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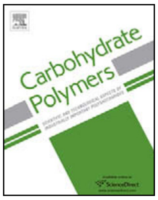

Cellulose fibers modified with nano-sized antimicrobial polymer latex for pathogen deactivation

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ABSTRACT

Antimicrobial cellulose fibers and paper products are of great importance for various applications. In this work, novel core–shell antimicrobial latexes based on hydrophobic acrylate monomers and antimicrobial macromonomer (GPHGH) were successfully prepared via a seeded semi-continuous emulsion copolymerization in the presence of a cationic surfactant. The surface properties as well as size of latex were tailored by varying the amount of GPHGH incorporated during the copolymerization. The resulting cationic nano-sized latexes showed the strong adsorption and formed monolayer on the surfaces of bleached sulfite fibers, thus rendering the cellulose fibers antimicrobial. An excellent antimicrobial activity (>99.99% inhibition) of modified fiber toward *Escherichia coli* was achieved at 0.3 wt% of latex dosage (on dry fibers). Results of transmission electron microscopy (TEM) observation confirmed that the particles obtained indeed possessed a desired core–shell structure. The latexes themselves exhibited high antimicrobial activities against *E. coli* with the minimum inhibitory concentration (MIC) as low as 6.25 ppm (similar to that of pure guanidine-based polymer). Moreover, the mechanical strength of the hand-sheets made from latex-modified cellulose fibers was also improved due to the filming of the latex on fiber surfaces.

1. Introduction

The lessons we leant from massive recalls on contaminated foods have raised the strong public demands on food packaging materials which enable to provide an excellent barrier toward bacteria or even deactivate the bacteria in contact. Over the past decades, several types of antimicrobial polymers have been developed and used in various circumstances, including the paint surfaces (Fulmer & Wynne, 2011), medical devices (Tilmaciu et al., 2015; Wang, Liu, Ji, Ren, & Ji, 2012) and hospital devices (Roquilly, Marret, Abraham, & Asehnoune, 2015; Yeroslavsky, Girshevitz, Foster-Frey, Donovan, & Rahimipour, 2015) in an attempt to eliminate the bacterial-induced infections. To date, the major antimicrobial polymer is quaternary ammonium compounds (quats)-based, which has been well document (Holappa et al., 2006). The other two types are the polymers consisting of phosphonium compounds (Zeng, Pignatello, Li, & Mitch, 2014) and halogenated sulfonamides (Limpachayaporn et al., 2014). The key advantages of polymer-based antimicrobial agents are relatively safe in use and long-term effectiveness against a broad spectrum of bacteria, i.e., both Gram-negative and Gram-positive ones. However, the relatively high minimum inhibition concentration (MIC) are often observed, particularly for the quats-based antimicrobial polymers (typical MIC > 100 ppm), resulting in relatively high dosage demanded during the application. Moreover, the deactivation process could be slow, taking hours to reach the maximum performance.

With the low MIC (<8 ppm), the guanidine-based polymers have been thoroughly investigated in our previous work (Guan, Xiao, Sullivan, & Zheng, 2007; Pan, Xiao, Zhao, & He, 2008; Qian, Guan, He, & Xiao, 2008; Wang et al., 2014) and reported by other groups (Coqueiro, Regasini, Stapleton, Bolzani, & Gibbons, 2014; Coquelle et al., 2015; Guan et al., 2007; Wang et al., 2015). The end products include cellulose fiber or paper, textile and plastic. The star polymer containing guanidine chains even showed high antiviral activity (Pan, Xue, Snow, & Xiao, 2015). However, the guanidine-based polymer itself is highly water-soluble and possesses low molecular weight, leading to the poor retention with substrates, particularly cellulose fibers for creating antimicrobial paper or packaging materials. To address this problem, the guanidine-based polymer could be grafted into a carrier in the presence of a proper coupling agent as we did previously using starch as a carrier

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(Guan, Qian, Xiao, & Zheng, 2008). Alternatively, the guanidine-based polymer could be converted into a macromonomer via introducing vinyl groups, enabling the polymer covalently bonded with carrier or functional substrates via copolymerization. The modification of cellulose fibers via grafting copolymerization has been well received (Dadkhah Tehrani & Basiryan, 2015; Guan et al., 2007; Rouabhia et al., 2014) though the relatively grafting efficiency remains as a key challenge. On the other hand, the latex particles obtained from the emulsion copolymerization using the functional macromonomers could be readily applied to papermaking process as wet-end additive or surface treatment agents, facilitating the modification of cellulose fibers with much higher efficiency.

Different from water-soluble polymer, the nano-sized latex, if designed properly, could form a thin functional layer on the substrates (e.g., cellulose fibers) upon being heated above its glass transition temperature (Tg). This requires the latex to possess cationic-charged groups and small particle size which ensure the strong adsorption of the latex particles on the surface of cellulose fibers via electrostatic association, followed by the filming formation at an elevated temperature above the Tg of latex (Li, Christian-Tabak, Fuan, Zou, & Cheng, 2014; Pan, Xiao, Zhao, & Wang, 2013). In such a manner, the latex acts as a functional carrier to immobilize antimicrobial agents, guanidine-based polymer in particular. Rahman and Elaissari (2012) produced submicron-sized core–shell temperature-responsive magnetic particles for controllable drug release. Garcia, Gonzalez, Marcipar, Vega, and Gugliotta (2014) covalently conjugated protein with latex complex for sensor application. However, the latexes mentioned above were used as supports; the bioactive materials were just immobilized or mixed into them. There are still some problems existed when they were used in the practice. For example, bioactive materials could not be dispersed in the latexes evenly and their bioactivity could not be stable over the prolonged period.

