



Synergistic antimicrobial and surface free energy of sol–gel coatings containing fluorosilanes and quaternary ammonium salts



Grant C. Daniels, Erick B. Iezzi, Preston A. Fulmer, James H. Wynne*

Chemistry Division, Code 6100, U.S. Naval Research Laboratory, 4555 Overlook Avenue SW, Washington, D.C. 20375, United States

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ABSTRACT

A need currently exists for chemical agent repellent coatings that also possess antimicrobial activity. Current coatings, primarily polyurethanes, lack chemical and antimicrobial resistance. With this in mind, herein a novel two component hybrid polysiloxane coating was prepared. Fluorosilane and quaternary ammonium salt (QAS) additives were incorporated in order to decrease the surface free energy and to impart antimicrobial activity. The inclusion of the additives independently showed a decrease in the surface free energy for the fluorosilane and antimicrobial activity for the QAS. A synergistic effect however was observed when both additives were used together in the polysiloxane. The combination of fluorosilane and QAS led to a further decrease in the surface free energy of the polysiloxane due to increases in both micro and nanoscale roughness as confirmed by confocal and AFM. Retention of antimicrobial properties was observed with log kills ranging from 3 to 5. The hybrid polysiloxane containing both additives provided a coating with enhanced chemical agent resistance and antimicrobial properties.

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1. Introduction

Polyurethane derived topcoats are the current technology of choice for providing protective camouflage, exterior durability to ultraviolet/sunlight, chemical agent resistance, flexibility, hydrocarbon resistance, and a host of other properties for military ground vehicles [1–6]. Although frequently referred to as chemical agent resistant, polyurethane topcoats used on military ground vehicles do not completely repel chemical warfare agents (CWAs), rather they retard the absorption into the coating matrix until a decontamination wash with chemicals and water can occur [7,8]. The absorption of agents into the coating in addition to corrosion of the substrate poses an exposure risk to those in proximity, as the off gassing of toxic agents could be undetected and a prolonged process. This leads to increased downtime for decontamination and continuous exposure issues [9]. Commercial coatings currently available offer similar performance to polyurethanes yet do not prevent the absorption of CWAs and biological warfare agents [10].

The threat of chemical and biological warfare remains high despite international treaties [11,12]. Biological defense and antimicrobial research in recent years has led to the development

of many coating additives that impart antimicrobial activity to polymer surfaces [13]. Imparting antimicrobial activity in the coating will not only protect vehicles and personnel against biological warfare, but could provide further chemical resistance. CWAs are categorized into broad classes depending on their symptomatic effects. Vesicant and nerve agents are of particular concern due to their persistence and lethality [14]. The most commonly stockpiled of these agents are sulfur mustard, bis(2-chloroethyl) sulfide, and VX, *O*-ethyl *S*-(2-diisopropylaminoethyl) methylphosphonothioate [15]. Chemical warfare agent simulants (CWS) are used to mimic these compounds because of their similar properties and lower toxicity [16]. 2-Chloroethyl phenyl sulfide (CEPS) is commonly used for sulfur mustard, while Malathion, diethyl 2-[(dimethoxyphosphorothioyl)sulfanyl] butanedioate, and Demeton-*S*, *O,O*-dimethyl *S*-2-(ethylsulfanyl)ethyl phosphorothioate, are used for VX [17].

A class of hybrid materials consisting of both organic and silicon–oxygen groups, known as polysiloxanes, are recently of interest to the scientific community due to the favorable properties (e.g., improved hardness, increased chemical resistance, reduced viscosity) they can impart to a coating system [2,18,19]. Polysiloxane-based polymers also have a lower surface energy than current military polyurethane polymers, thus providing for greater water and hydrocarbon repellency [18,20].

Due to the concerns about chemical and biological warfare agents and coating stability the development of a robust

* Corresponding author.

E-mail address: james.wynne@nrl.navy.mil (J.H. Wynne).

non-absorbing topcoat is necessary. In an effort to address this need, two-component ambient-curable polysiloxane topcoats were formulated using an amino-functional polysiloxane polymer and a cycloaliphatic epoxy. Polysiloxane coatings are typically crosslinked via dual reactions, which consists of sol–gel formation and reaction of organic functional groups [21]. The sol–gel formation occurs via hydrolysis of alkoxy silanes and condensation of the resulting silanols to form a three-dimensional polysiloxane network, whereas the reaction of organic functional groups, such as between epoxies and amines, are used to form a network of organic linkages at ambient conditions. Additives were added to further increase the polysiloxane resistance to chemical and biological agents.

2. Experimental

2.1. Materials

The amino-functional polysiloxane, which has a chemical structure of poly(2-aminoethyl)aminopropyl methylphenylpolysiloxane with terminal methoxy groups, was purchased from Wacker Chemical as Silres HP 2000. The cycloaliphatic epoxy, which is a hydrogenated bisphenol A diglycidyl ether, was purchased from Momentive as Eponex 1510. The tridecafluoro-1,1,2,2-tetrahydrooctyl triethoxysilane was purchased from Gelest, and the polymeric matting agent, apolymethyl urea powder, from Albermarle. Aromatic 100 solvent was purchased from Exxon. All were used as received. Titanium dioxide and coloring pigments were purchased from DuPont and Shepherd Pigments, respectively, to produce a pigmented coating. All other chemicals were purchased from Sigma–Aldrich and used as received unless otherwise noted.

