

Preparation and properties of antibacterial polyvinyl chloride

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Abstract. – **BACKGROUND:** Plastic products improve people's daily life, but microorganisms attaching to plastic product surfaces present health hazards. **Aim:** Our study aimed to design a new kind of antibacterial plastic products to promote a higher quality of life.

MATERIALS AND METHODS: Antibacterial polyvinyl chloride (PVC) composites were prepared using melt-blending. The antibacterial properties, mechanical properties, and optical transparencies of the PVC composites containing either silver-doped glass or silver-doped zirconium phosphate were studied, and the dispersal of these antibacterial agents throughout the PVC was also observed using scanning electron microscopy.

RESULTS: The results showed that the antibacterial agents were well-dispersed throughout the PVC matrix and that the antibacterial ratio of PVC-G against *Escherichia coli* and *Staphylococcus aureus* was over 99.0%, which was better than that of PVC-P. The antibacterial agents had little effect on the mechanical properties of the PVC; however, they decreased the optical transparency of PVC, and the transmittance of PVC-P was decreased by 28.3%.

CONCLUSIONS: Our results indicate that such kinds of antibacterial PVC composites have great potential in a wide variety of safer plastic applications.

Key Words:

Antibacterial properties, Polyvinyl chloride, Optical transparency.

Introduction

Plastic products make people's daily life and work increasingly convenient¹; however, microorganisms attaching to and/or breeding on plastic product surfaces present hidden health hazards including infection, which is a major cause of mortality and morbidity and which leads to increasing health care costs and decreasing quality of life²⁻⁵. In addition, as people increasingly focus on improving and maintaining their health, the safety of plastic products has become a topic of focus in

people's daily life. As a result, there is an increasing demand for the development of antibacterial plastic products to promote a higher quality of life.

"Antibacterial plastic products" refer to plastic products into which an inorganic or organic antibacterial agent has been added⁶⁻⁹. The antibacterial agent imparts an antibacterial property to the plastic products, enabling them to kill bacteria or inhibit bacterial growth over a certain timespan and, thus, reducing the risk of infectious disease. Current antibacterial plastic products are usually impregnated or compounded with some antibacterial or antimicrobial reagents¹⁰⁻¹¹ such as tea extract, chitosan, copper, silver, and zinc. However, these compounds require large quantities of antimicrobial reagents, and these reagents will be released gradually under many circumstances. Therefore, it is necessary to develop a safer and easier alternative to overcome these disadvantages.

Polyvinyl chloride (PVC) was one of the earliest industrial resins, accounting for 29% of the total plastic product consumption, which is less than the consumption of polyethylene (PE) but still ranks among the top five consumption rate for plastic products^{12,13}. PVC is a thermoplastic material widely used in water pipes, food packaging, medical equipment, and toys among other products because of its good mechanical properties and high chemical and abrasion resistance¹⁴. PVC products present potential hazards to human health when they come into either direct or indirect contact with the human body. For example, although medical polymers are very important in the treatment of diseases, they have a direct negative impact on a patient's health¹⁵⁻¹⁸. Therefore, improving the safety of such products could bring greater social and economic benefits. New antibacterial plastic materials can be developed using chemical modification and/or polymer blending¹⁹. However, developing new antibacterial polymers from new monomers often leads to high costs and changes in the polymer mechanical properties. Thus, the most frequently used method

of preparing antibacterial plastics is to incorporate various organic or inorganic substances such as tea extract, chitosan, copper, silver, and zinc into an existing polymer structure⁹. Among these additives, silver ions have long been known to have strong bactericidal effects as well as a broad spectrum of antimicrobial activities^{20,21}. Several studies have previously explained the inhibitory effect of silver on bacteria, and it is generally believed that silver ions denature proteins by reacting with the thiol groups in the methionine or cysteine amino acids over the active sites of the enzymes, leading to the inactivation of the proteins^{22,23}. In our study, silver-doped glass or silver-doped zirconium phosphate PVC compounds were prepared via melt-blending, and the dispersal, antibacterial properties, mechanical properties, and optical transparencies of the antibacterial PVC compounds were studied.

Materials and Methods

Materials

The materials used in this study were as follows: PVC SG-5 (Alkali Factory, Zunyi, Guizhou, China), dioctyl phthalate (DOP, a plasticizer, Jiaao Chemical Industry, Ltd., Zhejiang, China), an organotin stabilizer (Ya Chemical Industry, Ltd., Shanghai, China), zirconium phosphate (an antibacterial agent, Xindakang Inorganic Materials, Ltd.), and silver-doped glass (an antibacterial agent, Sanlian Chemical, Ltd.). *Escherichia coli* (*E. coli*, ATCC25922) and *Staphylococcus aureus* (*S. aureus*, ATCC6538) bacteria were purchased from ATCC. The specimens of antibacterial PVC, DOP plasticizer, organotin stabilizer, and other auxiliaries were mixed in a certain percentage (90%, 7%, 2%, 1%) in a high-speed mixer adding one mass fraction of either cooled silver-doped glass or cooled zirconium phosphate glass. The master batches of silver-doped glass PVC/(PVC-G) and silver-doped zirconium phosphate PVC/(PVC-P) were previously prepared using melt-extrusion with a twin-screw extruder and by stoving at 70°C. The molten glasses were injection molded, and the glass properties were tested using some samples among them.

