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Research Progress of Antimicrobial Nanomaterials and Polyurethane Coatings

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Abstract:

With the outbreak of various influenza and viruses, there is a growing concern about the mode of transmission of bacteria and the means of sterilization. Since antimicrobial coatings can be applied to a variety of materials and equipment in the fields of medical devices, food packaging, waterproofing systems, etc., there are many existing research studies and designs on antimicrobial surfaces. However, there are still some unresolved issues in the practical application and production of the current research. The research of nanomaterials applied in the field of antimicrobials is a relatively new technology. This study is based on polyurethane coating composite nanomaterials as the topic, respectively. It summarizes the research on three aspects of nanometallic materials composite polyurethane coating, organic nanomaterials composite polyurethane antimicrobial coating, and quantum dots modified polyurethane nanocomposites, and proposes the relevant ideas for improvement.

Keywords: antimicrobial coating, nanomaterial, polyurethane coating, metal-based nanocomposite coating, organic nanomaterials, quantum dots

1. Introduction

In recent years, outbreaks of influenza and viruses have increased awareness of the importance of antimicrobials. Microbial contamination has been related to various industries, such as medical device-related infections [1], prostheses, pipelines, and ships at sea [2]. The main cause of bacterial contamination is the attachment of bacterial spores to the surface of implants, which multiply, aggregate and form biofilms [3]. Biofilms are far more resistant to both antibiotics and human immune function than a single bacterium; therefore, conventional antibiotic administration cannot adequately meet the antimicrobial demand [4], and the use of frequent replacement of facilities and instruments produces a huge economic loss and waste of medical resources. Therefore, the use of antimicrobial coatings is considered an effective measure against bacteria and biofilm formation.

Antimicrobial coatings not only resist bacterial adhesion and avoid biofilm formation, but they can also be applied to a variety of surfaces, including glass, plastics, metals, and fabrics, for a wider range of uses. However, compared to other antimicrobial materials, nanomaterials have the advantages of a small size that facilitates charge transfer, a large surface area per unit mass [5], and produces fewer inflammatory effects [6]. Moreover, the application of polyurethane materials as coatings has the advantages of low cost, excellent mechanical strength and abrasion resistance, better adhesion, good flexibility and chemical resistance. This paper discusses several nanomaterials applied to polyurethane coatings and compares their advantages and disadvantages and the types of bacteria they can resist to facilitate subsequent research and application.

2. Metal nanomaterials composite polyurethane coating

2.1 Metal-based nanocomposite coating

Due to the small size and large specific surface area of metal nanomaterials, it is easy to contact with cells, and a large amount of metal ions can lead to cell toxicity and death. For example, Cu cations can interact electrostatically with negatively charged cell walls, resulting in membrane rupture [7]; and the conversion of Cu/Cu ions generates reactive oxygen species (ROS), which interact with the cell membrane of the phospholipid bilayer, leading to cell death [7]; and Cu can also bind to sites on nucleic acids with a double-helix structure, denaturing them and leading to cell death [7]. In addition, metals such as Ag, Sn, Al, Zn, Mn, Au and Ta have been shown to have antimicrobial activity [8].

Since the antimicrobial ability of composite metal films is better than that of single metal films, Rtimi et al. analyzed and characterized Cu-Ag sputtered urethane conduits and compared the surface characteristics and antimicrobial effects of different Cu:Ag atom ratios in Cu-Ag clusters. Cu-Ag 50%/50% samples were found to lead to faster bacterial inactivation [9]. The results demonstrated that an increase in the proportion of silver in them leads to a rise in the size and roughness of the Cu-Ag clusters (as shown in Figure 1). AgO is the most active silver oxide in the inactivated Escherichia coli [9]. Due to its optimal inactivation of bacteria, Rtimi et al. concluded from their analysis in Table 1 that the metal Cu appears to be necessary for effective charge transfer from the Cu-Ag surface to bacteria, and $Ag_2Cu_2O_4$ appears to play an important role in any catalyst/ photocatalyst-mediated charge transfer, as confirmed by comparing the different oxidation states occurring during bacterial inactivation of redox [9].

