Study on Antibacterial Durability of Waterproof Coatings with Different Base Materials

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Abstract: Microbial corrosion of waterproof coatings causes structural damage to buildings and renovation materials and severely threatens human health. In practical applications, coatings with different base materials show different durabilities to external environmental influences. There is little literature on the antimicrobial durability performance of waterproof coatings. Therefore, this paper selected four standard waterproofing coatings, including polyurethane coatings, cement-based coatings, asphalt-modified polymer coatings, and polymer emulsion coatings, as the main body of this study. Their antimicrobial abilities against Gram-negative Escherichia coli, Gram-positive Staphylococcus aureus, Candida albicans, and mold were tested after experiencing three kinds of harsh environments: Ultraviolet ray (UV), water immersion, and low temperature. The results show that the extreme climates significantly reduced the ability of the four coatings to resist mold, and the highest growth rate of bacteria was 54.64%. Under UV conditions, the polymer emulsion coatings were significantly more resistant to Candida albicans, and the optical density of the bacterial liquid showed a negative growth trend. The microstructural integrity of the polymer emulsion coatings was found to be damaged by Scanning Electron Microscope (SEM) observation. This work improves the durability application research on these coatings and provides a valuable reference for developing new environmentally friendly, antibacterial, and anticorrosive waterproof coatings.

Keywords: waterproof coatings; biocorrosion; durability; molds; bacteria; polymeric materials; photocatalysis; antimicrobial principle

1. Introduction

A waterproof coating comprises base materials, solvents, and additives, as well as a cured film formed on the surface of the grassroots level with a waterproof seepage control material function. According to their waterproofing principle, waterproof coatings are mainly divided into barrier types and water-repellent types. Coatings of the first type, such as ethylene-vinyl acetate copolymer (EVA) and acrylate emulsion coatings, a representative, are coated after molding to form dense polymer membranes. Water molecules in nature in conjugated form cannot pass through these films. The second category includes coatings containing water-repellent polymers, such as polyurethane coatings. These polymer molecules contain non-polar organic groups, and the polarity of water molecules is mutually exclusive, thus playing a waterproofing role. In addition to their primary waterproofing function, waterproof coatings have better extensibility, adhesion, and adaptability to structural changes. They are mainly used to protect the main structure of a building and interior decoration materials to prevent them from water erosion and to ensure the integrity of the appearance of the building materials while extending their service life. However, in the actual use process, due to long-term high-temperature sun exposure, extreme cold weather, or rain, the internal structure of a coating is easily damaged, and its waterproof seepage control function decreases.
Due to its functional properties, surface, and long-term surroundings in a humid environment, a waterproof coating allows the growth of microorganisms (such as fungi, bacteria, viruses, algae, etc.), providing favorable conditions [1]. Once microorganisms enter the material’s interior via cracks, they use the organic components in the material to grow and multiply in large quantities [2]. Studies have reported that microorganisms can easily hide in indoor walls and window frames, as well as in sewers and water storage tanks [3,4]. In addition to their application in the construction industry, coatings are also present in large quantities in the production and processing of food. For example, coatings for plastic food packaging and can packaging contain highly toxic chemicals, such as o-phenyl compounds and aldehydes [3,4], and they are often stored in environments with a temperature and humidity suitable for microbial growth. These compounds or parasitic microorganisms, once having migrated into food, can seriously threaten human health and induce fatal diseases such as cancer. Certain pathogenic bacteria such as *Escherichia coli*, *Pseudomonas aeruginosa*, *Candida albicans*, *Aspergillus*, and *Trichoderma* can be spread via the air, which can seriously contaminate our living environment and endanger human life and health [5].

