FY 2008 Project Proposal
Project No.
DAVI-08

Antimicrobial Coating Systems Based on Silver Nanorods.

Project Team:
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Objective:
The objective of this work is to develop new polymer nanocomposite blends based on silver nanorods and prepared through emulsion or suspension polymerization processes. These systems are expected to be attractive for the formation of antimicrobial coatings. The shape of the nanoparticle will reduce the loss of antimicrobial properties by wear through the formation of mechanical interlocks with the surface. The high aspect ratio of these systems is also expected to allow the systems to exhibit antimicrobial properties at low concentrations due to the significant reduction in the percolation threshold for rod shaped particles. Systems that are simply physical blends of dispersions of rods and latex, systems based on polymer encapsulation of silver rods, and mixtures of these systems will be developed and tested. To achieve the goal of this project the following specific aims will need to be met.

- A facile route to the production of silver nanorods suitable for dispersion in aqueous media and, in the case of encapsulation, for functionalizing the rod surface will be developed. Several methods for the production of silver rods can be found in the published literature including seed-mediated growth in a rodlike micellar media and various methods utilizing hard templates. These methods vary in yield, achievable length to diameter ratios and ease of dispersion of the finished product. For this work a rapid, microwave-assisted synthesis based on the polyol method will be utilized for preparation of silver rods. These rods will then be surface modified so that they can be encapsulated by emulsion or suspension polymerization processes.

- The retention of antimicrobial properties after wear process will be evaluated. Various wear processes, for example varying total deformation, frequency, or humidity conditions, would be expected to result in different rates of particle pull out of the nanorods from the surface. Development of controlled wear testing of coatings and correlation between the rod pull out rate as measured during the wear process and the retained antimicrobial properties of the surface are key to meeting the objective of the project. Correlations will be developed describing the rate of antimicrobial efficacy loss through wear processes for standard antimicrobial coatings and the proposed system.

State of the Art:
The preparation of polymer silver nanorod composite coatings is at the interface of the emerging technologies of emulsion polymerization in the presence of rod shaped particles and the development of antimicrobial coatings. To date developments in both emulsion polymerization in the presence of inorganic nanoparticles and silver based antimicrobial polymeric systems have focused on spherical shaped particles. This is largely due to the relatively new capability to produce and control morphology of rod shaped silver particles. However rod shaped particles have several attributes that make them particularly attractive in antimicrobial systems, among which are the low percolation threshold (concentration at which particle particle interactions become sufficiently probably that the particles can be said to form a continuous phase) of rods vs spheres and the ability of rods to form entanglements with polymeric systems. As the ability to produce these particles grows so to does interest in incorporating them into polymer systems.

A significant body of work has examined the emulsion polymerization in the presence of inorganic particles. This process has been utilized to encapsulate SiO_2 and TiO_2 in polybutyl acrylate[1], SiO_2 in polystyrene[2, 3], magnetite in PMMA, PolyHEMA and in polyacrylamide to create magnetic polymer particles[4, 5], alumina in PMMA to improve the curing and mechanical properties of bone cement[6], and $CaCO_3$ in PS[7], among many others. In almost every case, the literature reports the encapsulation of spherically, or roughly spherically, shaped particles. Two exceptions are the report of Zeng et. al. in 2005 on the preparation of core-shell alumina polystyrene composites that consisted of alumina needles surrounded by a PS shell[8] and the work conducted by Ham on the preparation of SWNTs covered with PS particles through the emulsion polymerization process[9, 10]. Outside of these two efforts little work has been performed on the emulsion polymerization in the presence of rod shaped particles. This work will seek to develop methods for encapsulation of rod shaped silver particles and thus increase the body of knowledge relating to emulsion polymerization in the presence of rigid rods.

In the field of antimicrobial systems there are three main techniques imparting antimicrobial properties to a surface, antiadhesive, biocide-releasing and contact active modifications. The typical process involves loading the surface with biocidal compounds such as halogens[11] or antibiotics[12] to create a biocide releasing system. Antiadhesive systems rely on coatings that limit the ability of a microorganism to attach and can be based on ultrahigh contact angle materials or coatings capable of creating noncharged hydrogells[13]. Contact active systems are capable of killing the microbe on contact and consist of antimicrobial polymers[14] and the photo catalytic production of $\cdot O_2^-$ and $\cdot OH$ radical by UV irradiated TiO_2 containing systems[15]. All of these systems suffer from non-optimum cost benefit considerations. Biocide release systems lose efficacy over time, antiadhesive systems are not 100% effective and contact active systems are often expensive.