2.2 Metal Oxide Nanocomposite Coating

Metal oxides, such as CuO, ZnO, TiO_2, NiO, and ZrO_2, can be designed and processed into various shapes and structures for incorporation into polymer matrices, offering enhanced corrosion resistance and mechanical characteristics over conventional fillers. Moreover, the use of metal oxides is prevalent in creating polymer composites that possess electrochemical, catalytic, photocatalytic, and antimicrobial characteristics, attributed to their semiconductive qualities [10]. Due to the versatility of metal oxide nanomaterials, they are widely used in metal corrosion protection coatings, medical sterilization coatings, water treatment membranes [11], etc.

Metal and metal oxide nanoparticles are capable of producing ROS and losing electrons, releasing metal ions in a solution, and metal ions interact electrostatically with negatively charged cell membranes, resulting in membrane rupture and the revelation of organelles and contents. Besides, ROS-induced cell membrane peroxidation also causes cell membrane rupture, leading to cellular dysfunction [10]. TiO_2 nanoparticles in aqueous solution can produce various ROS, including $\cdot OH$ and $\cdot O_2^-$ and H_2O_2, with $\cdot OH$ playing the main antimicrobial role [12]. As shown in Fig. 2, the antimicrobial mechanism of Ag, Au, Cu, Zn and TiO_2 is schematic. In addition, TiO_2 makes a good photocatalyst with better antimicrobial ability under ultraviolet (UVA) light. Nguyen and colleagues developed an integrated system using polyurethane and carbon nanotubes/TiO_2, aiming to enhance the interaction between polyurethane and TiO_2 and to better the coating's compatibility and stickiness [13]. It was demonstrated that the incorporation of carbon nanotubes not only improved the adhesion, tensile strength, impact resistance, and durability of the coating, but also provided good resistance to Staphylococcus aureus [13].

Daei et al. used polyols synthesized from epoxidized soybean oil to produce polyurethanes and added NiO nanoparticles synthesized by hydrothermal method to polyurethane resins [14]. The prepared coatings showed nickel oxide nanoparticles in a flower shape with relatively uniform distribution, large surface area and multiple reaction sites. The membrane kills the bacteria by increasing the contact area with the bacteria and promoting the production of hydroxyl radicals from nickel oxide, thereby oxidizing the organic structure of the cell. This nanocomposite coating serves dual purposes: shielding metal surfaces from corrosion and enhancing their capacity to inhibit both Gram-positive and Gram-negative bacteria.

3. Antimicrobial coating of polyurethane composite with organic nanomaterials

The positive charge of the polycation in the polymer will bind to the anionic sites on the bacterial cell wall in an electrostatic interaction, or the reactive groups of the polymer will come into contact with the bacterial cell membrane, causing it to rupture or restraining the activity of specific membrane proteins, resulting in bacterial death [15]. It has the advantages of flexibility, strength and durability and is able to maintain its antimicrobial properties

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for a long time without affecting other properties [11]. The antimicrobial mechanisms of the above nanometallic materials are generally release killing, contact killing and light-responsive antimicrobial approaches, while the polymers also have an anti-adhesion approach to prevent bacterial contamination. The adhesion energy of bacteria on coatings is related to van der Waals forces, electrostatic interactions, surface charge density, surface wettability, surface roughness, and so on [16], leading to differences in the adhesion ability of materials with different electrical properties and hydrophilicity to various bacteria (as shown in Figure 3).