Antimicrobial properties are an essential topic in the field of materials. When artificially chemically modified, specific polymers can exhibit various additional properties, such as preventing the attachment and proliferation of microorganisms, to resist the biological contamination of materials [6]. Polymeric antimicrobial materials have been widely used in the food and medical fields but less so in the field of building materials. “Durability” refers to the ability of a material or system to resist long-term damage by both the natural environment and its factors, and the durability of waterproof coatings is essential for their service life performance. Scholars undertaking waterproof coating durability research have focused on tensile strength, elongation at break, tear strength, and other physical indicators. Emphasizing research on the antimicrobial durability performance of coatings can contribute to building safety, environmental protection, and the medical, food, and chemical industries.

There is little literature on the antimicrobial durability performance of waterproof coatings. In this paper, three treatments of UV, water immersion, and low temperature were set up to simulate the extreme environments of sunlight exposure, drenching, and extreme cold in natural conditions. Four waterproof coatings most typical of industrial production were also tested for their antimicrobial activity against *E. coli*, *Staphylococcus aureus*, *Candida albicans*, and mold. Their microstructures were then observed by scanning electron microscopy to elucidate the waterproof coatings’ structural changes and antimicrobial principles under harsh conditions. This work fills the gap in the research on the antimicrobial durability of waterproof coatings and provides a reference for developing safer, environmentally friendly, and more adaptable antimicrobial coatings.

2. Materials and Methods

2.1. Pretreatment of Waterproof Coatings

There are many types of waterproof coatings. In this study, four standard waterproof coatings were selected for investigation according to the different base materials contained in the coatings, namely, I polyurethane coatings, II cement-based polymer coatings, III asphalt-based polymer-modified coatings, and IV other polymer emulsion coatings. The materials were obtained from Beijing Yuyang Zeli Waterproof Material Co., Ltd., Beijing, China; Beijing Jian Hai Zhong Jian International Waterproof Material Co., Ltd., Beijing, China; and Lang Fang Jian Jia Building Materials Co., Ltd., Lang Fang, China. The environmental conditions for the sample preparations were a temperature of 23 ± 2 °C and a relative humidity of 60% ± 15%. In the sample preparations, the test samples and the test apparatus used were stored in the above test conditions for 24 h. Afterward, the samples were stirred, according to the product manufacturer’s requirements for the ratio of mixing, mixing them for 5 min. In the case of not mixing with the air bubbles poured into the mold frame, the frame will not be warped, and the surface will be smooth. Following the actual
situation of the samples for several coatings (up to three times; each interval did not exceed 24 h), surface scraping was performed for the last time under the standard test conditions, followed by maintenance for 96 h, and then de-filming. The film coatings were turned over to continue under the standard test conditions, followed by maintenance for 72 h, to ensure that the final thickness of the films was $1.5 \pm 0.2$ mm.

2.2. Durability Treatment

The coated and molded paint samples were removed from the film frames, cut into small squares of $1 \times 1 \, (\pm 0.2) \, \text{cm}$, and divided into four groups. The first group was irradiated under a UV lamp, the second group was immersed in tap water, and the third group was frozen in a refrigerator at $-20^\circ \text{C}$. The above three durability treatments simulated the actual situations of outdoor sun exposure, rain, low temperature, and cold weather environmental conditions. The treatment time was $150 \pm 2$ h, and the fourth group of samples for the blank control group were placed in a typical environment for the same period. Three parallel control samples were set up for each treatment group.

2.3. Strains and Media

Pathogenic microorganisms in the environment pose a severe threat to human life. This study selected two types of bacterial and two types of fungal pathogens as strains for antimicrobial testing. The bacteria were *Escherichia coli*, represented by a Gram-negative strain from BNCC 352079 and another Gram-positive strain represented by *Staphylococcus aureus* from BNCC 186382; the fungal yeast was selected as *Candida albicans* from BNCC 263676; and the mold was selected as *Aspergillus heterophyllous* from BNCC 336544.

