the tested bacteria, that the addition of ZPT did not improve the antiviral efficacy of the samples against either tested bacteriophage.

Table 6. Antiviral activity of illuminated/non-illuminated PVC samples with ZnPTC-HEMA concentration scale and ZPT (0.005 wt %)

Sample →		**PVC-0.1-ZPT**	**PVC-0.2-ZPT**	**PVC-1-ZPT**	**PVC-3-ZPT**
Phage ↓	**ZnPTC-HEMA (wt %) →**	**0.1**	**0.2**	**1**	**3**

R Φ6	Illuminated	5.2±0.2	5.2±0.2	5.2±0.2	5.2±0.2
	Non-illuminated	0±0.0	0.1±0.0	0±0.0	0±0.0
R ΦX174	Illuminated	-	-	-	0.5±0.1
	Non-illuminated	-	-	-	0.4±0.1

The pronounced antiviral efficacy of singlet oxygen against bacteriophage Φ6 was expected, as its effectiveness against enveloped viruses has been documented in several studies.[52,53] Efimov et al. (2024) reported a 99.97% (3.4 log) reduction in the viral load of enveloped SARS-CoV 227 upon light exposure of fabrics functionalized with the tetracationic zinc phthalocyanine derivative LASU.[14]

Singlet oxygen is highly active and readily reacts with diverse biological macromolecules, including nucleic acids, proteins, and lipids. In DNA, it preferentially oxidizes guanine residues and can induce covalent cross-links between guanine and lysine.[25] In enveloped viruses, singlet oxygen also targets the lipid components of the viral envelope, a phospholipid bilayer embedded with membrane proteins and receptor-binding glycoproteins, leading to oxidative damage that compromises viral integrity and infectivity.[52,54]

Pyrithione has been shown to inhibit infection by human rhinovirus, coxsackievirus, and mengovirus, RNA viruses belonging to the Picornaviridae family. Additionally, Qiu et al. (2013) reported that pyrithione exhibits inhibitory activity against HSV-1 and HSV-2 at non-cytotoxic concentrations. These viruses, members of the Herpesviridae family, are large DNA viruses.[55] Although phage Φ6, a member of the *Cystoviridae* family, has been successfully used as a surrogate for enveloped viruses, incorporation of 50 mg of ZPT to PVC did not produce measurable antiviral activity. This concentration was selected in accordance with the manufacturer's recommendation (Alchimica CZ), but it appears to be insufficient to elicit an antiviral effect under the conditions tested. Moreover, in contrast to the bacterial assays, no

synergistic interaction was observed. Increasing the zinc pyrithione content to 0.01 wt % likewise failed to enhance antiviral efficacy.

Phage ΦX174 is one of the most resilient non-enveloped viruses, with an outer wall composed of a robust protein coat that withstands most disinfectants.[56] Our findings show that it resisted even the highest tested concentration of ZnPTC-HEMA in the PVC matrix at 3 wt % and the addition of ZPT (0.005 wt %).

3.6 Migration study evaluation

The objective of this study was to assess whether ZnPTC-HEMA migrates from PVC into an aqueous environment and, if so, to quantify its concentration. After 10 days of exposure (40 °C, distilled water), ZnPTC-HEMA was not detected in any of the eluates ($c < LOD$) by UV-Vis analysis and EDX method. These findings suggest strong retention of ZnPTC-HEMA within the PVC matrix, likely attributable to its high molecular weight and low aqueous solubility.

3.7. Limitations and future directions

Despite the promising performance demonstrated herein, several limitations should be acknowledged. Antiviral efficacy was evaluated using bacteriophage surrogates under controlled laboratory conditions; although Φ6 and ΦX174 are well-established models, confirmation against clinically relevant human viruses is necessary to fully establish translational relevance. In addition, long-term photostability, durability under repeated cleaning or mechanical abrasion, and performance in complex biological matrices were not assessed. Future work should therefore address real-world aging behavior, biofilm formation under continuous use, cytocompatibility and regulatory safety considerations, and

optimization of photosensitizer architecture to enhance activity against Gram-negative bacteria and non-enveloped viruses. Such investigations will be essential for advancing this platform toward practical medical and high-touch surface applications.

Conclusion

This study shows that incorporation of a methacrylate-functionalized zinc phthalocyanine (ZnPTC-HEMA) into PVC provides efficient, light-activated antimicrobial functionality at remarkably low additive loadings. Singlet oxygen generation increased sharply at 0.1 wt % and approached a plateau above approximately 1 wt %, identifying a practical composition window that balances photoactivity, processability, of material properties. Under visible light, the materials achieved complete photoinactivation (>5 log reduction) of the enveloped bacteriophage Φ6, while the structurally robust non-enveloped ΦX174 remained unaffected, underscoring the key role of lipid envelope oxidation in the antiviral mechanism.

The materials also exhibited pronounced photodynamic antibacterial activity, particularly against *S. aureus*, while *E. coli* required higher photosensitizer loadings, consistent with the grater permeability barrier of Gram-negative cell envelopes. Incorporation of ZPT at 0.005 wt % provided complementary dark-active antibacterial protection and broadened the antimicrobial profile without substantially reducing reactive oxygen species generation.

Materials characterization further confirmed good compatibility of the antimicrobial additives with the PVC matrix across the practically relevant concentration range. Noticeable structural disruption was observed only at the highest loading tested (3 wt % ZnPTC-HEMA), in agreement with the mechanical data. Statistically significant deterioration in mechanical performance was likewise detected only at this concentration, indicating that lower additive contents preserve the structural and functional integrity of the PVC foils. FTIR analysis showed that even the highest concentrations of ZnPTC-HEMA and ZPT did not measurably

alter the chemical environment of the PVC chains. In addition, migration experiments revealed negligible additive release, supporting the stability of the material system during prolonged aqueous exposure.

Overall, the combination of strong photodynamic antiviral activity against an enveloped virus surrogate, enhanced antibacterial performance, retained mechanical integrity at low additive content, and minimal additive migration establishes ZnPTC-HEMA-modified PVC as a promising platform for antimicrobial surfaces and medical-material surfaces. More broadly, these findings demonstrate the feasibility of integrating photoactive phthalocyanines into melt-processable PVC formulations to produce multifunctional materials for passive and light-triggered disinfection.

Notes

The authors declare no competing financial interest.

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Acknowledgments

Data will be made available on request.

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