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Antimicrobial surface coatings for polypropylene nonwoven fabrics

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ABSTRACT

Anionic and cationic N-halamine polyelectrolytes were synthesized, characterized and then immobilized onto melt-blown polypropylene fabrics having two different basis-weights. The coatings were rendered biocidal upon exposure to dilute sodium hypochlorite solution. The effect of single and multilayer deposition of the polyelectrolytes on the surfaces was investigated in terms of chlorine loadings, rechargeabilities, antimicrobial efficacies, and air permeabilities. It was found that all of the coatings provided remarkable biocidal efficacies with about six log reductions of bacteria within two min of contact time on filters having higher basis-weight, whereas slower inactivation was observed for lower-basis weight filters due to diminished surface areas and numbers of active halogen atoms. The antimicrobial coatings reduced the air permeabilities of the filters somewhat; however, the air permeabilities of the coated swatches were comparable to those of most protective textiles.

1. Introduction

Because prevention is a key concept to combat nosocomial infections, there is an increasing need for polymeric materials possessing antimicrobial functionality in order to minimize these infections. In this regard researches are centered on development of biocidal materials using organic and/or inorganic antimicrobials such as quaternary ammonium salts [1,2], silver [3,4], N-halamines [5–8], synthetic mimics of antimicrobial peptides [9,10] and chitosan [11,12]. Due to stability, rechargeability and rapid inactivation against a broad spectrum of microorganisms, N-halamines are of critical interest for development of superior antimicrobial polymeric materials. N-halamines are simply defined as halogen stabilizers, since inactivation of bacteria occurs through direct transfer of oxidative halogen to the cell membrane [7,13].

Because there are versatile applications in which bactericidal polypropylene (PP) is desired, antimicrobial treatment of PP polymers/fibers has been extensively studied. Russel et al. introduced quaternary ammonium salts on the surfaces of PP through surface-initiated atom transfer radical polymerization and obtained about a five log reduction of *Escherichia coli* using a dynamic shake flask test [14]. In another study, chitosan was coated on PP nonwoven fabrics in order to provide antifungal and antibacterial functionalities [15]. Silver was employed through compounding with molten PP, and the produced PP/Ag composite provided three log reduction of *E. coli* and *Staphylococcus aureus* within 24 h [16]. N-halamines were also utilized to impart biocidal activity to PP; Sun and Badrossamay studied radical graft polymerization of several cyclic and acyclic N-halamines to the PP backbone during a reactive extrusion process and obtained very effective biocidal efficacy results with around six log reductions of Gram-positive and Gram-negative bacteria within 30–60 min of contact time [17,18]. Zhao and Liu also used N-halamines to render woven PP fabrics antimicrobial by forming a surface semi-interpenetrating thermoplastic network on the fabrics, and the treated swatches provided a six log inactivation of methicillin-resistant *S. aureus* within 30 min of contact time [19]. Even though these previous studies successfully provided bactericidal PP, a more rapid inactivation provided by a less sophisticated and reasonable treatment procedure is desirable, since most of the applications for antimicrobial PP-based materials are usually single-use applications. Furthermore, because N-halamines are contact biocides, instead of using them as an additive, it would be preferable to apply these biocides on the surfaces of materials to provide sufficient contact with microorganisms. Therefore, there is a need for N-halamine surface treatments of PP based materials with facile procedures.

Recently we have reported a novel N-halamine monomer, hydantoin acrylamide (HA) [20] and its application as a surface coating for cellulosic materials through copolymerization with various monomers containing different tethering groups [21]. Polyelectrolytes of HA were also synthesized and immobilized onto cotton fabric through a layer-by-layer technique which provided rapid inactivation against Gram-positive and Gram-negative

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bacteria [22]. In this study, single and multilayers of anionic and cationic polyelectrolytes of HA were deposited on melt-blown PP nonwoven fabric surfaces through a pad-dry procedure and a layer-by-layer technique in order to provide rapid inactivating bactericidal PP webs that could potentially be used for air filters, face masks, hygiene products, and food packaging materials.

2. Experimental

2.1. Materials and instrumentation

All starting chemicals were purchased from Aldrich Chemical Company (Milwaukee, WI), TCI America (Boston, MA), and used as is unless otherwise noted. Charged, melt-blown polypropylene nonwoven fabrics having basis weights of 50 g/m^2 and 22 g/m^2 were used as N95 respirator and surgical face masks, respectively. These were kindly donated by Hollingsworth & Vose Company. Clorox® brand (Clorox, Inc., Oakland, CA) household bleach was used for chlorination. Bacteria cultures of *S. 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).

