

FINAL REPORT
March 4, 2014

Biodegradable Lactide Nanoparticles for the Destruction of Malodorous Organics

Principal Investigator(s): Daniel C. Whitehead, Assistant Professor
dwhiteh@clermson.edu
Department of Chemistry
467 Hunter Laboratories
Clemson University
Clemson, SC 29634
(864) 656-5765/(864) 656-6613 FAX

Collaborators: Frank Alexis, Assistant Professor
falexis@clermson.edu
Department of Bioengineering
203 Rhodes Annex
Clemson University
Clemson, SC 29634
(864) 656-5003

Date Submitted: March 4, 2014

Project Start Date: July 1, 2012

Duration of Project: 16 months

Lay Summary:

This project focuses on the development of new technologies to reduce odor emissions from the rendering industry. The main target of this work is to develop engineered, biodegradable poly(lactic acid) nanoparticles whose surface is decorated with appropriate reactive sites (*i.e.* functional groups) that are poised to destroy malodorous volatile organic byproducts of rendering processes. Briefly, by decorating the nanoparticles with appropriate reactive sites, offending volatile byproducts will be absorbed onto the particles by the formation of either ionic or covalent bonds. Alternatively, the offending odors will be chemically oxidized on the particle surface in order to generate less odorous byproducts. The malodorants will be chemically modified so as to both harness them onto the biodegradable particles for disposal, and to render them less odorous. This study will serve as a proof-of concept to demonstrate that functionalized biodegradable poly(lactic acid) nanoparticles have the potential to become a next-generation strategy for odor remediation in the rendering industry.

The technology being developed has the potential to be very beneficial to the rendering industry in terms of providing a next-generation alternative to established methods for odor remediation. The particles described herein might present several uses in an industrial setting. The particles could be employed as a rapid-use odor adsorbent in an emergency or spill situation. Further, the particles could, in principle, be incorporated into existing odor remediation equipment as an added means for odor elimination. The obvious long-term goal would be to develop an appropriate formulation of functionalized PLA nanoparticles that would compete with or ideally supplant existing odor elimination measures. One advantage of such an outcome includes the ability to land-fill the spent scrubbing material without further processing. Indeed, PLA polymers are biodegradable and non-toxic. Additionally, since their means of neutralizing malodorants is based on chemical reactivity instead of thermal degradation, the implementation of this strategy should return significant cost savings in terms of reduced energy consumption and reduced greenhouse gas emissions. Finally, the general strategy of surface decoration of polymer matrices with reactive sites is not limited to PLA polymers. One could envision the development of similar strategies for the preparation of “smart” clothing or other materials that are equipped with an odor elimination mechanism.

Objective (s):

To accomplish this project, we have set the following three long-term goals:

1. To assay the ability of amino-functionalized engineered poly(lactic acid) nanoparticles and thin films to sequester and destroy malodorous compounds. (Amino-functionalized nanoparticles and thin films will target 19 of the 26 most common malodorant organics from rendering emissions: the aldehydes and carboxylic acids).
2. To prepare and assay an ammonium peroxydisulfate functionalized poly(lactic acid) nanoparticle for the oxidative destruction of malodorants (ammonium peroxydisulfate-functionalized nanoparticles will target the 5 sulfur-containing malodorants that are common in rendering emissions).

3. To prepare and assay a hybrid poly(lactic acid) particle functionalized with amino and ammonium peroxydisulfate functional groups for the destruction of malodorants. (Hybrid nanoparticles will combine the strategies in goals 1 and 2 to target 24 of the 26 most common malodorants from rendering emissions.)

Project Overview:

1.1. Introduction: The Rendering Process and Malodorant, Environmentally Harmful Pollutants

Rendering is inextricably linked to the success and efficiency of the broader agricultural enterprise in the US. Roughly one third to one half of the live weight of livestock is not typically consumed by humans. Specifically, 49% of the live weight of cattle, 44% of the live weight of hogs, 37% of the live weight of broiler chickens, and 57% of the live weight of fish are not consumed by humans, and must therefore be processed by rendering methods. Indeed, 35 million cattle, 100 million hogs, and approximately 8 billion chickens are slaughtered per year in the US alone. The so-called co-products (or by-products) of slaughterhouse and butchering operations include hides, skins, hair, feathers, hooves, horns, feet, heads, bones, toenails, blood, organs, glands, intestines, extraneous muscle and fat tissues, egg shells, and whole carcasses (*i.e.* dead stock and slaughterhouse rejects). The total output of these materials from slaughterhouse operations exceeds 54 billion pounds per year. Rendering processes cook down these co-products (along with used restaurant cooking oils) in order to drive off moisture, separate the animal fats, and concentrate the protein-rich material into various dry meals including meat and bone meal, meat meal, poultry meal, hydrolyzed feather meal, blood meal, and fish meal.¹

