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Preparation of novel stable antibacterial nanoparticles using hydroxyethylcellulose and application in paper

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ABSTRACT

Taking advantage of the self-assembly between the components, novel stable antibacterial nanoparticles were efficiently fabricated via a facile one-step co-polymerization of acrylic acid (AA) and *N,N′*-methylenebisacrylamide (MBA) on a mixed aqueous solution of poly(hexamethylene guanidine hydrochloride) (PHMG) and hydroxyethylcellulose (HEC). The *z*-average hydrodynamic diameters of the nanoparticles ranged from 220 nm to 450 nm. The inner layer of the nanoparticles is composed of water-insoluble interpolymer complexes of PHMG and PAA networks, while the outer layer is composed of PHMG and HEC. The nanoparticles are stabilized by electrostatic interactions, hydrogen bonding interactions, and the chemical bonds. The nanoparticle solution remained stable in a wide pH range of 2.0–12.0 and at salt concentrations below 0.25 mol/L. The nanoparticles were incorporated into handsheets using a dipping treatment. The resulted handsheets exhibited excellent antimicrobial activities even after multiple water washing treatments. The nanoparticles are promising in fabricating paper, water-based coatings and textiles with permanent antibacterial activity.

1. Introduction

The disease transmission and the surface contamination by micro-organisms is an issue of enormous concern. The application of antibacterial coatings with bacteriostasis or bactericidal activity in the medical, packaging, house and public places is an efficient way to reduce the threat of various pathogenic bacteria to the health and safe of the mankind. Due to the renewability, biocompatibility and biodegradability, the antimicrobial cellulose-based products such as paper, membranes and fibers have attracted great interest in some high level of hygiene, such as hospitals, pharmaceutical production units, food factories, water treatment, etc.

The antibacterial coatings are usually fabricated by simply incorporating various antibacterial agents. The nanoparticles of silver (Martins et al., 2012; Youssef, Kamel, & El-Samahy, 2013), zinc oxide (Cheng et al., 2014; Khatri et al., 2014; Koga, Kitaoka, & Wariishi, 2009), copper (Dankovich & Smith, 2014), titanium dioxide (Luo & Huang, 2015), and copper oxide (Booshehri, Wang, & Xu, 2015), as well as antibacterial agent-loaded micro(nano)fibrillated cellulose (Lavoine, Desloges, Sillard, & Bras, 2014; Liu, Chen, Huang, Ni, & Sun, 2015) were incorporated into the surface coating or the matrix of the paper, rendering the paper with antimicrobial

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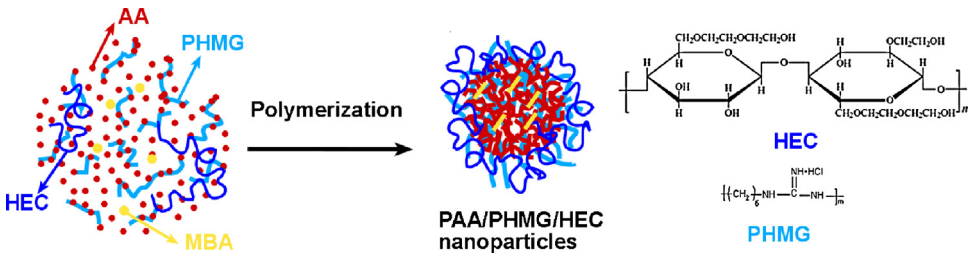

Scheme 1. The formation mechanism of PAA/PHMG/HEC nanoparticles.

properties. In addition, paper-based hygiene products have also been developed by using various modified paper additives, such as modified starch (Guan, Xiao, Sullivan, & Zheng, 2007; Guan, Qian, Xiao, & Zheng, 2008; Guan, Qian, Xiao, Zheng, & He, 2008), modified beeswaxes (Zhang & Xiao, 2013), chitosan and its derivatives (Chen, Li, Song, & Qian, 2014; Lv et al., 2014; Sun et al., 2010). Excellent antibacterial properties and non-leaching characteristics hold the important position in fabrication of the antibacterial paper.

Water-soluble polymeric guanidines are polycationic disinfectants with broad-spectrum activity against Gram-positive and Gram-negative bacteria, fungi, yeasts and viruses (Krebs et al., 2005; Müller & Kramer, 2005; Oulé et al., 2008). They have high binding affinities to the negatively charged cell walls and membranes of bacteria due to the positive charges, and the disruption is brought about by the perturbation of these sites (Gilbert & Moore, 2005; Qian, Guan, He, & Xiao, 2008; Zhou, Wei, Guan, Zheng, & Zhong, 2010). Polymeric guanidines also have low toxicity to humans and animals at the concentrations below 1% (Müller & Kramer, 2005; Oulé et al., 2008), and good thermal stability (Zhang, Jiang, & Chen, 1999). Therefore polymeric guanidines are widely used not only in the medicine, wound care, food industry and water treatment (Kratzer, Tobudic, Graninger, Buxbaum, & Georgopoulos, 2006; Oulé et al., 2008), but also in the fibers and plastics fields (Aleshina, Yudanova, & Skokova, 2001; Guan, Wang, & Zheng, 2003; Li, Hao, Chen, & Jiang, 2002; Wei, Zhou, Zhang, Guan, & Zheng, 2013).

