Next-generation Antimicrobial Waterborne

Polyurethane

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Microbial contamination on surfaces is a problematic and potentially deadly issue, particularly in high-risk settings such as healthcare, aged care, and food and beverage. In this research, we present an antimicrobial waterborne polyurethane additive that will be of interest to the coatings community due to its high compatibility with a variety of coating systems, which results in a range of highly diverse and useful applications.

This next-generation antimicrobial uses a nanocomposite approach to create a silver-based active ingredient that is non-toxic and truly non-leaching. The presented technology produces strong binding between silver and the polymer backbone. This prevents leaching while retaining high activity with proven results against a range of pathogens.

Introduction

Each day, approximately 1 in 31 U.S. hospital patients and 1 in 43 nursing home residents contract at least one infection associated with their healthcare.[1] Healthcare-associated infections accrue direct costs to U.S. hospitals of at least $28.4 billion each year.[2] Healthcare settings are just one example of a high-risk area where the transmission of disease is dangerous and expensive.

Silver is well known for its excellent antimicrobial properties, and many products have been produced that exploit this.[3–5] These products typically work via the controlled release of silver ions or nanoparticles, resulting in concerns over the release of silver into the environment and the interactions it subsequently undergoes.[6–8]

Countering this risk, a novel process has been developed that binds the silver active ingredient directly to a polymer backbone, creating a nanocomposite from which the silver does not leach.[9,10] This produces an antimicrobial material that is not only sustainable and environmentally friendly, but also displays incredible longevity as the active ingredient is not depleted.

In this research, a water-based silver-polyurethane nanocomposite material has been developed that displays antimicrobial activity against bacteria, viruses, and fungi. Its high potency means it can be utilized as an additive in other coating systems, and its compatibility with a range of materials has been shown, including acrylates, polyurethanes, and other waterborne systems.

As a result, this antimicrobial additive can be used effectively in a range of highly diverse applications (textiles, walls and floors, furniture, high-touch surfaces, filters, etc.).

Experimental

The silver-polyurethane composite was produced using Inhibit Coatings' proprietary functionalization process.

Characterization

X-ray diffraction (XRD) was used to confirm the crystalline structure and composition of the silver particles within the polymer. A PANalytical X'Pert PRO diffractometer was utilized with a copper K-alpha X-ray source at a wavelength of 1.5405 Å, operating at 45 kV and 40 mA.

A JEOL 2010 transmission electron microscope (TEM), operated at 200 kV, was used to visualize the silver particles within the polymer. The silver-polyurethane composite was diluted and then drop cast onto 200 mesh copper grids and plasma treated with a JEOL EC-52000IC ion cleaner prior to TEM analysis.

Independent Testing

Antimicrobial Testing

Antibacterial testing of the silver-polyurethane composite applied to a polyester textile was conducted according with the AATCC 100-2019 standard[11] by Microbe Investigations Switzerland (MIS). The sample was tested against *Escherichia coli* (*E. coli*) (ATCC 8739) for a contact time of 24 hours.

Antiviral testing of the silver-polyurethane composite in a polyurethane coating on acrylic was conducted according to the Japanese Industrial Standard JIS Z 2801 standard (modified for viruses)[12] by Microchem Laboratory. The sample was tested against Human coronavirus (ATCC VR-740, Strain: 229E) and Influenza A virus (H1N1) (ATCC VR-1469, Strain: A/PR/8/34), for a contact time of 2 hours.

Antifungal testing of the silver-polyurethane composite in a polyurethane coating on acrylic was conducted according to the ASTM G21 standard[13] by Microbe Investigations Switzerland (MIS). The test details utilised are provided in **Table 1.**

TABLE 1
Test Details for Antifungal Trials

Test Organism	*Aspergillus niger (A. niger)* (AATCC 16888)
Contact Time	28 days
Test Temperature	29 °C ± 1 °C
Relative Humidity	>85%

Leach Testing

Leaching of silver from the silver-polyurethane composite was conducted by Nanosafe, Inc. Testing of the composite applied to fabric samples followed U.S. EPA Method 1311 "Toxicity Characteristic Leaching Procedure,"[14] adapted for the assessment of silver-leaching potential from textiles.[15] Testing of the composite applied to wood samples was conducted under guidance of OECD 313 "Estimation of Emissions from Preservative-Treated Wood to the Environment."[16]

Toxicology Testing

Toxicology testing, as outlined in **Table 2**, was conducted by STILLMEADOW, Inc., on the silver-polyurethane composite.