The products of the rendering process, protein rich meals (11.2 billion pounds per year) and rendered animal fats (10.9 billion pounds per year), typically reenter the agricultural enterprise as feeds for livestock, poultry, aquaculture, and companion animals. Additionally, some rendering products including edible tallow (4.2 million pounds per year), lard (2.35 million pounds per year), and gelatin are suitable for human consumption.¹

The contribution of the rendering process to the sustainability of agriculture and food processes is two-fold. First, the process allows for the efficient removal, decontamination, and repurposing of the very large by-product stream from livestock and slaughterhouse operations. The cooking process serves to reduce the volume of the by-product stream by removing moisture (60% of gross weight) as well as to neutralize or deactivate biological contaminants including bacteria, viruses, protozoa, and parasites that would otherwise be deposited into the environment. Secondly, the products of the rendering process provide a nutrient-rich, high-energy food source for livestock, poultry, and aquaculture. In the absence of rendering operations, the alternative disposal strategies for slaughterhouse offal including landfilling or incineration, pose serious environmental concerns in terms of the potential for water and soil contamination and the venting of noxious gaseous emissions.¹

Significant efforts and capital are invested into controlling odor emissions that result from processing unused organic matter from livestock production, meat and food processing, and the food service industry. The positive environmental impact of the rendering process in terms of

reducing the amount of landfill and biological waste from the aforementioned operations is often overshadowed by negative perceptions of the environmental impact of the process in terms of wastewater and odor emissions. Concerns over odor emissions often play a large role in community resistance to site selection for new rendering operations.²

Indeed, *untreated* emissions from rendering operations can be detected up to 20 miles away from the source.³ Modern rendering facilities are equipped with sophisticated mechanisms for controlling odor and particulate emissions. Particulate emissions are controlled by filtering mechanisms called bag houses.² Malodorous vapors and contaminated air from the rendering process are controlled by means of several strategies. Common odor control methods include combustion/incineration, chemical oxidation, wet scrubbing, and biological scrubbing. Room air emissions are often treated with packed bed scrubbers containing chemical oxidants. Cooking vapors are often treated in two stages. First, vapors are cooled and passed through a venturi scrubber. The vapor effluent of the venturi scrubber is then treated with packed bed scrubbers filled with chemical oxidants. Other methods for treating cooking vapors involve the removal of condensable vapors followed by incineration of the non-condensable vapors in the plant boilers.^{2,3} Biological scrubbers remove plant odor emissions by passing odorous air through scrubbers containing bacterial biofilms that metabolize the odorous emissions.²⁻⁵

Despite their sophisticated nature, current odor remediation strategies suffer from some drawbacks. Combustion and incineration strategies are energy intensive processes that result in substantial venting of greenhouse gases. Chemical oxidation requires the use of strong oxidants. Spent chemical and biological packed bed scrubbers must be disposed of properly. Additionally, aqueous effluent from packed bed and venturi scrubbers contribute to the already substantial wastewater flow from rendering operations.² Finally, despite these technological advances the process nonetheless still suffers from a substantial odor problem.

Van Langenhove *et. al.* conducted a comprehensive study aimed at identifying the specific volatiles that contribute to malodorous rendering odors that vent from cooking processes. In total,

about 110 distinct volatiles were detected and identified, but 26 of that number were confirmed to contribute to the unsavory odors of cooking processes.⁶ Chart 1 includes a comprehensive list of the offending odorants as well as a general depiction of their common functional group. The list contains ten short chain aliphatic aldehydes ranging from three to ten carbons in

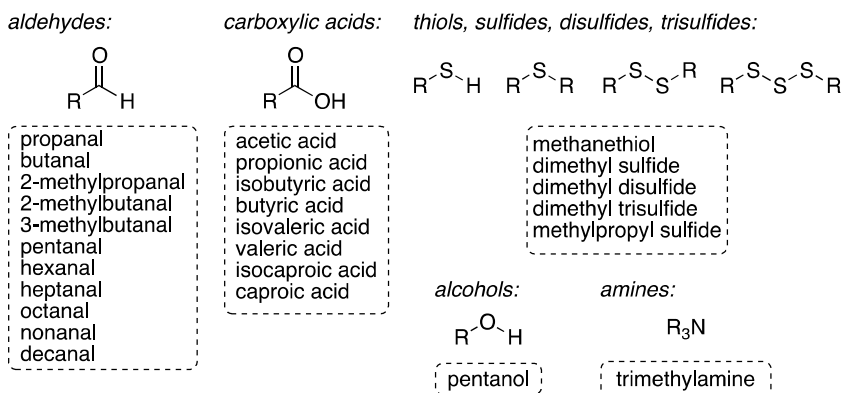


Chart 1. Volatile organics responsible for malodorous cooking emissions organized by functional group.

length. Carboxylic acids comprise the second most populous group, containing examples ranging from two to six carbons in length. Sulfur containing functional groups (including thiols, sulfides,

disulfides, and trisulfides) comprise the third largest group of offending odorants. Additionally, a single alcohol and a single amine were identified.⁶ Most of these volatile organics result from the thermal breakdown of protein and fats during the cooking process.⁴ Many of them are highly flammable, corrosive, carcinogenic, and/or toxic to both humans and animals.