The bacterial activation medium formulation (g/L) comprised 10.00 g of peptone, 3.00 g of beef meal, 5.00 g of sodium chloride, and 15.00 g of agar. The fungal activation medium formulation (g/L) comprised 200.00 g of potato (peeled), 20.00 g of dextrose, and 20.00 g of agar. The formulations of the media used in the antimicrobial test were as follows: the bacterial medium (g/L) comprised 4.72 g of ammonium sulfate, 35.60 g of sucrose, 3.00 g of potassium dihydrogen phosphate, 8.00 g of dipotassium hydrogen phosphate, 10 mL of magnesium sulfate heptahydrate, and 2 mL of the trace element solution; the fungal medium (g/L) comprised 40.00 g of glucose and 10.00 g of peptone. The pH value of the above medium was $7.3 \pm 0.1 \, (25^\circ \text{C})$.

The above strains were individually activated in a solid agar medium. Single colonies were picked and incubated in a liquid medium with a shake flask under shaking, set at 150 rpm and 28 $\, (\pm 1)$ $^\circ \text{C}$. The bacterial solution in the logarithmic growth phase was taken and diluted to $1.0~2.0 \times 10^6 \, \text{CFU/mL}$ for reserve.

2.4. Antimicrobial Performance Test

In this study, the bacterial growth rate was calculated by determining the bacterial liquid’s optical density (OD$_{600}$) value. The permanently treated materials and blank control group samples were sterilized with an alcohol wipe and placed in triangular flasks containing a sterilized liquid medium. The total area of the material placed in each flask was $3 \times 3 \, (\pm 0.2) \, \text{cm}$. An amount of 2.1 mL of the diluted bacterial solution was added to the medium containing the materials, respectively. Each triangular flask contained one material and one bacterial solution, which were cultured individually. The rotation speed was set at 150 rpm, the temperature was set at 28 $\, (\pm 1)$ $^\circ \text{C}$, and the culture was shaken for 12 h. The bacterial juice was collected for gradient dilution, and then the optical density (OD$_{600}$) value of the 10-fold dilution was measured by UV spectrophotometry. Three parallel controls were established for each treatment group.

2.5. Microstructural Analysis

SEM was performed on the coatings infiltrated with the bacterial solution and the uninfiltrated materials. The materials’ length, width, and height were less than 1 cm, and
the surfaces were sprayed with gold to increase the conductivity of the materials to obtain more precise images. The SEM instrument model was a HITACHI S4800 (Tókyô, Japan).

2.6. Data Analysis

The bacterial growth rate was calculated as:

\[ R = \frac{(B - C)}{B} \times 100\% . \]  

where \( R \) is the bacterial growth rate in \%; \( B \) is the optical density value of the samples in the treatment group in Abs; and \( C \) is the optical density value of the samples in the blank control group in Abs.

Statistical analysis in this study was performed using one-way ANOVA and Tukey’s multiple-comparison test. The GraphPad Prism 10.1.2 software was used for data processing and graphing. Significant differences between groups were shown by comparing the differences between the means of the groups two by two. \( p < 0.05 \) meant that there was a substantial difference between the groups, proving that the results of the experiment were valid.

3. Results

3.1. Microbial Growth Rate Analysis of Different Types of Waterproofing

In this experiment, four waterproof coatings commonly used in construction or decoration materials were selected as research objects, numbered as I polyurethane coatings, II cement-based polymer coatings, III asphalt-based modified polymer coatings, and IV other polymer emulsion coatings. A specific concentration of four different microbial (Escherichia coli, Staphylococcus aureus, Candida albicans, and molds) was artificially added for bio-contamination, and the growth of the bacteria was calculated to study the coatings’ antimicrobial durability to show the ability of the materials to resist bio-corrosion. This section focuses on the effects of the intrinsic properties of the materials on their antimicrobial effects.