Silver has long been recognized as a broad spectrum highly effective antimicrobial agent[16, 17]. Its ability to kill microbes has been explained through the activity of the Ag+ ions in denaturing the proteins by binding with their negatively charged components. For this reason silver is used as an antimicrobial agent in many articles such as wound dressings[18], catheters[19] and filters[20]. This mechanism requires the antimicrobial surface to remain wet in order to generate and transport the Ag+ ions to the bacterial cell walls.

There has been some effort on the preparation of antimicrobial wet coating systems based on the release of silver ions. In 2007 Davidson et. al. described an approach to formulating coatings based on the incorporation of zeolite supported silver though blending of the particles and prepared paints[21] and in 2008 Kumar described the preparation of coating systems based on the reduction of metal salts to colloidal silver in the presence of polymerizable vegetable oil derivatives[22]. In the case of Davidson the mechanism of action is the controlled release of silver ions when the surface is wet, thus a biocide releasing system. This suffers from two issues. The efficacy is lost with time and the antimicrobial properties require the surface to be wetted for a sufficient time to allow the release of the active agents. The method of Kumar creates an additional hurdle in that the hydrophobic surface can significantly reduce the rate of Ag+ ion release limiting the kill capability of the surface.

Alternative mechanisms for silver acting as an antimicrobial have been proposed including the generation of oxygen[23] or the lysing of the cell wall during contact between a silver surface and the cell[19, 22]. These mechanisms do not rely on water to generate and release Ag+ and thus allow silver to be used as a surface active antimicrobial agent. For these mechanisms to function the silver must be present at the surface of the article. However, silver typically has little if any affinity for the polymers of interest limiting attractive interactions. The spherical shape does not allow for mechanical entanglement and as a result the silver at the surface is lost through mechanical wear processes.

The approach of this project is fundamentally different from previous efforts in that we seek to prepare systems based on rod shaped silver particles. These systems are expected to display enhanced retention through wear processes as a result of entanglement with the polymer coating. In addition, the low percolation threshold and high aspect ratio of these particles means that it is more likely that at least a portion of the particle will be located at the coating surface were it can participate in the antimicrobial process in the absence of high humidity.

Approach:

To produce the rods a microwave assisted polyol process, as described by Gou[24], will be employed. This method is fast simple and can be tailored to produce rods of varying length. In this process microwave heating is utilized to accelerate the reaction when utilizing weak reducing agents. By adjusting the heating time the particle morphology can be varied from spherical to rod shaped. Examples of the differing structures available through this method are shown in Figure 1. Both rods and spheres are generated and some control over the rod length is possible.

The first and simplest approach to the preparation of the coatings will be the direct mixing of a latex paint binder with a colloidal suspension of silver rods. This mixture will be studied for stability and ability to form a fully cured film, likely affected by the rod length and rod concentration. Stability will be studied by monitoring sedimentation rates as a function of temperature. Wet coatings on temperature controlled surfaces will be used to measure the ability of the systems to form continuous cured films. The cured film morphology will be determined by SEM. The antibacterial efficacy of the coatings will be determined by monitoring the growth of gram positive bacteria on inoculated surfaces. Measurements of morphology and antibacterial efficacy will be performed prior to and during wear processes.

The second method of preparing these systems is to first encapsulate the silver particle in the polymer latex. These systems are expected to display enhanced stability and film forming capability. Stability of the system should be enhanced by the encapsulation, and polymer - polymer contact and molecular entanglement will not be impeded by the presence of the inorganic particles. It is expected that the maximum loading of silver particles in these systems may be reduced as compared to the direct blending process. The functionality of these systems will be determined in a similar fashion to the direct blends. However, their preparation will be considerably more complicated.

Figure 1 Product of Microwave Assisted Polyol Process as a Function of Heating Time (30 to 210 sec left to right.) Scale bars are 200 nm, 100 nm, 500 nm, 500 nm 1 mm, 1mm, and 1 mm in lower figures[24].