Performance tests

Antibacterial performance tests

The samples used for the antibacterial performance tests were injection molded to the dimension 50 mm × 50 mm × 2 mm and were tested ac-

ording to the light industry standard in People's Republic of China (China National Standard QB/T 2591-2003), using the methods of testing antibacterial plastics to test the antibacterial property and the membrane-filter procedure to test the performance. The antibacterial ratio after 24 h was calculated according to the following formula:

In the formula, R refers to the antibacterial ratio (%), B refers to the average bacterial count in a blank control (colony-forming units per milliliter, CFU/mL), and C refers to the average bacterial count in the antibacterial plastic samples (CFU/mL).

Mechanical performance tests

Sample tensile properties were tested according to the GB/T 1042-2006 standards. The tensile speed was 200 mm/min. The bending properties were tested according to the GB 9341-2000 standards. The bending speed was 2 mm/min. Shore hardness was measured according to the GB/T 2411-2008 standards.

Optical transparency tests

Optical transparency was tested according to the GB/T 2410-2008 standards, using a sample of thickness 1 mm.

Dispersal of antibacterial agents throughout the PVC matrix

Tensile samples were soaked in liquid nitrogen for 30 min to induce brittle fracture in the center of the samples, metal spraying was metal sprayed, and the dispersal of the antibacterial agents throughout the PVC was observed using scanning electron microscopy (SEM).

Experimental Apparatus

The instruments used in this study were as follows: a high-speed melangeur (SHR-50A, YILI Mechanism, Ltd., Zhangjiagang), a parallel double-screw extruder (CET-35, Kebeilongkeya Mechanisms Ltd., Nanjing), an injection molding machine (SA600, Haitian Molding Machine, Ltd., Ningbo), a universal testing machine (CMT-4104, Xingsansi Company, Shengzheng), a Shore hardness tester (LX-A, Edfort Machine, Ltd., Yueqing), a scanning electron microscope (ULTRA 55, ZEISS, Japan), a zero-degree program (NDH5000, Shouli BSQT Shanghai), an incubator (BSF-150, Boxun BSQT and Medical Apparatus Factory, Shanghai), and a clean bench (BIOSAFE-12, Likang Biology and Medical Tech group).

Results

Dispersal of Antibacterial Agents Throughout the PVC Matrix

SEM images of brittle fracture in the antibacterial PVC-G and PVC-P composite materials are shown in Figure 1. In the PVC-G samples, the silver-doped glass was uniformly dispersed throughout the PVC matrix, the dispersed medium was very uniform, the size of dispersed medium was ~ 500 nm, and the dispersed medium was very compatible with the PVC matrix. In the PVC-P samples, however, the agglomeration of silver-doped zirconium phosphate was more obvious, and the size of the dispersed medium was 500-800 nm. In addition, Figure 1(c) shows that the interface between the PVC matrix and the silver-doped zirconium phosphate was distinct, indicating that the compatibility between the PVC matrix and the silver-doped zirconium phosphate was inferior to that between the PVC matrix and the silver-doped glass.

Antibacterial Properties

The antibacterial properties of PVC/-G and PVC/-P against *E. coli* and *S. aureus* were mea-

sured in terms of the bacterial colony-forming units per milliliter (CFU/mL), and the results are listed in Table I. Images of bacterial colonies formed on samples are shown in Figure 2.

From Table I and Figure 3, we found that adding one mass fraction of either silver-doped glass or silver-doped zirconium phosphate increased the antibacterial effects of PVC against both *E. coli* and *S. aureus*. Especially, for PVC-G, the antibacterial ratio was more than 99.0%, and the antibacterial effect was evident.

Mechanical Properties

The mechanical properties of pure PVC and antibacterial PVC are listed in Table II. After the respective antibacterial agents were added to the PVC, the tensile and flexural strengths of the antibacterial PVC compounds had changed very little compared with those of pure PVC. Although the flexural modulus and rigidity were increased, the elongation to failure decreased.

