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TITLE

Distribution of Quaternary Ammonium Salt Encapsulated Polyoxometalates in Polyurethane Films

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ABSTRACT

The distribution behavior of amphiphilic quaternary ammonium salt (QAS) encapsulated nickel substituted polyoxometalates (Ni-POMs) in hydrophilic and hydrophobic polyurethane films for potential coating additive applications was investigated. The relative lengths of the alkyl and ethoxy tail moieties of QAS exhibited significant effects on additive distribution behavior within polyurethane. Nonpolar-polar interactions between the QAS(Ni-POM) additive and polyurethane matrix determined dispersion and segregation of the additives. Incorporation of QAS(Ni-POM) in polyurethane resulted in the formation of circular surface domains, the diameters of which were dependent on QAS composition, loading concentration, and solvent evaporation rate. XPS depth profiling analysis indicated that QAS(Ni-POM)s surface segregated in both hydrophilic and hydrophobic polyurethanes. Reduced antimicrobial activity of the QAS(Ni-POM) coatings relative to QAS coatings confirmed that QAS remained coordinated to POM during film preparation. Alkyl tail length affected the hydrophilic character of QAS(Ni-POM), while ethoxy tail length modulated effective molecular radius, both of which are facile means to control the dispersion and phase separation of encapsulated POMs in polyurethane coatings.

Keywords:

polyoxometalate; quaternary ammonium salt; polyurethane; phase separation; amphiphilic modification

INTRODUCTION

Recent developments in multifunctional materials have resulted in a broad range of materials that exhibit self-cleaning capabilities.[1] One specific class of materials that has been the focus of such research is polymeric coatings, i.e. paint, to impart additional properties such as water repellency, self-healing, antimicrobial activity,[2, 3] and chemical agent decontamination.[4, 5] While many approaches exist to impart multi-functionality, incorporation of additives into preexisting coating formulations offers the potential to create a functionalized coating surface while maintaining original properties. In this context, the distribution of molecular additives, including nanoparticles,[6] in solution and polymers, such as polyurethane,[7, 8] has been recently studied. The distribution of additives in polymer matrices depend on energetic interactions between the additive and polymer, as well as entropic effects.[9] However, the distribution of several new additives with promising properties have yet to be evaluated.

Polyoxometalates (POMs) are a broad class of metal oxide polyhedra that exhibit unique reduction-oxidation capabilities.[10, 11] Therefore, POMs are promising candidates for polymer coating additives to impart self-decontaminating functionality. Due to their complex metal oxide polyhedral composition, POMs afford oxidative catalysis of a range of molecules through a variety of reactions.[12] Specifically, Wells-Dawson type POMs can oxidize chemical warfare agent simulants.[13-15] Oxidation is the ideal degradation pathway for chemical warfare agents since it results in the least toxic by-products across a wide range of agents.[16, 17] However, POMs are incompatible with organic solvent based polyurethane coatings, such as those that are often employed in industrial and military applications because of their physical, chemical, and thermal robustness.[18]

Chemical modification of POMs is a promising route to improve their compatibility with organic solvent based polyurethane coatings. The ionic character of POMs allows for encapsulation with a variety of compounds through facile cation exchange reaction.[19] Specifically, quaternary ammonium salts (QAS) are promising species to encapsulate POMs as they have potential to improve dispersion in polymers and also exhibit biocidal properties. Amphiphilic QAS have been shown to automatically segregate to coating surfaces when mixed into existing formulations.[20] These compounds also demonstrate particular promise to improve dispersion of POMs via encapsulation. As such, recent work provided detailed characterization of the intermolecular coordination between Wells-Dawson type POMs containing Ni heterometal that were encapsulated with a series of amphiphilic QAS.[21]

Despite the breadth of research that has been performed, questions remain with regard to the polymeric distribution of additives resulting from the complex modification of POMs with amphiphilic QAS. It has been proposed that particle dispersion in polymers is dependent on the relative dimensions of the particle radius and the polymer radius of gyration, such that dispersion is favored when the particle radius is less than the polymer radius of gyration.[22] Other studies have shown that encapsulation of POMs can affect additive distribution based on chemical interactions. In one study, POMs encapsulated with fluorinated groups were found to segregate to the surface in epoxy resins.[23] While another investigation observed that spherical vesicles formed upon the incorporation of amphiphilic POM in polystyrene.[24] Therefore, the effect that encapsulation has on the distribution of POMs cannot simply be predicted.

