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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.

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1. 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

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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.

2. Experimental

2.1. 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.

2.2. 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 Fig. 1 [21]. Briefly, an ion exchange reaction occurred between quaternary ammonium salt and Wells-Dawson POM (α_2-$K_8P_2W_{17}O_{61}(Ni^{2+}\cdot OH_2)\cdot 17H_2O$) 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].

2.3. 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 × 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 min, respectively.

2.4. 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 °C. Surface texture, morphology, and roughness were investigated employing an Olympus LEXT OLS 4000 laser scanning digital microscope. 128 μm × 128 μm images were acquired at 2012 x 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 s 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 s/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.

2.5. 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 × g for 10 min, and resuspended in phosphate buffered saline (PBS) at a concentration of 1×10^9 CFU/mL. To prevent desiccation of the bacteria during testing, a hydration chamber was prepared consisting of a sterile 76 × 76 mm gauze pad placed in the bottom of a sterile 150 × 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 1×10^7 bacteria was added to each test film (approximately 188 mm^2), and then placed in a hydration chamber at room temperature. After 2 h of

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