Optical Transparencies

The optical transparencies of pure PVC and antibacterial PVC are listed in Table III. The optical transparencies of the antibacterial PVCs we-

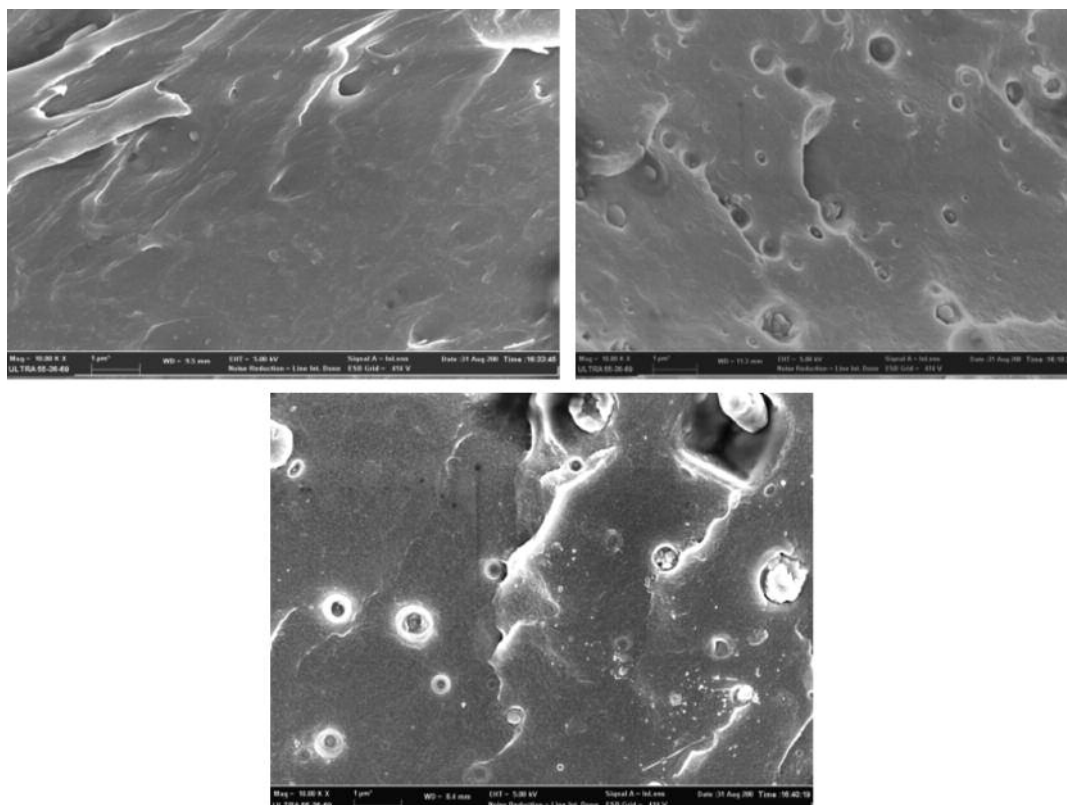
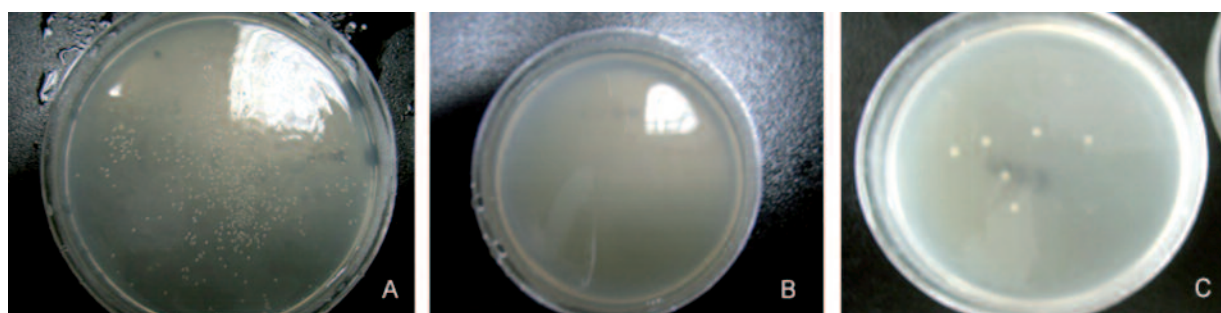


Figure 1. SEM images of PVC and antibacterial PVC samples: (A) pure PVC, (B) PVC-G, and (C) PVC-P.

Table I. Antidiabetic drugs associated with lactic acidosis in the study period.

Sample	<i>E. coli</i>		<i>S. aureus</i>	
	Number of bacteria colonies (CFU/mL)	Antibacterial ratio (%)	Number of bacteria colonies (CFU/mL)	Antibacterial ratio (%)
Pure PVC	5.2×10^8	–	1.72×10^8	–
PVC-G	5.7×10^4	99.9	5.9×10^5	99.6
PVC-P	6.0×10^6	98.8	2.3×10^6	98.6

**Figure 2.** The antibacterial efficiency of (A) pure PVC, (B) PVC-G, and (C) PVC-P against *E. coli*.

re lower than that of pure PVC because of the addition of the antibacterial agents. The optical transparency of PVC-P was especially low, namely, only 62.7, a decrease of 28.3% compared with the optical transparency of pure PVC.