POMS exhibit poor solubility and compatibility with organic solvents, which are components of many polymeric coating systems. Encapsulation of POMs with surfactants holds potential to improve their dispersion; however, the contribution of surfactant encapsulation on the distribution and activity of reactive substituents, such as POMs, in polymer matrices cannot be overlooked. In this work, the distribution of POMs encapsulated with amphiphilic QAS was investigated. Their compatibility with potential coating systems and the factors that affect distribution are reported.

EXPERIMENTAL

Materials

All solvents were reagent grade and used without further purification. Starting materials were purchased from Sigma Aldrich (St. Louis, MO) and used without further purification. Hydrothane AL 25-93A (AdvanSource Biomaterials, Wilmington, MA) and Tecoflex EG-100A (Lubrizol Corp., Wickliffe, OH) were generously donated by their respective companies and used without further purification.

Synthesis of QAS(Ni-POM) conjugates

The synthesis of the QAS was performed following a previously reported procedure.[20] Nickel containing POMs were synthesized based on established literature procedures.[25, 26] Coordination of QAS to POM has been reported in detail in a recent work and is shown in Figure 1.[21] Briefly, an ion exchange reaction occurred between quaternary ammonium salt and Wells-Dawson POM (α_2 - $\text{K}_8\text{P}_2\text{W}_{17}\text{O}_{61}(\text{Ni}^{2+} \cdot \text{OH}_2) \cdot 17\text{H}_2\text{O}$) in an aqueous solution of pH 6-7. Upon replacement of the potassium counterion of the POM with the quaternary ammonium cation of the QAS, the product QAS(Ni-POM)

precipitated and was isolated with subsequent extraction. Their full characterizations were reported in a previous related publication.[21]

Figure 1. General scheme and structure of QAS(Ni-POM) where $n = 6, 8, 10, \text{ or } 14$, and $m = 1, 2, 3, \text{ or } 4$.

Film preparation

Polymer solutions were first prepared by dissolving 5 g of either Hydrothane or Tecoflex in 50 mL of chloroform with a Teflon stir bar over 24 h to ensure complete dissolution. Hydrothane and Tecoflex were used because they are commercial polyurethanes that exhibit improved purity relative to comparable resin systems. To a scintillation vial containing QAS(Ni-POM), 2 mL of polymer solution was added and vortexed until additive was completely dissolved in the solution. The solution was then solvent cast into a 7.4 cm diameter aluminum pan covered with an 8.0 cm x 8.0 cm weigh boat and allowed to dry. Effects of solvent evaporation rate were evaluated by comparing identical polymer solution formulations that were cast under three different conditions in which the films were allowed to dry: uncovered, partially covered, and completely covered. These three conditions corresponded to dry-to-touch times of 5, 30, and 60 minutes, respectively.

Film analysis

Surface contact angle measurements were performed using a VCA Optima video contact angle system by AST Products, Inc. employing the sessile drop technique. Three replicate measurements were made of 4 μL of triple distilled water at 20 $^\circ\text{C}$. Surface texture, morphology, and roughness were investigated employing an Olympus LEXT OLS 4000 laser scanning digital microscope. 128 μm x 128 μm images were acquired at 2012x magnification with z-axis steps of 60 nm. Root mean square height surface roughness (Sq) was calculated by OLS software employing an 80 μm cutoff filter.

A Carl Zeiss SMT Supra55 scanning electron microscope (SEM) and a JEOL JSM-7600F Field Emission SEM were utilized to analyze morphology of the prepared films. Prior to SEM analysis, the polymer films were coated with a 5 nm layer of gold using a Cressington 108 auto sputter coater

equipped with a Cressington MTM-20 thickness controller. Accelerating voltage was set between 3 and 5 kV. Dimensions of surface features were measured using Image J analysis software calibrated to the image scale bar.