Other sources of odors in the rendering process include protein degradation products including amino acids and peptides, most notably present during blood storage. Wastewater treatment produces several noxious, toxic emissions including hydrogen sulfide and ammonia. Evaporation processes and animal waste product storage also emit hydrogen sulfide and ammonia along with various other amines, aldehydes, carboxylic acids, and thiols. Finally, smokehouse operations emit various aldehydes, acids, and other organic constituents including cresol and acrolein, a potent carcinogen.^{4,7}

The large number of offending chemical entities as well as their ill-defined and often variable relative concentrations complicate approaches toward the strategic remediation of rendering contaminant emissions. The situation is further complicated by the fact that the most offending odorants are not necessarily the major constituents of the emissions from rendering processes. For example, the human nose is capable of detecting odorants with thresholds as low as 0.1 parts per billion (v/v).⁸

In summary, the rendering process, while playing a vital role in handling animal by-products from slaughterhouse operations, results in the release of a complex mixture of small molecules that are malodorous. *This project has been devoted to demonstrating the potential of biodegradable functionalized poly(lactic acid) nanomaterials for rendering odor remediation in a series of proof-of-concept studies.*

1.2. Introduction: Poly(Lactic Acid) Polymers and Applications

Polymers of lactic acid (e.g. Figure 1) were first discovered in 1932, but their practical applications did not begin to emerge until the early 1970s when they found considerable use as dissolving sutures in surgical applications.^{9,10} Fermentation technology developed in the late 1980s resulted in affordable means for the preparation of the requisite monomer for PLA synthesis from D-glucose obtained from corn. Cheaper monomer sources for PLA catalyzed a renaissance of its

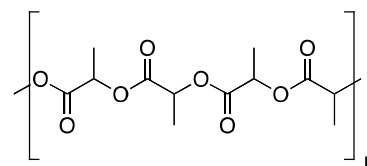


Figure 1. Poly(lactic acid) (PLA)

study, and numerous new applications of the polymer have recently emerged. Current applications include formulations for biodegradable trash/lawn care bags, water bottles, food storage containers, and various fiber products.^{11,12} Recent applications in medicine include applications for drug-delivery and controlled drug release. PLA polymers are particularly exciting due to their *biodegradability and toxicological safety*.⁹ PLA polymers can be engineered to degrade over a timeline of days, weeks, months, or even years depending on the specific formulation.^{9,13} *Their non-toxic nature and tunable degradation properties make them excellent candidates as a medium for the remediation of malodorous rendering emissions.*

2.1. Experimental Design

With the goal of investigating novel platforms appropriately functionalized to either chemically modify or sequester target malodorous rendering emissions, we designed a series of novel amino-functionalized poly(lactic acid) nanomaterials.

Figure 2 depicts the target materials in cartoon format.

The overall design strategy is based on a non-toxic, biodegradable poly(lactic acid) (PLA) substrate.

The PLA core of the materials is then coated with a polyethylene glycol layer, and is then capped with an appropriate functional group via a variable linker region. The functionalized PLA materials capped with amine (R-NH₂) functional groups are suitable for reaction with a large suite of the most common malodorous VOCs associated with rendering processes (*i.e.* short-chain fatty acids and aldehydes). Specifically, the choice of the amine group (see **1**, dashed box, Figure 3, formulation represented as a nanoparticle) was driven by considering the reactivity of the conglomerate of compounds collected in Chart 1 (*vide supra*, page 4). Considering conventional organic chemical reactivity, nineteen of the twenty-six VOCs associated with offending rendering odors, namely the aldehydes and carboxylic acids, are expected to react with an amino functionality and be sequestered (*i.e.* via chemical transformation). Aldehydes are known to undergo condensation with amines to generate imines (Scheme 2, eq. 1) via the expulsion of water. Reaction with an amino functionalized PLA nanoparticle like **1** (or with the analogous thin film) would result in the covalent sequestration of the offending odorant onto the surface of the nanomaterial. This interaction would prevent the emission of the compound as well as render it less volatile and therefore less odorous. The high surface-to-volume ratio of nanomaterials and their unique functionalities are expected to significantly reduce the emission of malodorous compounds.