TABLE 2
Test Details for Toxicology Tests

Test	Species	OCSPP Guideline
Acute oral toxicity	Rats	870.1100
Acute inhalation toxicity	Rats	870.1300
Acute eye irritation	Rabbits	870.2400
Acute dermal irritation	Rabbits	870.2500
Skin sensitization	Guinea pigs	870.2600

Acute toxicology testing was conducted to assess the possible health hazards that may arise from short-term exposure to the silver-polyurethane composite.

Preservative Testing

Preservative testing was run using a Difco Paddle Tester over three weeks, using three concentrations of the silver-polyurethane composite in a polyurethane dispersion, and testing weekly for bacterial growth.

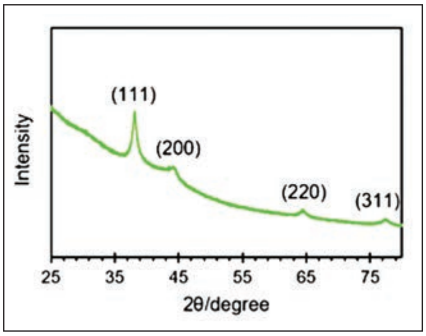
Results and Discussion

Silver Particle Characterization

Characterization techniques have verified that metallic silver nanoparticles have formed.

The XRD pattern of the silver-polyurethane composite has shown peaks with 2θ values of 38.2°, 44.3°, 64.5°, and 77.6° **(Figure 1)**, which can be attributed to the (111), (200), (220), and (311) crystallographic planes of face-centered cubic (fcc) silver crystals, respectively.[17]

FIGURE 1
XRD pattern of the silver-polyurethane composite.



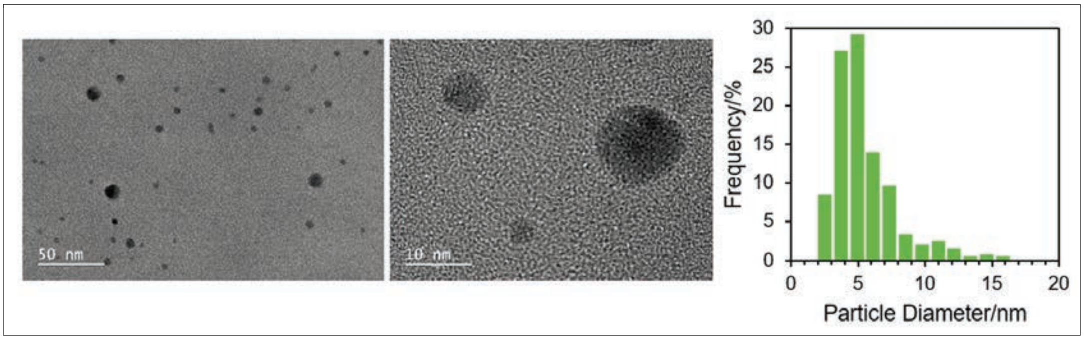


FIGURE 2
Representative low (left) and high (center) magnification TEM images of the particles in the silver-polyurethane composite, and the corresponding histogram (right) showing the particle size distribution.

TEM analysis of the silver-polyurethane composite revealed spherical/quasispherical silver nanoparticles **(Figure 2)**. An analysis of 385 of the particles observed via TEM gave an average particle diameter of 5.6 nm ± 3.3 nm. This relatively small size is well known to result in a superior antibacterial effect.[18,19]

Composite Properties

Antimicrobial Activity

Table 3 shows the silver-polyurethane composite to be effective against a range of microorganisms, including bacteria (*E. coli*), viruses (human coronavirus and influenza), and fungi (*A. niger*). For all these antimicrobial results, the silver-polyurethane composite was used as an additive, i.e., at the time of testing it was incorporated into different coating systems at various concentrations.

