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Rechargeable antimicrobial coatings for poly(lactic acid) nonwoven fabrics

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ABSTRACT

A novel heterocyclic N-halamine acetate homopolymer was synthesized and characterized by ATR-IR, NMR and MALDI-TOF spectroscopy and TGA and DSC analysis. The homopolymer was coated onto poly(lactic acid) (PLA) meltblown nonwoven fabric, and the surfaces were rendered biocidal upon exposure to dilute sodium hypochlorite solution. The coatings were quite stable versus UVA and florescent light exposure. Moreover, they exhibited long-term shelf-life stability, and they were rechargeable when oxidative chlorine on the surfaces was partially exhausted after three months storage. It was found that the chlorinated fabrics exhibited effective antimicrobial activity with about six logs inactivation of *Staphylococcus aureus* and *Escherichia coli* O157:H7 within 30 min of contact time. The coated PLA possesses potential for use in antimicrobial food packaging, filters, and hygiene products.

1. Introduction

Antimicrobial treatment of materials is of critical interest due to the increasing threat of infectious diseases transmitted through direct or indirect contact [1]. In this regard, several antimicrobials including quaternary ammonium salts [2–4], synthetic mimics of peptides [5], metal ions [6], light-activated compounds [7], and N-halamines [8–13] have been utilized to prevent contamination of surfaces. In these laboratories and elsewhere, N-halamine compounds have been studied extensively due to their superior bactericidal functionality, non-toxicity, long-term stability, and rechargeability [14]. N-halamine materials have been prepared primarily by three approaches; incorporation of N-halamines into polymers/fibers as additives [15], using N-halamine precursors as fiber-forming polymers [16], and applying surface coatings in which N-halamine compounds are covalently bonded [17] or physically immobilized [18] on materials. Several organic and inorganic materials including cellulose [19,20], polyester [21,22], nylon [23], polypropylene [24], polyacrylonitrile [25], polyurethane [26], cellulose acetate [27], polyethylene glycol [28], aramid [29], latex paint [30], stainless steel [31], silica gel [32], etc, have been functionalized by N-halamines using one of the approaches above.

Because it is biodegradable and sustainable, poly(lactic acid), PLA, has great potential to be used in food packaging materials, hygiene products, filters, wipes, and apparel [33], in which antimicrobial functionality is often desired. Therefore, several research projects have been performed to render PLA antimicrobial. Busolo et al. used silver based-nanoclay as an additive to prepare transparent PLA films [34]. Even though the films were antimicrobial against *Salmonella* spp., the migration of silver ions from the films to the environment limited its application. Sebastien et al. prepared chitosan/PLA biocomposite films and showed that the films effectively prevented the surface growth of mycotoxinogen fungal strains [35]. On the other hand, the physico-chemical properties of the heterogeneous films limited further development. Jin and Niemira prepared PLA coating formulations containing different antimicrobials, and they applied the coatings to apples on which about four logs reduction of *Escherichia coli* O157:H7 and *Staphylococcus stanley* were obtained within one day of contact [36]. Even though these previous studies were promising, there is a need for antimicrobial coatings on PLA which could simply be prepared, be effective within shorter contact times against a broad range of microorganisms, and be stable for longer use. In this regard, this study addresses synthesis and characterization of a new N-halamine homopolymer which was used to make surface coatings on PLA meltblown nonwoven fabrics through a simple pad-dry procedure. The stability, rechargeability, and antimicrobial activity of the coated PLA fabrics were evaluated. To the best of our knowledge, this is the first study reporting the use of N-halamines to prepare antimicrobial PLA.

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2. Experimental

2.1. Materials and instrumentation

All starting chemicals were purchased from VWR (Radnor, PA) or Aldrich Chemical Company (Milwaukee, WI) and used without further purification. PLA meltblown nonwoven fabrics (30 g/m^2) were kindly donated by the University of Tennessee Textiles and Nonwovens Development Center. Clorox® brand (Clorox, Inc., Oakland, CA) household bleach was used for chlorination. Bacteria cultures of *Staphylococcus aureus* ATCC 6538 and *E. coli* O157:H7 ATCC 43895 were purchased from American Type Culture Collection (Rockville, MD), and Trypticase soy agar was obtained from Difco Laboratories (Detroit, MI).

NMR data were collected using a Bruker 400 MHz spectrometer, and a Nicolet 6700 FT-IR spectrometer with an ATR (Attenuated Total Reflectance) accessory utilizing a diamond crystal was used to record ATR-IR data (collected with 32 scans at 16 cm^{-1} resolution). TA Instruments Q500 and DSC Q2000 were employed for thermal analysis (data were collected at a heating rate of 10 °C/min under nitrogen atmosphere).