Similarly, carboxylic acids ought to undergo an acid-base reaction

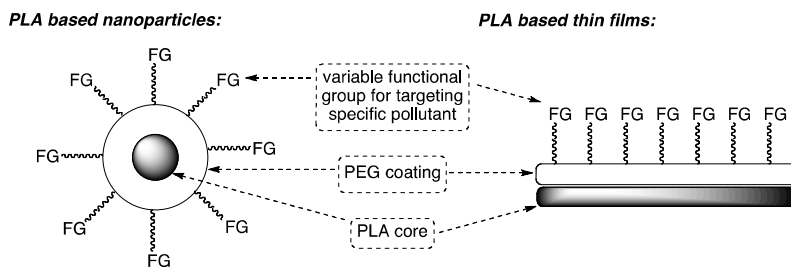


Figure 2. Cartoon depiction of poly(lactic acid) (PLA) nanomaterials highlighting design elements. The core substrate for both the particles and films is PLA. The PLA is coated with polyethylene glycol (PEG) to promote water solubility. The variable functional group region can be tuned for compatible reactivity with target pollutants.

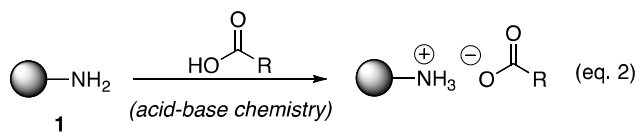
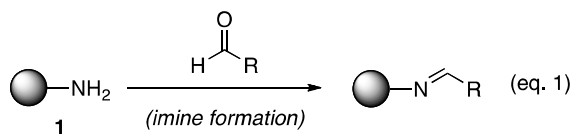
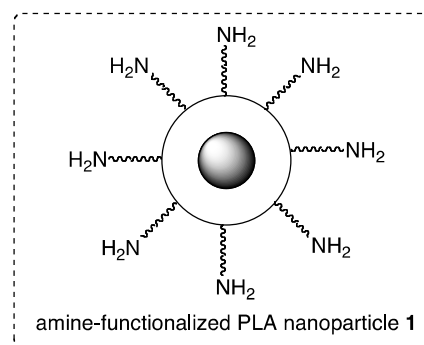
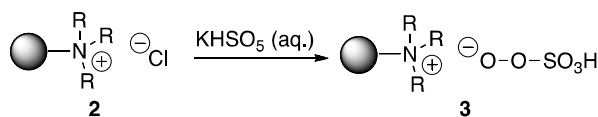


Figure 3. Amine functionalized PLA nanoparticle **1**, and predicted reactivity with aldehyde and carboxylic acid odorants.

with the amino functionalized PLA nanomaterials (Figure 3, eq. 2). The resultant ammonium carboxylate ionic compounds would effectively sequester the odorant VOC onto the surface of the nanoparticle or thin film.

Additionally, We designed an oxidant-functionalized PLA nanomaterial to target the five sulfur-containing compounds (see Chart 1, page 4) associated with rendering operations. The compounds are particularly noxious, emitting an overwhelming, putrid odor that is detectable even at miniscule concentrations. In order to target these contaminants, we designed PLA nanoparticles and thin films that are end-capped with ammonium peroxyulfates that can serve as the requisite oxidant for odorant destruction.

Briefly, proposed to prepare engineered PLA nanoparticles and thin films functionalized with quaternary ammonium salts (Scheme 1, 2). In short, we proposed to cap our base formulation, PLA-PEG-COOH with an appropriate linker that displays a quaternary amine. Employing the method developed by Travis and Borhan,¹⁴ we would then generate the requisite ammonium peroxyulfate functionalized PLA nanoparticles and thin films. Specifically, the active oxidant of commercial Oxone®, potassium peroxyulfate, would be isolated. The PLA nanoparticles and thin films functionalized with quaternary ammonium salts (e.g. 2) would then be treated with an aqueous solution of potassium peroxyulfate in order to displace the counterion (represented in Scheme 1 as Cl⁻). The extent of peroxyulfate incorporation onto the PLA nanoparticle or thin film (e.g. formation of 3) could then be determined by iodine titration.¹⁴



Scheme 1. Strategy for the preparation of ammonium peroxyulfate functionalized PLA nanoparticles poised to react with sulfur containing odorants.

Finally, a logical extension of the approach would be to engineer a hybrid PLA nanoparticle or thin film that contains both the amine functional group as well as the ammonium peroxyulfate functional group. This hybrid PLA material would then be adequately equipped to capture aldehyde and carboxylic acid contaminants as well as to oxidize sulfur-containing agents, thus demonstrating the tunability of PLA-based adsorbents. The methods developed for the preparation of the nanomaterials (*vide infra*) are uniquely designed to allow for such fine-tuning of the surface functionalization of the nanoparticles and thin films. Essentially, the nanomaterials can be capped with a statistical mixture of two or more unique functional groups by simply controlling the ratio of the incoming capping groups during the fabrication process. By simultaneously capping the PLA nanoparticle or thin film with a mixture of the appropriate amine and quaternary ammonium salts, a hybrid nanomaterial can be prepared in one operation. Subsequent treatment of the quaternary ammonium sites with potassium peroxyulfate as described above would then produce a hybrid PLA nanoparticle or thin film equipped with both amines and ammonium peroxyulfates (See 4, Figure 4). Described below is our progress toward achieving the preparation and validation of these three formulations of nanomaterial formulations as a next-generation strategy for odor remediation in the rendering industry.