- I polyurethane coatings

The antimicrobial durability of the polyurethane coatings was investigated first. The experimental results in Figure 1 show that the antifungal ability of the polyurethane coatings significantly decreased after UV irradiation. Combined with the results in Table 1, compared with the blank control group, the OD\(_{600}\) values of Candida albicans and molds reached 0.879 and 0.549, and the growth rates of the bacteria were 23.73% and 54.65%. Moreover, after UV irradiation under the same conditions, the inhibitory ability of the polyurethane coatings against E. coli and S. aureus was enhanced, and the bacterial growth rates showed a negative growth trend. According to Table 1, the growth rates of Candida albicans on the polyurethane coatings were 23.73% under UV conditions, 0.07% after water immersion, and 4.86% after freezing. The Candida albicans growth rate was only 0.07%. After 120 h of freezing treatment, the same growth trend of Candida albicans was observed, with a growth rate of 4.86%. Water immersion had little effect on the polyurethane coatings’ antimicrobial properties. The results show that materials containing polyurethane coatings are not suitable for exposure to outdoor environments or UV exposure in clean rooms.

### Table 1. Microbial growth rates on I polyurethane coatings.

<table>
<thead>
<tr>
<th>Process Group</th>
<th>UV</th>
<th>Soaking</th>
<th>Freezing</th>
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<tbody>
<tr>
<td>E. coli (%)</td>
<td>−38.86</td>
<td>−37.47</td>
<td>−7.09</td>
</tr>
<tr>
<td>S. aure (%)</td>
<td>−44.04</td>
<td>−53.31</td>
<td>−36.75</td>
</tr>
<tr>
<td>Candida albicans (%)</td>
<td>23.73</td>
<td>0.07</td>
<td>4.86</td>
</tr>
<tr>
<td>Fungus (%)</td>
<td>54.65</td>
<td>−26.76</td>
<td>−18.03</td>
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</table>
In summary, extreme environmental conditions had the strongest–weakest effects on the antimicrobial properties of polyurethane coatings in the following order—UV radiation > freezing > water immersion—which proved that the material has excellent waterproofing antimicrobial properties. From the perspective of bacterial strains, polyurethane coatings are superior to fungi in their resistance to bacteria. Chen Miao [7] and others prepared a high-strength one-component polyurethane waterproof coating and found that the film performance at $-5^\circ$ was lower than that at $23^\circ$, and the strength and elongation were lower at low temperatures. The mechanisms of the effects of UV irradiation and low temperature on the antimicrobial properties of polyurethane coatings should be further investigated.

Pawinee Siritongsuk et al. [8] proposed that adding AgNP chitose to polyurethane (WPU) composites could self-sterilize them. The average inhibition rates of the coatings against *Enterobacter coli* and *Staphylococcus aureus* were $81.72 \pm 3.15\%$ and $82.07 \pm 3.01\%$, respectively, which provided solid short- and long-term antimicrobial effects. Guofei Jiang et al. [9] synthesized a CuZnO@RGO water-based polyurethane (WPU) composite coating (CuZnO@RGO/WPU). The experiments showed that the nanocomposites exhibited the highest antimicrobial rate of 99.70% and a corrosion inhibition rate of 93.30% in circulating cooling water. The polyurethane coating showed good antimicrobial performance under extreme conditions.

- **II cement-based polymer coatings**

Polymer–cement waterproof coatings have become one of the most widely used coatings in construction projects, such as interior and exterior walls and roofs, due to their environmental-friendliness and low cost. Combining the results shown in Figure 2 and Table 2, this antimicrobial durability study found that harsh environments highly affected the cement-based coatings. In addition to Candida albicans, there was a significant increase in *E. coli* Gram-negative bacteria, *S. aureus* Gram-positive bacteria, and molds. Of note was the spike in *E. coli* to 218.66% and 110.05% after the material was exposed to water immersion and cold temperatures, presumably significantly weakening the ability of the cement coatings to resist the Gram-negative bacteria. The optical density value
of the bacterial fluid reached 0.586 after UV irradiation, an increase of 31.28% compared with the control group. In comparison, the growth rate of *S. aureus* on the cement-based paint reached 18.21% in the case of freezing temperatures. Of interest was the growth rate of *Candida albicans* on the cementitious paints being −1.35% under UV conditions. According to the durability test, the Gram-negative bacterium *Escherichia coli* can severely attack cementitious paints. It was found that the growth rate of *E. coli* was 218.66% and that of *S. aureus* was 10.71% in underwater immersion conditions. The water repellency can be improved by adding other polymer components during manufacturing to avoid microbial attack.