XPS analysis was performed using a Thermo Scientific K-Alpha XPS spectrometer. For each sample, a low resolution survey was performed with a pass energy of 200 eV and step size of 1.0 eV. High resolution region scans were performed for all samples, each with a pass energy of 30 eV and a step size of 0.15 eV. XPS emission angle was 54.7°. XPS depth profiling was performed with a 3000 eV ion gun set to low current. An ion sputter cycle of 10 sec was performed, followed by survey and elemental scans. High resolution region scans during depth profiling were performed in multichannel snapshot mode employing a 150 eV pass energy, 10 frames, 1 sec/frame, over 128 channels. Peak fitting was performed with Avantage computer software, specifically smart fitting algorithm.

A Carl Zeiss SMT Supra55 SEM equipped with energy dispersive X-ray detector with an accelerating voltage set to 10 keV was utilized to perform energy dispersive X-ray spectroscopy (EDS). Data was collected and analyzed on Spirit Software. Attenuated total reflectance infrared (ATR-IR) spectra were measured utilizing a Nicolet 6700 FT-IR with ATR attachment equipped with a Ge crystal from Thermo Scientific. 64 scans were compiled for each spectrum with resolution of 4 cm⁻¹. A TA Instruments Discovery TGA was utilized to perform thermogravimetric analysis at a heating rate of 10 °C/min under nitrogen from room temperature to 600 °C. Data was analyzed utilizing TA Instruments Trios software.

Anti-microbial testing

Staphylococcus aureus (*S. aureus*, ATCC 25923) was utilized in bacterial challenges for the polymer films. Bacteria were grown at 37 °C. Log phase cells were harvested by centrifugation, counted on a hemocytometer using phase contrast microscopy, pelleted by centrifugation at 4,000 xg for 10 min, and resuspended in phosphate buffered saline (PBS) at a concentration of 1 x 10⁹ CFU/mL. To prevent desiccation of the bacteria during testing, a hydration chamber was prepared consisting of a sterile 76 x 76 mm gauze pad placed in the bottom of a sterile 150 x 15 mm Petri dish. The gauze pad was saturated with 5 mL of sterile water and the test samples placed on top. A 10 µL aliquot containing 1 x 10⁷ bacteria was added to each test film (approximately 188 mm²), and then placed in a hydration chamber at room temperature. After 2 h of incubation, bacteria were recovered by placing the film in a tube containing 5 mL sterile Lethen media, followed by 30 sec of vortexing. Serial dilutions were carried out, and incubated for 18 h at 37 °C with agitation. Following incubation, the cultures were examined for the

presence of turbidity, indicating bacterial growth. Each film was tested in triplicate. Log kill was determined by the following: Log kill = 7 - highest dilution exhibiting bacterial growth. All bacterial challenge procedures were conducted using standard aseptic techniques in a BSL-2 hood.

RESULTS AND DISCUSSION

Hydrothane and Tecoflex films containing QAS(Ni-POM) additives were analyzed at a variety of loading concentrations to determine factors that affect their distribution behavior in polymer matrices. Hydrothane and Tecoflex differ in their chemical structure (Figure 2) in that they are hydrophilic and hydrophobic resins, respectively. The effects of polymer hydrophilicity on additive distribution were determined by comparing QAS(Ni-POM) behavior between both resin systems.

Figure 2. General chemical structures of Hydrothane (top) and Tecoflex (bottom).

Effect of QAS(Ni-POM) Concentration

Hydrothane films with 0 – 21 wt% C₁₆EO₁(Ni-POM), neat C₁₆EO₁, and neat Ni-POM were analyzed via SEM (Figure 3). C₁₆EO₁(Ni-POM) loading in Hydrothane resulted in surfaces that exhibited circular surface domains, which were absent in films containing neat C₁₆EO₁ and neat Ni-POM. Diameters of surface domains increased linearly with C₁₆EO₁(Ni-POM) loading concentration (Supporting Information), indicating that the surface domains were composed of C₁₆EO₁(Ni-POM). The distribution of QAS(Ni-POM) were further analyzed by mapping the tungsten (W) signal via EDS. Strong overlap of W signal concentrations with the surface domains in Hydrothane films containing mixtures of QAS(Ni-POM) (Supporting Information) confirmed that the surface domains were indeed composed of QAS(Ni-POM). The three-dimensional morphology of the domains could not be determined by SEM. To determine the morphology of the domains on the surface, the experimentally measured diameters were used to calculate areas of hypothetical two dimensional circles and three dimensional spheres, which were compared to actual loading concentration (Supporting Information). A strong correlation was found