2.2. Synthesis

The hydantoin acetate homopolymer (HyAc), poly (2-(4,4-dimethyl-2,5-dioxoimidazolidin-1-yl)acetate), was synthesized in three steps (Fig. 1). First, the potassium salt of 5,5-dimethylhydantoin was prepared by mixing 6.40 g (50 mmol) of 5,5-dimethylhydantoin with 2.80 g (50 mmol) of KOH in 100 mL of ethanol and subsequently refluxing for 10 min. After removal of the solvent by reduced pressure, the salt was obtained as white crystals with a yield of 92% and further dried in a vacuum oven at 50 °C for 2 d.

Second, vinyl chloroacetate was polymerized by free radical polymerization in methylene chloride using azobisisobutyronitrile (AIBN) as an initiator. In brief, 2.41 g (20 mmol) of vinyl chloroacetate and 0.02 g of AIBN were dissolved in 10 mL of CH_2Cl_2, and nitrogen was flushed through the solution for 10 min for deoxygenation. After refluxing the solution for 7 h under nitrogen protection, the polymer was precipitated by drop-wise addition of 10 mL of hexane, filtered, and then dried under reduced pressure.

In the last step, the potassium salt of 5,5-dimethyl hydantoin was reacted with the homopolymer of vinyl chloroacetate; 1.66 g of homopolymer, and 2.29 g of hydantoin salt were dissolved in 30 mL of anhydrous DMF, and the solution was stirred for 5 h at 75 °C. After filtering the byproduct KCl, HyAc was precipitated by drop-wise addition of 50 mL of distilled water, filtered, and then dried in a vacuum oven (the yield was 73%).

The synthesized homopolymer, HyAc, was converted to an N-halamine compound through a chlorination procedure with sodium hypochlorite solution; 2 g of HyAc were stirred in 20% of NaOCl solution at room temperature for 4 h, and then the polymer was recovered by filtration, washed vigorously with distilled water, and dried at 45 °C for 2 h. The oxidative chlorine loading on the polymer was found to be 9.15 wt%.

2.3. Coating and chlorination procedure

The homopolymer, HyAc, was dissolved (1.5 wt%) in a 50/50 EtOH/water mixture at 40 °C, and the poly(lactic acid) nonwoven fabric was soaked in the solution for 10 min. Then the fabric was put

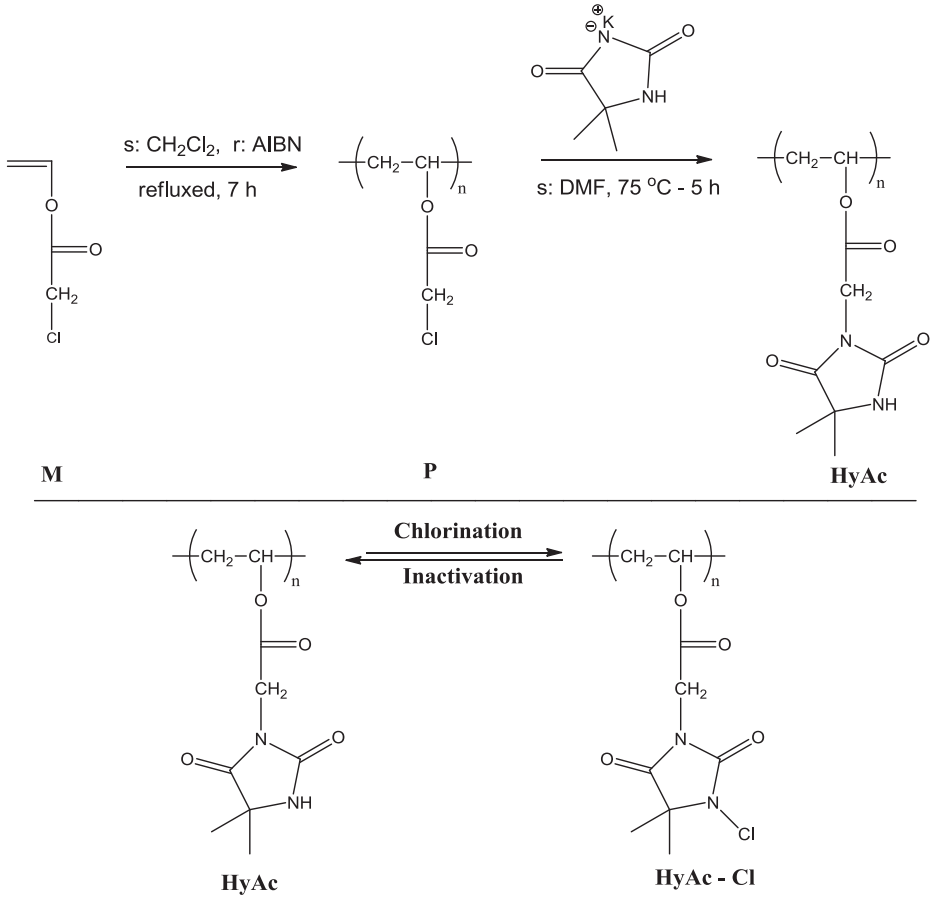

Fig. 1. Synthesis of the hydantoin acetate homopolymer.