![Figure 2](image)

**Figure 2.** Effects of extreme environmental conditions on the antimicrobial properties of cement-based polymer coatings, expressed as the optical density values of bacterial fluids. (a): *Escherichia coli*, (b): *Staphylococcus aureus*, (c): *Candida albicans*, and (d): molds. (One-way ANOVA followed by Tukey’s multiple-comparison test. Data are expressed as mean SEM, *p < 0.05, **p < 0.01, ***p < 0.005, ****p < 0.0001).

<table>
<thead>
<tr>
<th>Process Group</th>
<th>UV</th>
<th>Soaking</th>
<th>Freezing</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>E. coli</em> (%)</td>
<td>22.73</td>
<td>218.66</td>
<td>110.05</td>
</tr>
<tr>
<td><em>S. aure</em> (%)</td>
<td>11.07</td>
<td>10.71</td>
<td>18.21</td>
</tr>
<tr>
<td><em>Candida albicans</em> (%)</td>
<td>−1.35</td>
<td>−16.61</td>
<td>−17.26</td>
</tr>
<tr>
<td>Fungus (%)</td>
<td>31.28</td>
<td>23.99</td>
<td>29.04</td>
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Scientists have found that microorganisms and ions are the leading causes of the structural deterioration of cement, and the addition of a gelling material of modified polyacrylate (MXene-PG/PA) can effectively protect the coating and enhance its waterproofing and antimicrobial properties [10]. The durability of cement or concrete coatings on highway pavements determines their safety performance. Kyungnam Kim introduced a novel polymer into concrete coatings to increase their adhesion by varying the amount of spray [11], which has great potential to improve the durability of cement concrete pavements. Some researchers synthesized calcium-based cement using eggshells as a component, showing significant effects and specificity against *Streptococcus* and *Enterococcus faecalis* in bactericidal activity tests [12].
III asphalt-based polymer-modified coatings

Asphalt is a significant component of highway pavements. To date, researchers have conducted fewer antimicrobial studies on asphalt-based polymer-modified coatings. As shown in Figure 3 and Table 3 in this study, in the antimicrobial research on asphalt-based polymer-modified coatings, it was found that the bacterial inhibition ability of the material was significantly weakened after experiencing freezing. The growth rates of *E. coli*, *S. aureus*, and mold were 18.88%, 22.46%, and 7.35%, respectively, compared with the blank control group. The optical densities of the bacterial solutions in the water immersion and UV irradiation groups did not show significant growth, and the material’s antimicrobial properties were even increased (the negative growth rate of *E. coli* was 11.89% after UV treatment; the positive growth rates of *Staphylococcus aureus* and *Candida albicans* in the water immersion treatment were 18.64% and 11.93%, respectively). However, for the asphalt-based modified coatings, the growth rate of *Candida albicans* under UV conditions was 6.37%. The experiments showed that the asphalt-based polymer-modified coatings had better antimicrobial durability, probably because the polymer materials were modified to improve their ability to resist microbial infestation. However, one should try to avoid applying this coating at low temperatures, which may harbor bacteria.

**Figure 3.** Effects of extreme environmental conditions on the antimicrobial properties of asphalt-based polymer-modified coatings, expressed as the optical density values of bacterial fluids. (a): *Escherichia coli*, (b): *Staphylococcus aureus*, (c): *Candida albicans*, and (d): molds. (One-way ANOVA followed by Tukey’s multiple-comparison test. Data are expressed as mean SEM, *p* < 0.05, **p** < 0.01, ***p*** < 0.005, ****p*** < 0.0001).