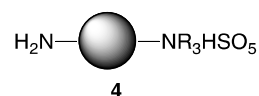


Figure 4. A hybrid PLA nanoparticle equipped with an amine and an ammonium peroxyulfate.

2.2. Preparation of Amine Functionalized Nanomaterials

Our initial efforts on the project were directed toward preparing the amine functionalized nanomaterials that were suitable for sequestration of the aldehyde and carboxylic acid malodorants (nineteen of the twenty-six target malodorants). Six amine-capped formulations were targeted for study. We prepared PLA nanoparticles that were end-capped with ethylenediamine (EDA), presenting a single primary amine functionality at the end of each tether region. Similarly, we generated EDA end-capped PLA thin films. Additionally, we end-capped PLA nanoparticles and thin films with low molecular weight polyethyleneimine (LMWPEI) and high molecular weight polyethyleneimine (HMWPEI). LMWPEI and HMWPEI are dendritic polyamines that present a number of primary amines (and secondary and tertiary amines) on the surface of the particles and films. The methods described below for their fabrication are robust, reliable, and thoroughly optimized.

Functionalized thin films were prepared by first dispersing a 100 mg/mL dichloromethane solution of PLA-PEG-COOH polymer (prepared via ring opening polymerization)¹³ onto a glass slide, followed by overnight drying to generate the thin films. The slide containing the carboxylate-terminated polymer film was then incubated in a 10X molar excess of 1-ethyl-3-(3-

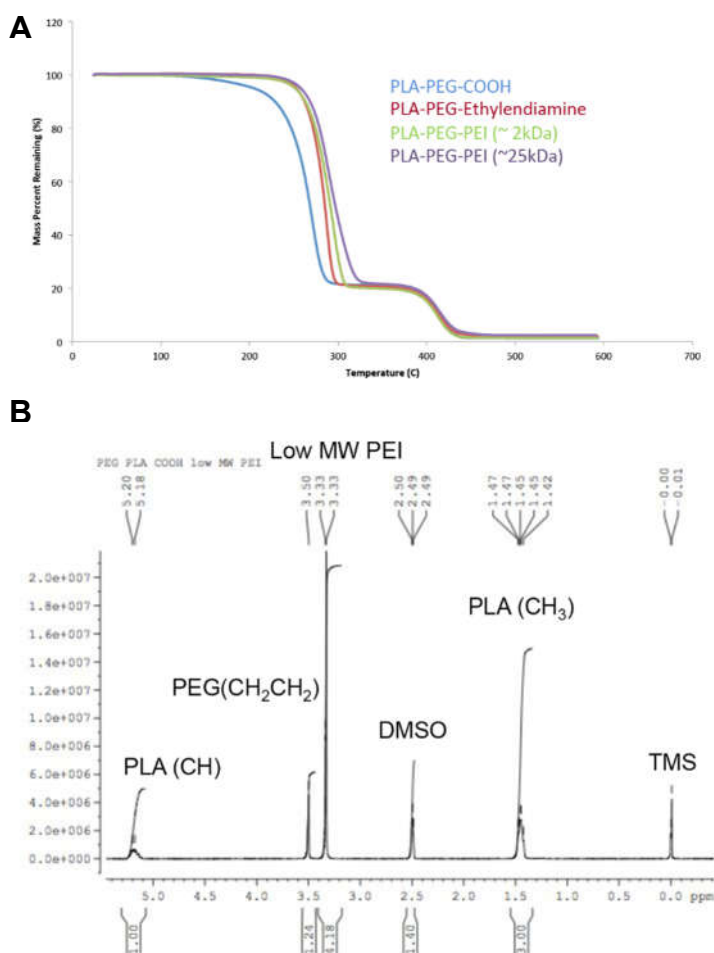


Figure 5. Representative characterization data for functionalized PLA nanoparticles and thin films. **Panel A:** TGA analysis of four thin film formulations. Blue: PEG-PLA-COOH film, Red: PLA-PEG-EDA film, Green: PLA-PEG-LMWPEI film, Purple: PLA-PEG-HMWPEI film. **Panel B:** ¹H NMR spectrum of PLA-PEG-LMWPEI thin film. Key resonances are indicated on the spectrum. Abbreviations: PLA = poly(lactic acid), PEG = polyethyleneglycol, Low MW PEI = Low molecular weight polyethyleneimine, DMSO = dimethylsulfoxide (NMR solvent), TMS = tetramethylsilane (NMR standard).

dimethylaminopropyl]carbodiimide (EDC) in phosphate buffered saline (PBS) (pH 7.4) to generate the activated ester. The amine cap (EDA or PEI) was then added as a 10X excess to the activated ester and incubated for six hours in order to load the amine cap via amide formation. The resulting amine capped PLA thin film was then washed three times with distilled water to remove excess coupling reagents. Finally, the thin films were removed from the glass slide and subjected to freeze-drying to remove residual water. The films were characterized as described below.