Discussion

Antibacterial polyvinyl chloride composites were prepared by melt-blending PVC with either silver-doped glass or silver-doped zirconium

phosphate. The antibacterial agents had dispersed uniformly throughout the PVC matrix, increasing the antibacterial ratio of PVC against *E. coli* and *S. aureus*. The antibacterial ratio of PVC-G against *E. coli* and *S. aureus* was over 99.0%. Previous studies have shown that silver ions have strong antibacterial effects as well as a broad spectrum of antimicrobial activities²⁰⁻²¹. The silver ion was the main active ingredient in the antibacterial PVC. The silver ion could rapidly combine with the mercaptan –SH functional group of bacterial zymoprotein, or it could combine with a

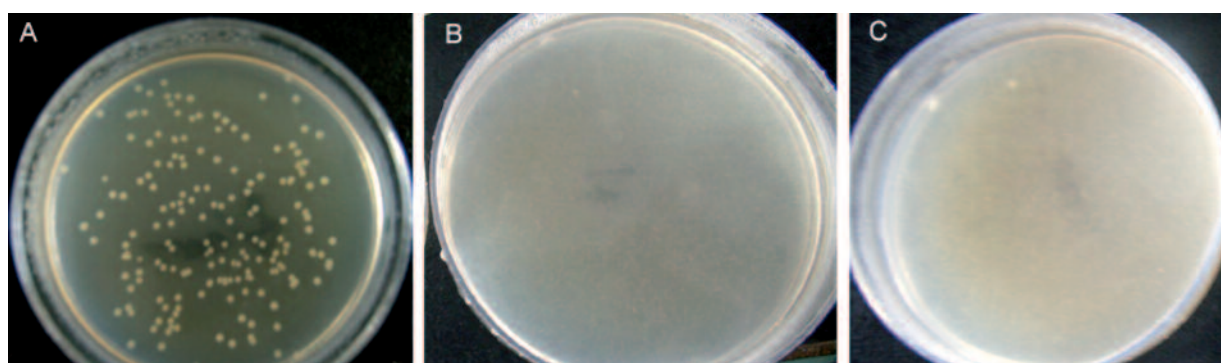
**Figure 3.** The antibacterial efficiency of (A) pure PVC, (B) PVC-G, and (C) PVC-P against *S. aureus*.

Table II. Mechanical properties of pure PVC and antibacterial PVC samples.

Sample	Tensile strength (MPa)	Elongation to failure (%)	Flexural strength (MPa)	Flexural modulus (MPa)	Shore A
Pure PVC	19.9	232	4.1	83.8	88
PVC-G	20.1	213	4.0	92.1	89
PVC-P	20.2	212	4.1	92.0	89

Table III. Optical transparencies of pure PVC and antibacterial PVC samples.

Sample	Optical transparency
Pure PVC	87.4
PVC-G	82.0
PVC-P	62.7

general bacterial protein to produce a silver metaprotein, thus killing the bacteria. Silver ions could also react with $-NH$, $-COOH$, and other organic functional groups, thereby killing the bacteria and mold^{22,23}. From Table I, the antibacterial efficiencies of both PVC-G and PVC-P were slightly higher against *E. coli* than they were against *S. Aureus*.

Compared with the tensile and flexural strengths of pure PVC, those for the antibacterial PVC compounds had changed very little. Although the flexural modulus and rigidity increased, the elongation to failure decreased. The silver-doped glass and zirconium phosphate additives imparted a significant amount of rigidity to the antibacterial polymer compounds materials, enabling the materials to withstand an increased amount of external force by increasing the material strength and flexural modulus and decreasing the amount of tensile strain within the materials, leading to the decreased elongation to failure.

The optical transparency of the PVC-G was slightly lower than that of the pure PVC, while the optical transparency of the PVC-P was 28.3% lower than that of the pure PVC. The optical transparency of the antibacterial PVC compounds is closely associated with the difference between the refractive index of pure PVC and that of the antibacterial additives: the larger the difference between the refractive indices, the less optically transparent the antibacterial compound will be²⁴. The refractive index of pure PVC is 1.52-1.55, and that of the silver-doped glass is

1.57. The refractive index of the silver-doped glass is closer to that of the PVC than is the refractive index of the silver-doped zirconium phosphate, so the silver-doped glass does not affect the optical transparency of the antibacterial compound nearly as much as the silver-doped zirconium phosphate does.

Conflict of Interest

The Authors declare that there are no conflicts of interest.

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