**Table 3.** Microbial growth rates on III asphalt-based polymer-modified coatings.

<table>
<thead>
<tr>
<th>Process Group</th>
<th>UV</th>
<th>Soaking</th>
<th>Freezing</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>E. coli</em> (%)</td>
<td>−11.89</td>
<td>5.59</td>
<td>18.88</td>
</tr>
<tr>
<td><em>S. aureus</em> (%)</td>
<td>2.54</td>
<td>−18.64</td>
<td>22.46</td>
</tr>
<tr>
<td><em>Candida albicans</em> (%)</td>
<td>6.37</td>
<td>−11.93</td>
<td>−0.33</td>
</tr>
<tr>
<td>Fungus (%)</td>
<td>0.15</td>
<td>3.25</td>
<td>7.45</td>
</tr>
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</table>

Hongfeng Li developed an asphalt nano-TiO<sub>2</sub> superhydrophobic coating (PSC) [13]. The PSC coating was tested to have strong hydrophobicity, which can reduce puddles on pavements, thus protecting the pavements to prevent the occurrence of deformation and...
other damages and improve their safety performance and service life. In winter, pavements are prone to snow and ice exposure. Xijuan Zhao developed an asphalt coating with strong hydrophobicity [14], which can produce ice adhesion at sub-zero temperatures and remained effective after seven test cycles in a durability test. A cold composite coating (composition: polyurethane resin, TiO$_2$, hollow glass microspheres, etc.) [15] applied to asphalt pavement had excellent thermal insulation properties, suppressed solar radiation absorption, and prevented permafrost thawing. The development of asphalt coatings with increased durability in extreme environments could lead to significant progress in the field of road maintenance.

- IV other polymer emulsion coatings

Material IV is another polymer emulsion coating. According to the experimental results in Figure 4 and Table 4, it can be found that the inhibitory ability of the material against *E. coli* was significantly weakened after experiencing an extreme environment in which the optical density values of the bacterial liquids in the water immersion and low-temperature groups were 0.588 and 0.586, which were more than five times that of the blank control group (0.113). The bacterial growth rate also increased to 170.97% and 170.05%. Moreover, the optical density values of molds also increased, and the growth rates of bacteria after UV irradiation and water immersion were 32.78% and 29.12%, respectively. Notably, there was a very significant increase in the ability of the material to inhibit *Candida albicans* after UV irradiation, with a negative growth rate of 96.57%, a phenomenon that deserves further investigation. Studies have confirmed that metal and metal oxide nanoparticles, such as silver or zinc oxide, can penetrate the cell membranes of microorganisms and destroy the organelles due to their spiky structure on the outside, ultimately leading to the inactivation of the bacteria [16]. For example, adding metal oxide (e.g., MgO or ZnO) nanoparticles to acrylic latex adhesives significantly improved their antimicrobial properties and physicochemical properties [17]. Nanoparticles improve the tolerance of building materials to biological factors by providing antimicrobial functionality [18,19]. Therefore, the durability of building materials can be improved by combining nanoparticles with cement matrices and polymer emulsions in the production stage.

![Figure 4. Effects of extreme environmental conditions on the antimicrobial properties of other polymer emulsion coatings, expressed as the optical density values of bacterial fluids. (a): *Escherichia coli*, (b): *Staphylococcus aureus*, (c): *Candida albicans*, and (d): molds. (One-way ANOVA followed by Tukey’s multiple-comparison test. Data are expressed as mean SEM, *p < 0.05, **p < 0.01, ***p < 0.005, ****p < 0.0001).](image-url)
Table 4. Microbial growth rates on IV other polymer emulsion coatings.