ATR-IR data recorded with 32 scans at 16 cm^{-1} resolution were obtained with a Nicolet 6700 FT-IR spectrometer with an ATR (Attenuated Total Reflectance) accessory using a diamond crystal. NMR data were recorded using a Bruker 400 MHz spectrometer. A Frazier air permeability tester was used to measure air permeability.

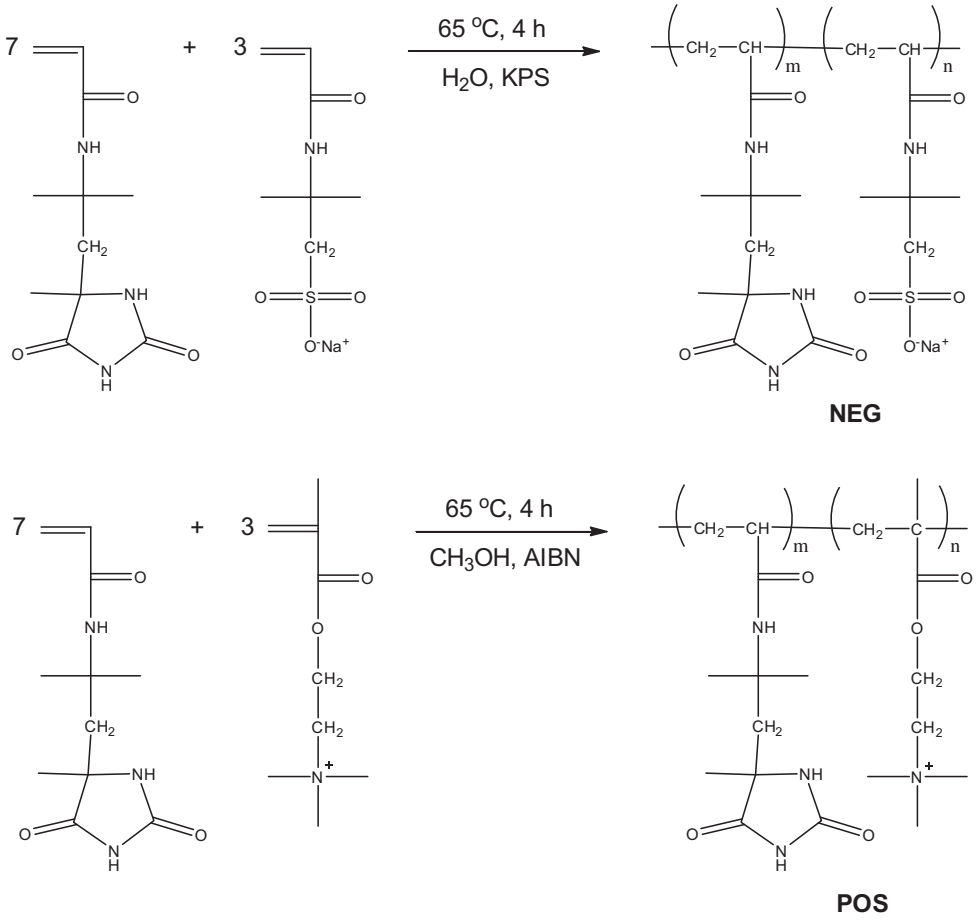
2.2. Synthesis of the copolymers

The copolymers were synthesized by free radical polymerization using azobis (isobutyronitrile) (AIBN) or potassium persulfate (KPS) as initiators. HA was synthesized by following a procedure outlined previously [20]. To synthesize hydantoinyl acrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid, sodium salt (NEG), 7 mmol of HA and 0.01 g of KPS were mixed with 3 mmol of 2-acrylamido-2-methyl-1-propanesulfonic acid, sodium salt in 50 mL water. After 15 min of N_2 flushing through the solution, the mixture was stirred for 4 h at 65 °C, and then the reaction mixture was cooled to room temperature, and the copolymer was obtained as a white solid after solvent evaporation under vacuum. The copolymer hydantoinyl acrylamide-co-trimethyl-2-methacryloxyethylammonium chloride (POS) was synthesized similarly, except the reaction was carried out using AIBN as the initiator and methanol as the solvent (Scheme 1).

2.3. Coating and chlorination procedure

Single layer coatings were obtained using a pad-dry procedure; 1 wt% of the copolymer POS or NEG along with 0.1% Triton X nonionic surfactant was dissolved in 10% Clorox solution buffered to pH 8.2 using $NaHCO_3$. Then the solution was applied on fabric swatches using a laboratory type wringer, and then dried at 45 °C for 2 h.

Multilayer deposition of the copolymers was achieved via layer-by-layer coatings. Briefly 0.2 wt% of copolymer POS or NEG and 0.1 wt% Triton X were dissolved in water in 300 mL glass



Scheme 1. Synthesis of the copolymers.