The amine capped PLA-PEG nanoparticles were generated by dissolving the PEG-PLA-COOH polymer in acetonitrile (~ 5 mg/mL). This acetonitrile solution was then added dropwise into water to allow for the polymeric nanoparticles to form over the course of about 1.5 hours. The individual polymer strands self-assemble into nanoparticles by hydrophobic-hydrophobic interactions between the PLA polymer chain such that the hydrophilic PEG outer layer is projected into the aqueous solvent.¹³ After the 1.5 h incubation, the nanoparticles were washed by ultracentrifuge filtration to remove residual solvents. The particles were then resuspended in PBS (pH 7.4) and treated sequentially with the EDC and amine end-cap solutions analogous to the thin film preparation described above. The amine-capped PLA-PEG nanoparticles were then washed three times with distilled water using ultracentrifugation and dried using a freeze dryer.

After preparation, the particles and films were characterized by ¹H nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy, and thermogravimetric analysis (TGA). The presence of the desired amine functionality on the surface of the particles was further verified by zeta potential measurements. Figure 5A (previous page) shows the TGA data for the capped thin film formulations (including the carboxylic acid terminated film prior to EDC treatment), and Figure 5B shows an ¹H NMR spectrum for the PLA-PEG-LMWPEI thin film as representative examples of the characterization. Nanoparticle size was judged by zetasizer measurements and was found to range from 100 to 500 nm depending on the formulation. Nanoparticle size is further evaluated in solution utilizing Clemson University's NSF-funded hyperspectral microscope.

2.3. Demonstration of Desired Reactivity for Capture of Rendering Contaminants with Small Molecule Mimics

While the preparation of the desired amine functionalized nanomaterials was underway, we sought to demonstrate the desired reactivity of amines with several malodorous, environmentally harmful contaminants associated with rendering off-gases. Recall from Chart 1 (*vide supra*, page 4) that short chain aldehydes (R-CH=O) and carboxylic acids (R-CO₂H) are among the most prevalent constituents of malodorous emissions from rendering operations.⁶ We hypothesized that amine capped PLA nanomaterials would readily capture aldehydes and carboxylic acids via the rapid formation of imines (R-CH=N-R') and ammonium carboxylates (RNH₃⁺ R'CO₂⁻), respectively. To demonstrate the high likelihood of this predicted reactivity, we conducted small molecule experiments in dichloromethane where we mixed 0.01 M butyraldehyde (a common malodorous emission of the aldehyde class) with 1, 1.1, 1.5, 2, 3, 5, and 10 equivalents of butylamine, a small molecule surrogate for the functionalized nanomaterials. These mixtures were assayed by gas chromatography in triplicate, and in each case revealed complete or nearly complete imine formation. Similar experiments with butyric acid (a common malodorous emission of the carboxylic acid class) produced nearly identical results: only a slight excess of 1.1

equivalents of the amine surrogate was necessary to promote complete formation of the ammonium carboxylate salt. These experiments with small molecule mimics indicated that it was highly likely that similar reactivity could be expected on the surface of the amine capped nanomaterials discussed in the previous section, resulting in the capture of environmentally harmful malodorants of the aldehyde and carboxylic acid classes.

2.4. Development of an Aqueous Testing Platform for Hexanal

Significant effort was invested in the development of an aqueous solution-phase assay for the removal of hexanal with our functionalized nanomaterials. This effort spanned several months and roughly 1000 gas chromatography experiments. Briefly, standard stock solutions of 0.005 M hexanal and 0.005 M tetraglyme (internal standard, ISTD) were prepared in an 0.025% aqueous tetra-*n*-butylphosphonium bromide solution. (Note: The tetra-*n*-butylphosphonium bromide was added as a phase-transfer catalyst to facilitate the dissolution of the hexanal into water at room temperature.) Next, an appropriate aliquot of the 0.005 M hexanal stock and 0.005 M tetraglyme stock were diluted to generate a standard curve ranging from 5 to 50 μM hexanal with 50 μM tetraglyme in each sample. Ten 1 mL samples were prepared containing 50 μL hexanal and 50 μL of tetraglyme (ISTD). These samples were subjected to GC analysis (ZB-Wax column, FID detection) to assess our ability to recover untreated hexanal samples. Based on this analysis, we were able to recover $40 \pm 0.5 \mu\text{M}$ of hexanal from untreated 50 μM hexanal samples. Therefore, 40 μM hexanal was used as our baseline concentration for treatment with our nanomaterials.