Yang et al. prepared oxidatively modified bacterial cellulose nanocrystals (NBC) by pulverization-oxidation, grafted biguanide compounds (BG) by hydrothermal method, and then compounded NBC-BG in different ratios with medical polyurethane coating (PU) to prepare PU-NBC-BG antimicrobial coating [1]. The guanidine-containing compounds have the advantages of good antimicrobial properties, less toxicity and a friendlier environment, while bacterial cellulose nanocrystals are easily modified and are hydrophilic by the presence of abundant hydroxyl structures, and the appropriate hydrophilicity can hinder bacterial adherence and improve the antimicrobial capacity [1]. This study demonstrated that the PU-NBC-BG antimicrobial layer had good antimicrobial effects against S. aureus and E. coli, but due to the high surface energy of the nanomaterials that can be easily agglomerated, a large amount of nanomaterials may be shed after immersion and washing if the NBC-BG content continues to be increased, resulting in a decrease in the stability and a reduction in the longevity of the coating utilization [1].

4. Carbon based quantum dots modified polyurethane nanocomposites

Another category of optically active nanomaterials, carbon-based quantum dots, hold promise for antimicrobial coatings owing to their non-toxic nature, compatibility with biological systems, extensive specific surface area, unique physicochemical properties and demonstrated modifiability. The development of graphene quantum dots (GQDs) and carbon quantum dots (CQDs) has resulted in amazing advances in the realm of medicine. Graphene quantum dots (GQDs), as derivatives of graphene, have a larger specific surface area than graphene, allowing for better adsorption of bacteria and inhibiting their growth [17]. The photothermal and photodynamic effects, as well as the structure of the GQDs themselves, all contribute to their inhibitory action. To be specific, The ROS generated by GQDs under the photothermal and photodynamic effects oxidize with the intracellular substances of E. coli, causing cell membrane damage, while the sharp edge structure of GQDs destroys the integrity of the bacterial cellular structure, inhibiting bacterial growth [17]. In addition, Wei et al., in their experiments, found that increasing the mass concentration of quantum dots or extending the duration of light exposure under 808 nm laser irradiation can effectively improve the sterilization efficiency of GQDs [17].

Carbon quantum dots (CQDs) are zero-dimensional carbon-based nanomaterials with a diameter of less than 10 nm [18]. CQDs' antimicrobial mechanisms include the impact of their surface charges and functional groups on bacterial growth, division and gene expression, and the induction of photodynamic antibacterials [18]. Since hydrophobic CQDs (hCQDs) can dissolve effectively in organic solvents like toluene and chloroform, Kováčová et al. found that hCQDs/polyurethane nanocomposites have a certain antimicrobial property and a strong potential for resistance to biological contamination. Nanocomposites of hCQDs/PU demonstrated bactericidal properties against S. aureus and E. coli following an hour of BL irradiation at 470 nm, while also showing resistance to the attachment and growth of eukaryotic cells [19]. However, it was observed that hCQDs were distributed irregularly and clustered within the PUs, as determined by analyzing their surface structure [19].

5. Summary and Prospects

Although a review of the literature reveals that the excellent antimicrobial properties of nanomaterials have been discovered by researchers in earlier years, nanomaterials are not well dispersed in polyurethanes due to their high surface energy and susceptibility to agglomeration. Therefore, I envision a possible approach to fluorine-modified nanocomposites. Because elemental fluorine has the advantages of low surface energy, high hydrophobicity and excellent self-cleaning ability, Han et al. found that fluorine-containing polymer antimicrobial materials, in addition to their own fluorine-containing material properties, also have the advantages of anti-adhesion and synergistic reactive group surface enrichment, which strengthens the antimicrobial properties of the materials [20].