2.2. General polysiloxane coating formulation

Two-component polysiloxane topcoats were formulated using an amino-functional polysiloxane polymer and a cycloaliphatic epoxy presented in Fig. 1. The H-amine to epoxy ratio was 1:1. Titanium dioxide, carbon black and chromium green–black hematite were mixed into the cycloaliphatic epoxy using a high-speed stirrer to achieve a dark green color, followed by addition of the polymeric flattening agent and Aromatic 100 solvent. The amino-functional polysiloxane and dibutyltin dilaurate catalyst were then added while mixing. The coatings were then applied over 3 × 6" tinplate and aluminum panels at 3 mils (~75 μ) wet film thickness using a drawdown bar, then allowed to cure (crosslink) at ambient conditions (50% R.H., 72 °C) for at least 7 days prior to evaluation.

2.3. General procedure for the preparation of quaternary ammonium salts

QAS were prepared as previously reported [22,23]. Briefly the amphiphilic biocides were prepared by reacting monodispersed methoxy-terminated oxyethylene bromides with tertiary amines in ethanol to afford the desired ammonium bromide salt (QAS) in high yield. The QAS synthesized for these polysiloxanes was *N*-(methoxyethyl)-*N,N*-dimethylhexadecane-ammonium bromide QAS.

2.4. Modified polysiloxane coatings

Addition of hydrophobic and low surface free energy additives is predicted to increase the coating's ability to prevent adsorption of chemical warfare agents. Traditionally fluorinated species are the most commonly utilized additive to reduce surface free energy

in polymer systems [24–26]. Tridecafluoro-1,1,2,2-tetrahydrooctyl triethoxysilane, a fluoroalkylsilane, was chosen since the silane allows for ease of crosslinking into the polysiloxane coating. Amphiphilic quaternary ammonium salts (QAS) have been shown to surface segregate, be non-leaching and have broad spectrum antimicrobial activity [22,23,27,28]. The ability to surface segregate in a coating allows for a simplified drop in additive approach with QAS in addition to preserving bulk properties [22,28]. The polysiloxane coating (PS) was modified by adding various percentages (by weight) of a fluorinated silane, quaternary ammonium salt (QAS) or combination in effort to reduce the surface energy to prevent the absorption of chemicals (e.g., chemical warfare simulants), in addition to providing a surface with anti-microbial activity. These additives were mixed into the coatings before the catalyst was added. All modified coatings are referred to as PS-F2.4 through PS-QF4.6, identities of which can be found in Table 1.

2.5. Surface characterization

Surface measurements were taken with confocal microscopy using an Olympus OLS4000 3D Measuring Laser Microscope with 108–2150× magnification. Images for roughness analysis were taken at 1076× magnification with an area of 715 × 720 μm and a height step of 60 nm. The roughness was calculated by the LEXT software using the root mean square deviation from the surface.

Atomic force microscopy (AFM) imaging was performed using a Cyphre atomic force microscope from Asylum Research operating in tapping mode. Images were collected using a rectangular cantilever with a silicon tip (225 × 40 × 7.0 μm, Micromasch) with a nominal spring constant of 40 N m⁻¹ and a resonant frequency of 170 kHz. Roughness was calculated by WSxM 5.0 software using the root mean square equation.

Contact angle measurements were obtained using a VCA 2500 goniometer. Measurements taken employed the sessile drop technique; 2 μL droplets were deposited for multiple liquids including distilled water, hexadecane, and diiodomethane. Geometric mean, Owens–Wendt theory, was used to determine the surface free energy of the coatings.

2.6. CWS wettability testing

Demeton-S, Malathion, and chloroethyl phenyl sulfide (CEPS), 99.9% purity, were each independently tested for wettability on the coatings. Wettability is broadly described as the ability or degree to which something can be wet or absorbs a liquid. For our purposes, wettability will be determined by the initial contact angle of the CWS and any changes in the contact angle measurements over periods of time. 1 μL drops were deposited on the coatings and the contact angle of the CWS was monitored over 24 h. As previously determined the amount of simulant used and dwell times correspond to the convention used for contamination of coatings with CWS [8,29]. Between measurements the drop was covered with a small petri dish to minimize evaporation. Contact angle of the CWS on the coatings was observed at times of 10 min, 1 h, 3 h, and 24 h to determine the CWS wetting of the surface.

2.7. Bacterial challenges

Bacterial surface challenges were done with *Staphylococcus aureus*, for all Gram-positive, and *Escherichia coli*, for all Gram-negative. The bacterial challenges were conducted using a previous reported technique that reports high log kills more efficiently than plate counts [22,30]. *S. aureus* and *E. coli* were grown at 37 °C in LB media. Log phase cells were harvested by centrifugation, counted on a hemocytometer using phase contract optical microscopy, pel-

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