2.5. Screen of Functionalized Thin Films for Removal of Hexanal

Here, we attempted to demonstrate the ability of our amine functionalized thin film formulations to remove hexanal from aqueous solutions. Briefly, microscope slides were prepared that contained the three amine-decorated thin film formulations: PLA-PEG-EDA, PLA-PEG-LMWEDI, and PLA-PEG-HMWEDI (Figure 6). Each formulation was treated with 1 mL aqueous samples containing 50 μM hexanal and 50 μM tetraglyme and allowed to react for 10 minutes. The aqueous analyte was then removed from the thin film and subjected to GC analysis (ZB-wax column, FID detection).

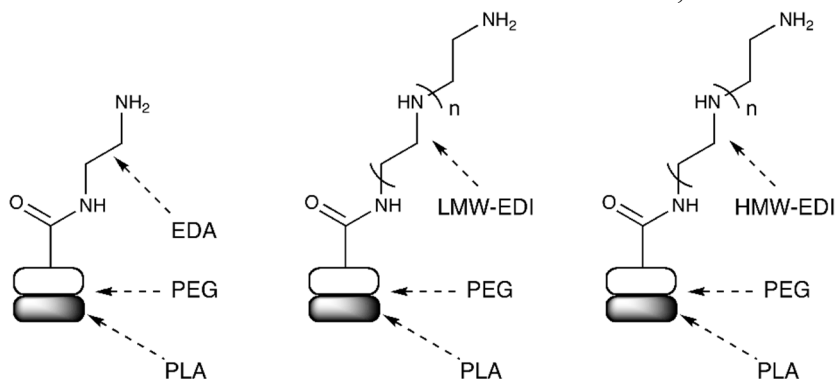


Figure 6. Amine-functionalized thin film formulations for aqueous hexanal removal screen. EDA = ethylenediamine; LMW-EDI = low molecular weight polyethyleneimine; HMW-EDI = high molecular weight polyethylene imine.

After 10 minutes of treatment, GC analysis revealed that all three thin-film formulations resulted in the reduction of the concentration of hexanal relative to the $40 \pm 0.5 \mu\text{M}$ recovery of untreated hexanal samples. Table 1 indicates the results from this study. After treatment with the PLA-PEG-EDA formulation for just 10 minutes, the concentration of hexanal in the aqueous sample was reduced to 11 μM , corresponding to a 72% reduction relative to the $40 \pm 0.5 \mu\text{M}$ recovery of untreated hexanal samples. Similarly, the PLA-PEG-LMWEDI reduced the

concentration of hexanal to 25 μM (37% reduction), while the PLA-PEG-HMWEDI reduced the malodorant concentration to 18 μM (55% reduction).

Table 1. Removal of hexanal from aqueous samples with amine functionalized thin films

	PLA-PEG-EDA	PLA-PEG-LMWEDI	PLA-PEG-HMWEDI
hexanal concentration (μM)	11	25	18
percent reduction	72%	37%	55%

3. Conclusions

The efforts over the past 16 months culminated in first evidence that appropriately designed functional poly(lactic acid) nanomaterials are capable of sequestering a volatile molecule known to contribute to rendering malodors. Initial efforts centered on the preparation of a number of nanoparticle and thin-film formulations. Additionally, we found that the desired reactivity could be demonstrated with a small molecule mimic. Finally, a significant amount of time was invested in developing and verifying an aqueous testing platform for the sequestration of hexanal. Finally, we demonstrated the ability of functional thin films to remove hexanal from aqueous media. These efforts have laid a solid footing for the continued investigation of PLA nanomaterials as a next generation strategy for odor remediation in the rendering industry.

Impacts and Significance:

The technology that is being developed has the potential to be very beneficial to the rendering industry in terms of providing a next-generation alternative to established methods for odor remediation. The particles described herein might present several uses in an industrial setting. The particles could be employed as a rapid-use odor adsorbent in an emergency or spill situation. Further, the particles could, in principle, be incorporated into existing odor remediation equipment as an added means for odor elimination. The obvious long-term goal would be to develop an appropriate formulation of functionalized PLA nanoparticles that would compete with or ideally supplant existing odor elimination measures. One advantage of such an outcome includes the ability to land-fill the spent scrubbing material without further processing. Indeed, PLA polymers are biodegradable and non-toxic. Additionally, since their means of neutralizing malodorants is based on chemical reactivity instead of thermal degradation, the implementation of this strategy should return significant cost savings in terms of reduced energy consumption and reduced greenhouse gas emissions. Finally, the general strategy of surface decoration of polymer matrices with reactive sites is not limited to PLA polymers. One could envision the development of similar strategies for the preparation of “smart” clothing or other materials that are equipped with an odor elimination mechanism.

Publications:

While we have not submitted a manuscript on this project yet, we are very close to completing our first paper. Additionally, we have begun initial work with the Clemson University Research Foundation (CURF) in order to protect the technology with a patent.