There are several methods available for the encapsulation of inorganic particles by a polymer. The encapsulated product can be broadly classified as physical, where the polymer simply surrounds the particle or as chemical, where there is covalent bonding between the polymer and the particle surface. In the case of chemical encapsulation there are two main approaches. The first is the introduction of a coupling agent, typically bearing a double bond, to the surface of the particle followed by emulsion or suspension polymerization. The second method is atom transfer radical polymerization starting from the surface of the particle with initiating groups. For this work both physically and chemically encapsulated silver nanorods will be prepared. In both cases stable silver particles capable of participating in the emulsion or suspension polymerization processes will need to be prepared. There are several processes in the literature that, after appropriate modification, should be capable of producing the required modified silver rods.

For the preparation of encapsulated particles two types of polymerization processes will be utilized, emulsion polymerization and suspension polymerization. In the emulsion polymerization process it is desired to stabilize the silver particles in the continuous aqueous phase. By modifying the surface appropriately the polymer can be bound to the surface during the initial phase of the polymerization process. As the polymer chains grow the oligomers will be stabilized by surfactant. Eventually this process will result in silver stabilized in growing latex particles. To encapsulate the particle using a suspension polymerization scheme the particle needs to be stabilized in the discontinuous organic phase. In this process surface modification can be used simply to stabilize the particle or can also be selected to participate in the reaction.

To chemically bond the polymer to the surface of the silver particle through emulsion polymerization a method similar to that of Bao et.al.[25] will be developed. Their approach was to immobilize azo-initiators on the surface of spherical silver particles by chelating the carboxylate group to the silver surface. This was followed by stabilization with poly(acrylic acid) and polymerization of styrene and 4-styrenesulfonic acid sodium salt. In the proposed work the procedure will be modified in several ways. First, the starting silver particles will be rod shaped. The lower percolation threshold of rods will limit the loading of the system and alter the stabilization dynamics both during the modification of the silver surface and the emulsion polymerization process. Second, the polymer used to coat the particle surface will be more typical of those currently used commercially in latex paint systems, acrylate styrene blends. Finally, the PAA stabilizer will be replaced with ionic surfactants. This will allow charge stabilization of the particle without the need of resorting to components such as styrenesulfonic acid sodium salt to increase charge density. The effect of initiator and surfactant concentration, reaction conditions, and polymer composition will be studied in regards to stability, coating thickness and efficacy.

The second method for encapsulating the silver rods will utilize suspension polymerization. For this process to encapsulate the particle it must be stabilized in the organic phase. This will be accomplished by the modification of the surface with ligands such as dodecanethiol to render the surface hydrophobic. The methods of Brust et.al.[26] and Sarathy et.al.[27] will both be tested. Brust reduced hydrogen tetrachloraurate trihydate with sodium borohydride in the presence of a thiol compound to produce a thiol modified surface on colloidal gold. This process will be modified by using a seed solution of silver rods produced by the microwave assisted polyol method and by replacing the gold precursor with silver chloride. Sarathy utilized a two phase process with silver particles located in an aqueous phase and the thiol compound located in an upper organic phase. Upon addition of HCl the particles migrate to the upper phase were they react and are stabilized by the thiol compound. We will replace the spherical colloidal particles with rod shaped particles in this process to produce rod shaped organic soluble silver particles.

Outreach to Industry:

Antimicrobial coatings have several industrial and commercial applications. Contamination of surfaces in hospitals with multi-drug resistant isolates has been a significant cause for alarm[28, 29]. Cross contamination of meats in packing plants by E. coli have sparked several high profile recalls in recent years. As a result, new technologies to reduce microbial colonization of surfaces are needed. Industry will be involved in this work through the development and testing of the coating systems developed. For example Scott Lambert of Sealed Air has expressed an interest in evaluating the technology after initial development has been completed.

New Resources Required:

Several pieces of equipment are required to effectively perform the work proposed.

- To measure particle size and size distribution dynamic light scattering equipment is required. A combined unit capable of measuring zeta potential, an indication of stability, would be of great use.
- Equipment to produce uniform coatings and measure required conditions to form continuous coatings will be required.
- All reactions performed will require excellent temperature control. A high quality temperature controlled water bath is required.

To effectively perform the work described in the attached proposal 1 graduate student and 2 undergraduates will work on the project. The graduate student together with the PI will develop the synthesis methods while the undergraduates will work on the characterization of the wet coating systems.

BIBLIOGRAPHY SECTION
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