between the calculated areas and $C_{16}EO_1(Ni-POM)$ concentration as both increased linearly with increased loading with slopes of approximately 0.33. In contrast, calculated spherical volumes increased with an approximate slope of 0.60. Therefore, the physical dimensions of the domains were likely that of a flattened disc shape, suggesting that the domains do not penetrate significantly down into the polymer bulk.

Figure 3. SEM micrographs of Hydrothane films with increasing concentration of $C_{16}EO_1$ (left column), Ni-POM (center), and $C_{16}EO_1(Ni-POM)$ (right column) dried at intermediate (30 min) conditions.

Tecoflex films were loaded with 5, 10, 15, and 20 wt% $C_{16}EO_2(Ni-POM)$. Increased loading of $C_{16}EO_2-POM$ in Tecoflex was confirmed by increased W-O vibrational modes at 979, 931, and 900 cm^{-1} in ATR-IR analysis (Supporting Information) that corresponded well with previously reported IR spectra of the QAS(Ni-POM).[21] $C_{16}EO_2-POM$ loading was further confirmed by TGA analysis. Since approximately 40 % of the molecular weight of the $C_{16}EO_2-POM$ was composed of thermally unstable $C_{16}EO_2$, only approximately half of the mass was expected to remain at 600 °C due to the temperature stable POM core. Indeed, the mass of Tecoflex films remaining after temperature ramps to 600 °C corresponded to approximately half of the loading concentrations of QAS(Ni-POM) (Table 1). Morphology (diameter and

height) of surface domains on Tecoflex films with increasing concentration of $C_{16}EO_2(Ni-POM)$ were analyzed via confocal microscopy (Figure 4). The average diameter and height of surface domains increased with increasing loading of $C_{16}EO_2(Ni-POM)$ in Tecoflex films up to 15 wt% loading. The height of the surface domains did not increase with increasing loading concentration, while the surface domain diameters increased. As such, the ratio of height to diameter decreased with increasing concentration. In addition to surface domain height, the depth of the surface domains were measured after the application and removal of adhesive strips from the surface to remove portions of the surface domains, which exposed the cavity in which they resided (Supporting Information). Surface domains exhibited an average depth to diameter ratio of 0.05, compared to the average height to diameter ratio of 0.03. Therefore, the surface domains protruded into the polymer film more than they projected above its surface. From this, an estimation of the cross sectional morphology of an average surface domain was determined to be a flattened disc shape (Supporting Information). Furthermore, the fact that an adhesive strip was able to remove intact surface domains from the polymer surface indicated a lack of covalent bonding of the surface domains to the polymer.

Figure 4. Surface domain diameter (D) and height (H) measured from laser confocal microscopy of $C_{16}EO_2(Ni-POM)$ loaded Tecoflex films dried at intermediate (30 min) conditions.

Table 1. TGA and contact angle analyses of Tecoflex loaded with C₁₆EO₂(Ni-POM) dried at intermediate (30 min) conditions.

Tecoflex Additive	Final Mass (%)*	Contact Angle (°)
Control	0.624	92.2 ± 1.2
5 % C₁₆EO₂(Ni-POM)	3.644	87.3 ± 0.8
10 % C₁₆EO₂(Ni-POM)	5.928	87.7 ± 0.5
15 % C₁₆EO₂(Ni-POM)	8.041	88.4 ± 0.3
20 % C₁₆EO₂(Ni-POM)	9.233	85.2 ± 1.5

*At 600 °C

Table 1 presents a slight reduction in contact angle with incorporation of C₁₆EO₂(Ni-POM) into Tecoflex films. A decrease in water contact angle would typically suggest a more hydrophilic polymer surface; however, QAS(Ni-POM)s have been shown to demonstrate hydrophobic exteriors that would be expected to result in increased contact angles.[21] Concurrently, surface morphology analysis indicated that the surface roughness of Tecoflex films increased with increased loading of C₁₆EO₂(Ni-POM) (Figure 5). Contact angle is dependent on both solid surface tension and surface roughness.[27] Also, increased surface roughness yields decreased water contact angles for surfaces with water contact angle close to 90°.[28] Therefore, decreased contact angle on the Tecoflex films with increased C₁₆EO₂(Ni-POM) was caused by the surface roughness imparted by the surface domains.