Outside funding:

To date, we have used preliminary data generated through FPRF/ACREC support as the basis for four federal research proposals:

1. “Biodegradable Functionalized Nanomaterials for the Remediation of Agricultural and Food Process Pollutants”, (2013) Sponsor: USDA/NIFA Foundational Program Strengthening Grant, \$500,000, Declined.
2. “SusChEM: Functionalized Biodegradable Nanomaterials for the Remediation of Environmental Pollutants”, (2013) Sponsor: NSF, \$330,000, Declined.
3. “SusChEM: Functionalized Biodegradable Nanomaterials for the Remediation of Gaseous Environmental Pollutants”, (2014) Sponsor: NSF, \$380,000, under review.
4. Letter of Intent: “Biodegradable Functionalized Nanoparticles for the Remediation of Agricultural and Food Process Pollutants”, (2014) Sponsor: USDA/NIFA Foundational Program. Full proposal submission was encouraged; deadline April 9, 2014.

Future Work:

There is much left to do with this project. The data described herein lay a strong foundation for the development of these materials into a viable strategy for odor remediation. Further, our team is committed to pursuing the latter long-term aims described above. Upon completion, these aims will have confirmed the ability of the functional PLA nanomaterials to capture or destroy rendering malodors in a proof-of-principle capacity. What lies ahead after that are efforts aimed at realizing the true potential of these materials in a more practical setting. We are working toward scale-up experiments and physical measurements that will evaluate the potential of these materials in industrial settings. We hope to continue our relationship with the FPRF and ACREC for the foreseeable future so that we can see these materials through to their true potential.

Acknowledgments:

Many Thanks to the following students who have participated in this project: McKenzie Campbell (Chemistry), Samuel Rackley (Chemistry undergraduate), Timothy Gibson (Chemistry Undergraduate), Eric Drew (Chemistry Undergraduate), Thomas Moore (Bioengineering), Jhilmil Dhulekar (Bioengineering).

References:

- (1) Meeker, D.L., Hamilton, C.R. An Overview of the Rendering Industry In *Essential Rendering: All about the Animal By-Products Industry*. Meeker, D.L. Ed. Kirby Lithographis Company, Inc. Arlington, VA, 2006. p 1-16.
- (2) Sindt, G.L. Environmental Issues in the Rendering Industry. In *Essential Rendering: All about the Animal By-Products Industry*. Meeker, D.L. Ed. Kirby Lithographis Company, Inc. Arlington, VA, 2006. p 245-258.

- (3) Bethea, R.M., Murthy, B.N., Carey, D.F. Odor Controls for Rendering Plants. *Environmental Science & Technology*. 1973. 7, 504-510.
- (4) Shareefdeen, Z, Herner, B, Webb, D, Verhaeghe, L, Wilson, S. An odor predictive model for rendering applications, *Chemical Engineering Journal*. 2005. 113, 215-220.
- (5) Shareefdeen, Z, Herner, Wilson, S. Biofiltration of nuisance sulfur gaseous odors from a meat rendering plant, *Journal of Chemical Technology and Biotechnology*. 2002. 77, 1296-1299.
- (6) Vanlangenhove, H.R., Vanwassenhove, F.A., Coppin, J.K., Vanacker, M.R., Shamp, N.M. Gas-chromatography mass-spectrometry identification of organic volatiles contributing to rendering odors. *Environmental Science and Technology*. 1982, 16, 883-886.
- (7) Pearson, A.M., Dutson, T.R. *Inedible Meat By-Products*. Elsevier Applied Science, London, 1998.
- (8) Fazzalari, F.A. *Compilation of Odor and Taste Threshold Data*, ASTM Data Series DS 48A, ASTM, Philadelphia, PA, 1973.
- (9) Alexis, F. Factors affecting the degradation and drug-releasae mechanism of poly(lactic acid) and poly[(lactic acid)-co-(glycolic acid)] *Polymer International* 2005, 54, 36-46.
- (10) Griffith, L.G. Polymeric biomaterials *Acta Materialia* 2000, 48, 263-277.
- (11) Drumright, R.E, Gruber, P.R., Henton, D.E. Poly(lactic acid) technology *Advanced Materials* **2000**, 12, 1841-1846.
- (12) Lunt, J. Large-scale production, properties and commercial applications of poly(lactic acid) polymers *Polymer Degradation and Stability* **1998**, 59, 145-152.
- (13) Pridgen, E., Alexis, F., Farokhzad, O.C., Langer, R. *Methods in Bioengineering Book Series. Nanoscale Bioengineering and Nanomedicine*, Artech House; Boston, MA, 2009.
- (14) Travis, B.R., Ciaramitaro, B.P, Borhan, B. Preparation of purified KHSO₅ center dot H₂O and nBu(4)NHSO(5) from oxone by simple and efficient methods *European Journal of Organic Chemistry* **2002**, 3429-3434.