<table>
<thead>
<tr>
<th>Process Group</th>
<th>UV</th>
<th>Soaking</th>
<th>Freezing</th>
</tr>
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<tbody>
<tr>
<td>E.coli (%)</td>
<td>1.61</td>
<td>170.97</td>
<td>170.05</td>
</tr>
<tr>
<td>S. aure (%)</td>
<td>-61.68</td>
<td>-35.93</td>
<td>-9.88</td>
</tr>
<tr>
<td>Candida albicans (%)</td>
<td>-96.57</td>
<td>-16.02</td>
<td>-22.87</td>
</tr>
<tr>
<td>Fungus (%)</td>
<td>32.78</td>
<td>29.12</td>
<td>-11.72</td>
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</table>

The experimental results in this chapter show that, among the four base materials of waterproof coatings studied, the antimicrobial performance of the polymer emulsion coatings was seriously affected by external environmental conditions. Based on the above experimental conclusions, material IV was selected as the research object, and further SEM observation was carried out to discuss the relationship between the microstructure of the inner layer of the coatings and their antimicrobial performance.

3.2. Influences of Extreme Environmental Conditions on the Antimicrobial Properties of Coatings

- UV

In the SEM results in Figure 5, it can be seen that the polymer emulsion coatings, after UV irradiation, with or without the addition of bacteria, were altered to a great extent, and multiple hollow pores appeared on the surface and in the cross-section of the material. However, according to the results of the previous experiment in Table 4, the antimicrobial capacity of the coatings after UV irradiation, on the contrary, significantly increased. The polymer emulsion coatings were better adapted to UV exposure than the other components.

Figure 5. SEM observations of polymer emulsion coatings after exposure to extreme environments. (a,b): Blank control group, (c,d): UV, (e,f): water immersion, and (g,h): low temperature. (a,c,e,g) were treated with addition of bacterial solution; (b,d,f,h) were not treated with addition of bacterial solution.
Light (sunlight or UV) is a catalyst for certain antimicrobial materials. Under normal conditions, oxygen metabolism in microbial cells generates ROS, and ROS-scavenging enzymes are produced during the repair of cell damage. A moderate amount of ROS is involved in cell signaling and immune function. At the same time, excessive accumulation of ROS causes oxidative stress within a bacterial or fungal cell, which constitutes a significant injury to the cell membrane \[20,21\]. It destroys the cell membrane’s structure and degrades proteins and nucleic acids that are essential for cell function. More seriously, this process triggers a series of lethal stress reactions that are interrelated and cascading, ultimately leading to irreversible cell rupture and death \[22\]. ROS mainly include superoxide anion radicals (\(O_2^-\)), hydroxide ions (OH\(^-\)), hydroxyl radicals (-OH), and hydrogen peroxide (\(H_2O_2\)). The superoxide anion breaks the peptide bond by interacting with the carbonyl group of the peptide bond in the cell wall, causing the cell to disintegrate \[23\]. It has been shown that various wavelengths of visible light (e.g., green, blue, and red) possess weak bactericidal mechanisms, in addition to violet light. However, photocatalytic materials exert the most potent antimicrobial activity at wavelengths of <400 nm (ultraviolet) \[24\]. Modified materials with smaller particle diameters and pores absorb less energy from UV radiation to achieve optimal antimicrobial performance \[25,26\], such as metal oxide nanoparticles including ZnO, MgO, and TiO\(_2\) \[27\]. The process of microbial destruction by nanoparticles is shown in Figure 6. In addition, due to their smaller particle size, nanoparticles can easily pass through the cell membrane and pierce the intracellular organelles, leading to the rupture and death of the bacterium through specific physical effects \[16\]. The antimicrobial principle of ROS can also be used to produce building materials by adding appropriate antimicrobial agents. However, at the same time, attention should be paid to protecting the environment and human health.

**Figure 6.** Schematic of UV-induced sterilization of metal oxide nanomaterials. Reprinted with permission from Ref. \[16\]. 2023, Elsevier.

- **Water immersion**

  Figure 5e,f show that after water immersion treatment, the original tightly bonded coatings showed obvious cracks and rotting patterns, the surfaces changed from flat to flocculent, and holes appeared. The previous experimental results of the polymer emulsion coatings after water immersion showed a significant decrease in antimicrobial activity against *E. coli*, with a bacterial growth rate of 170.97%. The change in the material’s microstructure aggravates the rate of its biological corrosion, and it is hypothesized that the antimicrobial ability of polymer emulsion coatings has a particular relationship with the bond strength.