Figure 5. 3D Confocal microscopy images of Tecoflex films with 0 wt% (top) and 10 wt% $C_{16}EO_2(Ni-POM)$ (bottom) dried at intermediate (30 min) conditions. Z-axis dimensions are magnified 25x in both to highlight roughness.

Effect of QAS Composition

The role of QAS alkyl and ethoxy tail lengths on the distribution of additive in hydrophilic polyurethane were examined by loading Hydrothane films with QAS(Ni-POM)s of differing QAS composition. The selection of QAS(Ni-POM)s comprised $C_8EO_1(Ni-POM)$, $C_8EO_2(Ni-POM)$, $C_8EO_3(Ni-POM)$, $C_8EO_4(Ni-POM)$, $C_{10}EO_1(Ni-POM)$, $C_{12}EO_1(Ni-POM)$, $C_{12}EO_2(Ni-POM)$, $C_{16}EO_1(Ni-POM)$, and $C_{16}EO_2(Ni-POM)$. SEM analysis, shown in Figure 6A-F, clearly demonstrated that distribution of QAS(Ni-POM) in Hydrothane was significantly affected by QAS composition. Between QAS(POM) of equal ethoxy length, increased alkyl tail length from 12 to 16 carbons resulted in an increased quantity of surface domains, yet the average domain diameter remained constant. Domain diameters significantly increased when the ethylene oxide tail was lengthened by a single unit, from $C_{12}EO_1(Ni-POM)$ to $C_{12}EO_2(Ni-POM)$ and from $C_{16}EO_1(Ni-POM)$ to $C_{16}EO_2(Ni-POM)$. QAS(Ni-POM) of alkyl tail length less than 12 carbons in length did not exhibit surface domains. Greater hydrophilicity of the shorter alkyl chain QAS(Ni-POM)s improved mixing with Hydrothane and resulted in absence of domains. Correspondingly, increased nonpolar character from longer alkyl tails resulted in aggregation of QAS(Ni-POM) into surface domains in Hydrothane. Therefore, surface domain formation was caused by polar-nonpolar repulsive interactions between QAS(Ni-POM) and Hydrothane, which was controlled by relative alkyl and ethoxy tail lengths. Considering that the ethylene oxide tail was coordinated to the POM surface,[21] increasing the length of the ethylene oxide tail did not increase the hydrophilic character of the QAS(Ni-POM) molecule as expected. Rather, longer ethylene oxide tail increased the molecular weight and effective

radius of the QAS(Ni-POM), both of which contributed to reduced solubility that lead to aggregation of QAS(Ni-POM) into larger surface domains.

Figure 6. SEM micrographs of 6 wt% QAS(Ni-POM) Hydrothane films (A-F) and 10 wt% QAS(Ni-POM) Tecoflex films (G-L) dried at intermediate (30 min) conditions.

Hydrothane films were prepared with mixtures of $C_{16}EO_1$ (Ni-POM) and $C_{16}EO_2$ (Ni-POM) at varying ratios (total 10 wt%) to further examine effects of ethoxy tail length. Surface domain diameters increased linearly with increased $C_{16}EO_2$ (Ni-POM): $C_{16}EO_1$ (Ni-POM) ratio (Figure 7). The line equation in Figure 7 describes the average domain size at specific $C_{16}EO_2$ (Ni-POM): $C_{16}EO_1$ (Ni-POM) ratios and

suggests an additive effect in which both coalesce in the formation of each domain. Therefore, the QAS(Ni-POM) species of different ethylene oxide tail lengths mixed with each other into surface domains to minimize additive-polymer interactions.