In this work, we aimed at developing a new type of latex containing antimicrobial property and core–shell structure. The latex was used as wet-end additive to modify the surface of natural fiber in an attempt to render the cellulose fibers highly antimicrobial. The polymeric monomers were selected based on the consideration of sufficiently high hydrophobicity, excellent filming capability and antimicrobial activity. Therefore, acrylate-type monomers such as butyl acrylate were chosen for hydrophobicity and filming whereas the antimicrobial macromonomer, i.e. the reactive modified guanidine polymer, was prepared as the key component for pathogen deactivation. Compared with general polymer latex particles, the latex with core–shell structures has significant advantages, such as minimum filming temperature or low glass transition temperature and improved filming properties created by proper copolymer in the core; meanwhile the hydrophilic shell, mainly consisting of guanidine polymer, facilitate the bonding to the substrates or specifically strong adsorption on cellulose fiber addressed in this work. Therefore, a range of polymer latexes bearing core–shell particles with hydrophobic core and antimicrobial shell were synthesized in this work, followed by comprehensive characterization. The novelty of this work represents the first attempt on rending cellulose fiber antimicrobial using the functional latex with tailored core–shell structures.

2. Materials and methods

2.1. Materials

Butyl acrylate (BA) and ethylhexylacrylate (EHA) monomers as well as glycidyl methacrylate (GMA) for reacting with guanidine-based polymers were purchased from Sigma–Aldrich, washed with alkali solution and distilled under reduced pressure before use. The initiator, 2,2′-Azobis (2-methylpropion-amidine) dihydrochloride (AIBA) (assay, 97%), used in preparing cationic PBA-co-EHA/GPHGH (CPBA-co-EHA/GPHGH) latex via emulsion polymerization, and the emulsifier, cetyl trimethyl ammonium bromide (CTAB) (assay, ≥99%) and crosslinker, ethylene glycol dimethacrylate (EGDMA) (reagent grade) were also obtained from Sigma-Aldrich and used as received without further purification. The condensation polymerization of hexamethylene diamine and guanidine hydrochloride led to the antimicrobial polyhexamethylene guanidine hydrochloride (PHGH) of low molecular weight (Pan et al., 2008). The cellulose fibers used in this work were bleached sulfite pulps, obtained from Twin-River Papers in Canada.

2.2. Synthesis of cationic PBA-co-EHA/GPHGH latex with core–shell structure

To incorporate vinyl groups into PHGH, GMA was used to react with PHGH to generate macromonomer GPHGH according to our previous work (Pan et al., 2015).

To create the desired core-shell structure of the latex with the low Tg of the core and antimicrobial shell, a seeded emulsion polymerization technique was adopted. The emulsion polymerization was conducted semi-continuously in the presence of a cationic emulsifier (CTAB) via a two-stage process. The monomer ratios were changed to produce the core–shell latex particles with different structures, shell ones in particular. In a typical copolymerization process with overall monomer molar ratio at BA:EHA:GPHGH = 15:10:1, 30.0 g of BA/EHA mixture at molar ratio of 15:10 (or 16/14 g) was first added to 180 ml of distilled water containing 0.3% to 4.0% of CTAB (wt on monomers) along with 0.15 g of initiator (0.5 wt% on monomers) and 0.3 g of EGDMA (1.0% of the monomer weight) as a crosslinker. This first-stage emulsion polymerization was performed in a 250 ml of glass flask equipped with a reflux condenser; and the nitrogen purging was applied to the mixture of monomers to remove oxygen for 30 min. The system was then heated to 60 °C to induce the copolymerization; and the polymerization proceeded for 2 h to obtain the core latex with a high monomer conversion. In the second stage of emulsion polymerization, 4.2 g (about 7.0 mmol) of macromonomer GPHGH, 0.021 g of initiator (0.50% of the monomer weight) were added the system above in an attempt to synthesize the shell of the latex. The initiator, dissolved in 16 ml of distilled water, along with GPHGH solution were placed in funnels and dropped into the emulsion containing core latex over 2 h period at 60 °C, i.e. a semi-continuous process.

Afterward, the emulsion polymerization was continued at 80 °C for another 2 h to ensure the high conversion of shell monomer. The chemical structure of resulting antimicrobial latex and the schematic of core–shell structure are shown in Fig. 1.

2.3. Characterization of latex with core–shell structure

The as-synthesized latex above was characterized in 0.1 mM KCl aqueous solution using a Malvern Nano-ZS to determine the zeta potential, mean particle size and size distribution. Particle charge detector PCD 03 (Herrsching, Germany) was used to determine the surface charge density of latex using potassium polyvinyl sulfate (PVSK from Alchi-Sigma) as a standard anionic polyelectrolyte.

The core–shell structure of the latex was visualized using a transmission electron microscope (TEM – JEOL 2011 STEM). The diluted samples were dropped onto copper grid and then stained with 2% phosphotungstic acid (PTA), dried overnight in a desiccator and analyzed.