  Scientists have proposed that the hydrophobicity of a material’s surface is related to cell adhesion \[28,29\]. Coatings with rough surfaces are highly hydrophobic and have low surface wettability, which are not conducive to bacterial colonization. The antimicrobial capacity of materials with high hydrophobicity is superior to that of hydrophilic materials \[29,30\]. High hydrophobicity, low surface energy, and high surface roughness should be
sought in developing antimicrobial coatings or other materials. The immersion of materials in water provides an aqueous phase to the surrounding environment, which may enhance the growth and reproduction of algal organisms. It can be seen that the presence of water or moisture has a significant effect on the mechanical properties or antimicrobial capacity of coatings. James Redfern et al. suggested that the antimicrobial effect of a material’s surface can be evaluated by building a mathematical model and setting up experimental environmental conditions, e.g., humidity, airflow, temperature, etc. [31].

- Temperature

Temperature is one of the most critical factors affecting the properties of materials. In this study, the internal structural changes in polymer emulsion coatings after low-temperature treatment were observed. It can be seen that Figure 5g,h show a large fracture in the material before the addition of bacteria, and the internal structure of the coating was loose and irregular in shape after the addition of bacteria. This microstructural change resulted in a sudden decrease in the antimicrobial capacity of the polymer emulsion coatings against *E. coli* after exposure to low temperatures, with a bacterial growth rate of 170.05%. Too high or too low a temperature can have different effects on the antimicrobial activity of the material. It has been found that when heated, the particle size of some silver nanomaterials becomes more prominent, with a diameter of about 400 times that at room temperature, the particles are unable to pass through the cell membrane, and the rate of bacterial inhibition significantly decreases [32,33]. Energy shortage is a major problem faced by the world today, and the thermal insulation performance of building materials has also become an essential aspect of energy conservation and emission reduction. Most of the fire-resistant coatings on the market have to withstand high temperatures of 400 °C or more, and researchers need to put more effort into finding coating components that are both heat-insulating and heat-retaining, fire-resistant, and antimicrobial at the same time. This will contribute to several fields, such as construction, healthcare, and environmental protection.

4. Discussion

From the literature reviewed in this paper, it can be found that most of the research on antimicrobial coatings has been conducted on their development process or antimicrobial performance under normal conditions, and there are very few studies reporting on the antimicrobial durability of waterproof coatings, which was the primary motivation for writing this paper. From the experimental results in this paper, it can be concluded that after experiencing harsh environments, the durability of the antimicrobial capacity of the four types of waterproof coatings against Gram-negative bacteria *Escherichia coli* and mold substantially decreased, while the Gram-positive bacteria *Staphylococcus aureus* inhibition rate did not change significantly. UV irradiation can significantly improve the durability of the antimicrobial performance of polymer emulsion waterproof coatings. The SEM microstructures of the waterproof coatings were found to have excellent antimicrobial performance under SEM observation after undergoing UV irradiation, immersion in water, and low-temperature environmental exposure. The internal structure of the material showed different degrees of disintegration, a large number of voids and cracks, and a decreased antimicrobial capacity.

Biological corrosion of waterproof coatings seriously affects the service life of buildings and decorative materials. In recent years, the resistance of microorganisms has gradually increased, and the addition of antimicrobial agents will cause some pollution in the human living environment. Most of the research on antimicrobial coatings is limited to the laboratory stage. In the future, damage mechanisms can be simulated by computer modeling, using modern artificial intelligence and digital tools to support the study of the antimicrobial properties of materials [27]. In this paper, by understanding the antimicrobial effects of waterproof coatings for different substrates, we studied the effects of internal structural changes in the materials on their antimicrobial properties, which provides a reference for studying the durability applications of waterproof coatings.
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