Figure 7. Relationship between $C_{16}EO_2(Ni-POM):C_{16}EO_1(Ni-POM)$ ratio and domain diameter in Hydrothane films dried at intermediate (30 min) conditions.

Tecoflex films were also loaded with a range of QAS(Ni-POM)s, as well as neat $C_{16}EO_1$ and neat Ni-POM to understand the role of alkyl and ethoxy tail length on additive behavior in a less polar matrix. QAS(Ni-POM) and Ni-POM loading had minor effects on contact angle of Tecoflex surfaces, whereas incorporation of neat $C_{16}EO_1$ resulted in a significant decrease in water contact angle (Table 2). These results support previous structural characterization of these compounds in which the more polar regions of the molecule were found coordinated to the POM.[21] QAS(Ni-POM)s with carbon tail lengths of 8 did not result in any observed surface features in Tecoflex. Surface features were observed in Tecoflex films loaded with QAS(Ni-POM)s of the longest alkyl tail lengths, C_{12} and C_{16} (Figure 6G-L). The average domain diameters increased with increasing ethylene oxide tail length from EO_1 to EO_2 . Increased domain quantity and diameter signified phase separation of QAS(Ni-POM)s from the Tecoflex polymer matrix. Since domain diameter increased with increasing alkyl tail length, the aliphatic character of QAS was attributed to play a major role in the phase separation of QAS(Ni-POM). This likely occurred not through solvophobic interactions between QAS(Ni-POM)s and Tecoflex, since Tecoflex is relatively hydrophobic, but through attractive non-polar interactions between the aliphatic chains of proximal QAS(Ni-POM)s. Furthermore, increased domain diameter with increased ethoxy tail length indicated

that increased molecular radius from longer tail length decreased solubility of QAS(Ni-POM)s in Tecoflex solution to segregate into surface domains.

Table 2. Contact angle of Tecoflex films loaded with 10 wt% additive dried at intermediate (30 min) conditions.

Additive	Contact Angle (°)
Tecoflex Control	92.2 ± 1.2
C₈EO₁(Ni-POM)	103.2 ± 2.3
C₈EO₂(Ni-POM)	91.5 ± 2.0
C₈EO₃(Ni-POM)	100.2 ± 3.7
C₈EO₄(Ni-POM)	98.3 ± 2.7
C₁₀EO₁(Ni-POM)	100.0 ± 2.4
C₁₂EO₁(Ni-POM)	98.2 ± 2.6
C₁₆EO₁(Ni-POM)	99.2 ± 2.5
C₁₆EO₂(Ni-POM)	87.7 ± 0.5
C₁₆EO₁, Neat	33.0 ± 0.8
Ni-POM, Neat	92.6 ± 2.0

Effect of Drying Time

The effect of drying time (i.e. solvent evaporation rate) on the formation of surface domains was investigated. Domain diameters were compared between Hydrothane films loaded at 10 wt% C₁₆EO₁(Ni-POM) that were subjected to relatively slow (1 h), intermediate (30 min), and fast (5 min) drying times. Previous work demonstrated that QAS(Ni-POM) coordination occurs between the ethylene oxide moieties of QAS and the POM surface with the alkyl tails are oriented outward, which suggested that QAS(POM) would exhibit effectively non-polar behavior.[21] Domain size increased with increasing drying time (Figure 8); therefore, additional drying time allowed QAS(Ni-POM) to reach thermodynamic equilibrium in polymer solution, during which minimization of non-polar QAS(Ni-POM) and hydrophilic Hydrothane polymer interactions drove the QAS(Ni-POM) to accumulate into surface domains. The thermodynamic phase separation of C₁₆EO₁(Ni-POM) into aggregates at the surface of Hydrothane polymer film supports the structural model that was proposed in previous work.[21]

Figure 8. Histogram of domain diameters for 10 wt% $C_{16}EO_1(Ni-POM)$ Hydrothane films allowed to dry at various rates.