TABLE 3
Results of Antimicrobial Testing Conducted on the Silver-Polyurethane Composite

Microorganism	Result
E. coli	99.999% reduction
Human coronavirus	99.86% reduction
Influenza A (H1N1)	98.61% reduction
A. niger	No growth detected

The antibacterial test run against *E. coli* was completed on a textile substrate designed for furnishing applications. The material demonstrated excellent antibacterial activity without compromising the look or feel of the fabric. Further, when the composite was incorporated into a polyurethane coating designed for floors and other hard-wearing surfaces, it also demonstrated excellent antifungal properties, preventing the growth of *A. niger.* This fungus causes black mold infections and has been associated with cases of pneumonia.[20]

Leach Testing

The silver-polyurethane composite, at its highest possible concentration, was applied to textile and wood substrates and tested for silver leaching. Briefly, the textile samples were submerged in water (pH unadjusted) and also in water (pH adjusted to 2.9). The vessels were then rotated end-over-end for a period of 18 hours, and then the amount of silver that leached from the composite into the water was measured. The wood samples were submerged in water, and in substitute ocean water, for a period of 29 days. The silver leached into the water was measured at various intervals over that time.

All textile samples were found to release < 0.11% of the silver they contained over the period of the test, independent of the water's pH. Also, all wood samples leached < 0.25% silver into water and substitute ocean water over the full 29-day period. This can be compared to silver composites tested for leaching in the literature, including commercially available products, which have been shown to release significantly larger rates of silver, often under milder washing conditions.[6–8]

Toxicology Tests

Acute toxicology testing was conducted to assess the possible health hazards that may arise from short-term exposure to the silver-polyurethane composite. The material fell into the lowest (safest) category in all tests administered **(Table 4)**, indicating that it is safe to use and interact with. This distinguishes the material from commonly used biocides, for example, isothiazolinones, which are well-known sensitizers.[21]

Scale Up & Applications

Typically, nanomaterials involve expensive multistage synthetic procedures that make them unscalable. However, the process used to produce the silver-polyurethane composite presented in this work utilizes an in-situ method that removes many expensive handling and processing steps, enabling high scalability at low cost using standard processes. To date, the synthesis methodology has been successfully scaled from 10 g to 25 kg.

We have found that the silver-polyurethane composite can be added to coating systems at addition rates as low as 1%(w/w) of the composite, while retaining antimicrobial activity. It is easily dispersible during formulation, and the range of systems with which the composite is compatible has led to a broad variety of potential applications. By addition to different coating systems the composite has been successfully applied to a number of substrates including textiles (cotton, polyester, leather, faux leather, filters), wood, walls and floors, high-touch surfaces, etc.

In addition to causing harm through disease, bacteria and fungi are responsible for significant material damage and

TABLE 4
Results of Toxicology Testing Conducted on Silver-Polyurethane Composite

Test	Result
Acute oral toxicity	LD_{50} of >5000 mg/kg (no deaths observed)
Acute inhalation toxicity	LC_{50} of >2.03 mg/L (no deaths observed)
Acute eye irritation	Rated as practically non irritating (Category IV)
Acute dermal irritation	Rated as non-irritating (Category IV)
Skin sensitization	Not a sensitiser

LD_{50} dose lethal to approximately 50% of test animals.
LC_{50} concentration lethal to approximately 50% of test animals.

TABLE 5
Results of Preservative Testing

	Week 1	Week 2	Week 3
Control (no biocide)	H	H	H
Silver-polyurethane composite–concentration 1	N	N	N
Silver-polyurethane composite–concentration 2	N	N	N
Silver-polyurethane composite–concentration 3	N	N	N

Growth: H=heavy, M=moderate, L=light, N=no growth.

degradation. This is another area where the reported silver-polyurethane composite may be applied, preventing the growth of microorganisms to extend product lifetimes and reduce waste. For example, it has been shown that the composite is effective as an alternative to traditional wet and dry film preservatives, preventing bacterial growth within water-based coatings **(Table 5)**. Small amounts of the composite may be a viable alternative to replace the organic preservatives currently utilized (e.g., isothiazolinones), which are well-known sensitizers and are subject to ongoing regulatory scrutiny.[21]

Conclusions

Antimicrobial silver-based technologies are well-established in the prevention and treatment of human infections. We report the development of a silver-polyurethane composite that demonstrates high efficacy against bacteria, viruses, and fungi, even at low concentrations. Utilizing cutting-edge polymer chemistry that is both low cost and readily scalable (2500x to date), strong polymer-nanosilver interactions were achieved. Rigorous examination denotes a material additive that is durable and, most importantly, safe to use. The composite is compatible with a wide range of substrates and coating formulations, offering the potential for extensive protection. ❊

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