Solvent-based polyurethane (PU) coatings exhibit superior resistance to abrasion, cold, chemical, and corrosion, along with diverse mechanical strengths [2]. However, because they contain organic solvents, they produce volatile organic compounds (VOCs) as well as hazardous air pollutants (HAPs) during use, which is detrimental to environmental protection and life and health. Managing and using solvent-based PUs can lead to harmful side effects, like the vaporization of organic solvents elevating atmospheric concentrations of VOCs and HAPs, with the majority of these volatile substances being cancer-causing

[2]. Therefore, switching to waterborne polyurethanes for coating substrates can be considered. Waterborne polyurethane can enhances the coating film's resistance to abrasion, flexibility, and cracking by adding polyurethane dispersions to the base resin [2]. Since the dispersion medium is water, the emission of VOCs can be reduced to a greater extent [2], and therefore, the application of waterborne polyurethane coatings is safer, healthier, and more environmentally friendly. However, the development of waterborne polyurethane composite coatings still holds great research promise because the compounds used to synthesize WPU are both expensive and non-renewable [21].

Positioning Figures and Tables:

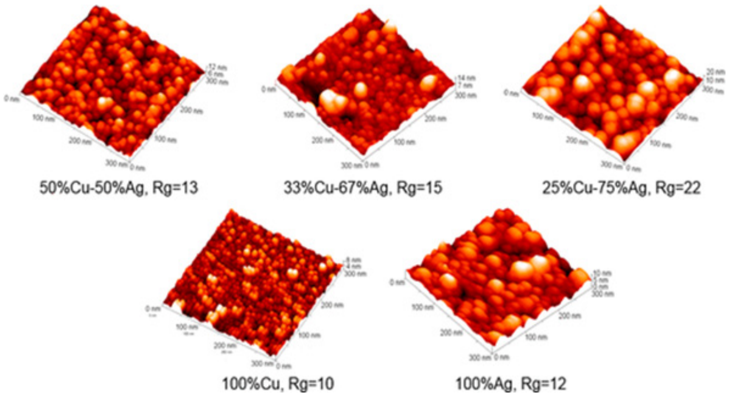
50%Cu-50%Ag, Rg=13
33%Cu-67%Ag, Rg=15
25%Cu-75%Ag, Rg=22
100%Cu, Rg=10
100%Ag, Rg=12

Figure 1 Atomic force microscopy (AFM) of Cu–Ag at different atomic ratios[9]

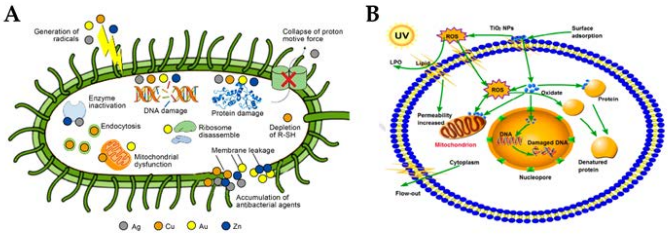

Figure 2 Schematic diagrams of antimicrobial mechanism of metal ions Ag, Au, Cu, Zn (A [22]) and TiO2 (B [23])

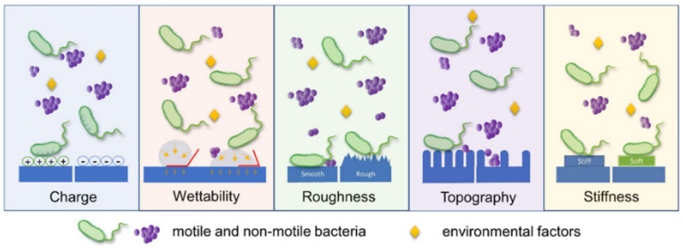

Figure 3 Effect of surface charge density, wettability, roughness, morphology and stiffness on bacterial adhesion[16]

Table 1 Cu and Ag species present of Cu–Ag films with varying atomic ratios of Cu:Ag[9]

	Cu–Ag (50%-50%)	Cu–Ag (33%-67%)	Cu–Ag (25%-75%)
Cu species	CuO, Cu_2O, Cu	CuO, Cu_2O	CuO, Cu_2O
Ag species	AgO, Ag	AgO, Ag_2O, Ag	AgO, Ag_2O, Ag
mixed phase	$Ag_2Cu_2O_4$	Ag_2Cu2O_4	

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