Solvent evaporation rate (i.e. film drying time) significantly affected distribution of QAS(Ni-POM) in Tecoflex. Surface domain diameters decreased with increased drying time in Tecoflex films containing $C_{16}EO_2(Ni-POM)$ (Figure 9), which contradicted the behavior of $C_{16}EO_1(Ni-POM)$ in Hydrothane. When afforded more time, nonpolar interactions between Tecoflex and $C_{16}EO_2(Ni-POM)$ caused increased mixing and smaller surface domains.

Figure 9. Surface of Tecoflex films loaded with 10 wt% $C_{16}EO_2-POM$ after 5 (a), 30 (b), and 60 min (c) drying times.

Surface Concentration

XPS was utilized to determine the presence of QAS(Ni-POM) at the surface. Figure 10A presents the W 4f XPS signal from each Hydrothane film loaded with QAS(Ni-POM) at 10 wt%. Hydrothane films that contained $C_{12}EO_1POM$, $C_{16}EO_1POM$, and $C_{16}EO_2POM$ indicated progressive increases in tungsten surface concentration. In contrast, control Hydrothane (0 wt% QAS(Ni-POM)) and $C_8EO_2(Ni-POM)$ Hydrothane films did not exhibit a W4f signal, indicating an absence of QAS(Ni-POM) at the surface. W4f signal intensity corresponded with increased quantity and area of surface domains that were previously observed with SEM, providing complimentary evidence to the EDS results that the surface

domains were composed of QAS(Ni-POM). It was expected that the additives segregated to concentrate at the polymer-air interface (i.e. surface) of the film instead of being buried within the bulk. Indeed, XPS depth profiling confirmed that the quaternary ammonium nitrogen XPS signal (402 eV) was present only at the surface (Figure 10B & C). These results combined with EDS, which provided lateral distribution, demonstrated that the circular domains were present only at the surface of the polymer and composed of QAS(Ni-POM).

Figure 10. XPS W 4f signal from Hydrothane films loaded with QAS(Ni-POM)s (A) and comparison of N 1s from surface (B) and bulk (C) of $C_{16}EO_1$ POM loaded Hydrothane dried at intermediate (30 min) conditions.

XPS depth profiling was used to examine the distribution of $C_{16}EO_2$ (Ni-POM) loaded at 10 wt% in Tecoflex films by monitoring the N 1s signal. A peak at 402 eV, which corresponds to quaternary ammonium nitrogen, was present at the top surface (Figure 11A) and absent in the bulk (Figure 11B), the bottom surface (Figure 11C), and the bottom bulk (Figure 11D). These results confirmed that QAS(Ni-POM) resided only at the top surface of Tecoflex film, in support of the ATR-IR comparative analysis, and provided evidence of surface segregation. Surface segregation of QAS(Ni-POM)s in Tecoflex films was further examined by comparative ATR-IR analyses of the top and bottom surfaces of $C_{16}EO_2$ (Ni-POM) loaded Tecoflex films (Supporting Information). The IR spectrum of the top surface of the film contained vibrational modes that corresponded to the tungsten oxide POM (979, 931, and 900 cm^{-1}) and ether stretching from the ethylene oxide tail ($\sim 1120 \text{ cm}^{-1}$). These characteristic bands unique to $C_{16}EO_2$ (Ni-POM) were not observed on the bottom of the film, which indicated that the QAS(Ni-POM) additive was concentrated at the surface likely from segregation during film drying.

Figure 11. XPS nitrogen 1s signal of 10 wt% C₁₆EO₂(Ni-POM) in Tecoflex a) top surface, b) sputtered top, c) bottom surface, and d) sputtered bottom.

Antimicrobial Activity of Films Containing QAS(Ni-POM)

Since QAS are known to exhibit antimicrobial activity, Hydrothane and Tecoflex films containing QAS(Ni-POM) additives were subjected to antimicrobial challenges. Figure 12 presents the efficacy of Hydrothane films against *S. aureus* (Gram-positive) and *E. coli* (Gram-negative) challenges. Hydrothane films loaded with less than 15 wt% C₁₆EO₁(Ni-POM) did not statistically reduce bacteria at loading levels. Yet, the 15 and 21 wt% C₁₆EO₁(Ni-POM) Hydrothane films exhibited 6 log reduction of *S. aureus* and 1-2 log reduction of *E. coli*. Tecoflex films containing QAS(Ni-POM) additives at 10 wt% loading exhibited antimicrobial activity (Supporting Information) similar to Hydrothane films of comparable loading. In addition to the QAS(Ni-POM)s, neat C₁₆EO₁ and neat Ni-POM were incorporated into separate Tecoflex films for comparison (Supporting Information). As expected, Tecoflex films containing neat C₁₆EO₁ exhibited potent antimicrobial activity against both Gram-positive and Gram-negative bacteria, while incorporation of neat Ni-POM imparted insignificant activity.

Antimicrobial activity against Gram-positive bacteria was dependent on QAS(Ni-POM) concentration, though inhibitory concentration of QAS(Ni-POM) at the surface of the coatings was not achieved until loading levels of 15 wt%. In contrast, activity against Gram-negative bacteria was independent of QAS(Ni-POM) loading and polymer composition, with average log kill of less than 1. Amphiphilic QAS are known to be more effective against Gram-positive than Gram-negative.[29] Therefore, due to the diminished antimicrobial activity of QAS from coordination to POM and the reduced efficacy of QAS against Gram-negative bacteria, QAS(Ni-POM) was below the minimum inhibitory concentration for the Gram-negative challenge in both Hydrothane and Tecoflex for all loading concentrations examined. The lack of significant antimicrobial activity of films containing

QAS(Ni-POM)s at loadings less than 10 wt% confirmed the previously proposed structured model of QAS(Ni-POM)s, in which the quaternary ammonium nitrogen atom was coordinated in close proximity to the POM counter anion. QAS antimicrobial behavior has been proposed to result from the ionic disruption and subsequent lysis of the bacterial cell membrane facilitated by the quaternary ammonium ion.[30] Therefore, The lack of antimicrobial activity of the polymer films containing QAS(Ni-POM) indicated that coordination of the ammonium ion of the QAS to the Ni-POM remained intact and effectively shielded quaternary ammonium interaction with bacteria. The QAS(Ni-POM) containing films did not exhibit antimicrobial activity to the same degree as films cast with neat QAS, further indication that the QAS remained coordinated to the POM during film formulation. The combination of significant antimicrobial activity on the most loaded Hydrothane films and that QAS did not dissociate from Ni-POM suggested that the unique surface morphology from domain formation may have contributed to antimicrobial activity. This relationship will be the subject of future study.

Figure 12. Antimicrobial activity of Hydrothane films of various loadings of C₁₆EO₁(Ni-POM).

CONCLUSION

Polyurethane films loaded with QAS(Ni-POM) additives demonstrated the formation of surface domains dependent on a variety of factors. Intermolecular interactions between QAS(Ni-POM) and polyurethane were the primary factor in the additive distribution for this system. Specifically, the hydrophilic character of polyurethane was found to play a significant role in the distribution and phase segregation of QAS(Ni-POM) into surface domains in polyurethane films. The additives separated from the additive/polyurethane solution to segregate into a surface layer at the polymer-air interface during film drying. Subsequently, additives aggregated into surface domains to reduce thermodynamically

unfavorable hydrophilic-hydrophobic interactions. This proposed mechanism of QAS(Ni-POM) dispersion was confirmed when surface domain diameters increased with increased Hydrothane film drying time and decreased with increased Tecoflex drying time. The distribution behavior of QAS(Ni-POM) additives in polyurethane matrices was also dependent on the alkyl tail length of QAS, ethoxy tail length of QAS, and QAS(Ni-POM) concentration. Alkyl tail length affected the hydrophilic character of QAS(Ni-POM), while ethoxy tail length effectively modulated molecular radius. Therefore, alkyl tail length can be used to tailor distribution of QAS(Ni-POM) by modulating its polar/nonpolar character relative to the polymer matrix. Whereas, increased ethoxy tail length can be used to increase domain formation, irrespective of polymer hydrophilicity, as a function of its reduced solubility from the larger molecular radius. This work presented that modification of QAS is an easy method through which distribution of QAS(Ni-POM) additives can be controlled in polyurethane coatings for potential self-decontaminating applications.

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Supporting information is available online.

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