Although the antibacterial coatings could be fabricated expediently by directly mixing polymeric guanidines with the coatings, the antibacterial activity will gradually reduce and lose after washing or exposure to rain due to the water solubility of polymeric guanidines. A method to avoid the leaching of polymeric guanidines is to prepare water-dispersible nanoparticles. To this end, water-dispersible poly(acylic acid)/poly(hexamethylene guanidine hydrochloride) (PAA/PHMG) nanoparticles with a narrow size distribution ($\langle D_h \rangle$ = 190 nm, P.D.I. = 0.09) were synthesized by a facile co-polymerization of acrylic acid (AA) and *N*,*N*′-methylenebisacrylamide (MBA) in an aqueous PHMG solution (Zhang, Chen, & Zhao, 2014). The nanoparticles displayed excellent antibacterial activities against *Staphylococcus aureus* and *Escherichia coli* (antibacterial rates >99.0% at a concentration of 5 g/L). However, the nanoparticles exhibited a limited stability, which might constrain their practical applications.

In this work, a small amount of hydroxyethylcellulose (HEC), which is not only widely used as stabilizers and protective agents for the colloids, but also can interact with PAA via formation of hydrogen bonds (Dou, Jiang, Peng, Chen, & Hong, 2003; Khutoryanskiy, Mun, Nurkeeva, & Dubolazov, 2004; Nikolava, Budtovam, Alexeev, & Frenkel, 2000), was introduced to improve the stability of the nanoparticles. Specifically, the stable PAA/PHMG/HEC nanoparticles were fabricated via a self-assembly-assisted polymerization, i.e., the co-polymerization of AA and MBA in a mixed aqueous solution of PHMG and HEC. Dynamic light scattering, transmission electron microscopy, and Fourier transform infrared spectroscopy were used to characterize the size, structure, and morphology of the nanoparticles, as well as the interactions between the components. The stability of the nanoparticle solution against the storage, pH value, and salt was also investigated in detail. Furthermore, the potential application of the PAA/PHMG/HEC nanoparticles as a novel antibacterial additive for the fabrication of antibacterial paper was evaluated.

2. Experimental

2.1. Materials

Hexamethylene diamine and guanidine hydrochloride were purchased from Sinopharm Chemical Reagents Co. Ltd. (Shanghai). Polyhexamethylene guanidine hydrochloride (PHMG) oligomer (Scheme 1) was prepared by condensation polymerization of hexamethylene diamine and guanidine hydrochloride according to the procedure reported in the literature (Wei et al., 2009), with $\bar{M}_n$ = 771 g/mol and $\bar{M}_w/\bar{M}_n$ = 1.31 estimated by electrospray ionization time-of-flight mass spectrometry. Hydroxyethylcellulose (HEC, M_η = 90,000, Aldrich) with an average number of substituted hydroxyl groups and molar substitution degree of 1.5 and 2.5, respectively, was used after desiccation to remove the absorbed moisture. Acrylic acid (AA) from Shanghai Reagent Company was distilled under reduced pressure prior to use. The initiator ammonium persulfate (APS, Shanghai Reagent Company) and the crosslinker *N*,*N*′-methylenebisacrylamide (MBA, Acros) were purified by re-crystallization in water and methanol, respectively. The accelerator *N*,*N*,*N*′,*N*′-tetramethyl ethylenediamine (TEMED, Acros) was used as received. A cellulose dialysis membrane bag with a cut-off molecular weight of 14,000 was used. Deionized water was used in all experiments.

2.2. Preparation of PAA/PHMG/HEC nanoparticles

The typical procedure was as follows: a mixture of 0.54 g of PHMG, 60 mg of HEC and 60 mL of aqueous hydrochloric acid (HCl) solution of pH 3 was first placed into a three-necked round-bottomed flask (100 mL) equipped with a magnetic stirrer and a thermometer. The mixture was stirred under constant agitation (300 rpm) over night to ensure the complete dissolution of HEC. Then, 0.6 mL of AA and 30 mg of MBA was added successively under gentle stirring and nitrogen bubbling. Polymerization was initiated at 35 °C by adding APS and TEMED successively. The reaction lasted for 2.5 h, followed by dialyzing against aqueous HCl solution of same pH value for 3 days to remove impurities.

Fixing the target degree of crosslinkage (i.e., $W_{MBA}/(W_{MBA} + W_{AA})$) at 5%, four series of PAA/PHMG/HEC nanoparticles were prepared by varying the amount of HEC, the pH value of the reaction medium, the weight ratio of AA to the sum of PHMG and HEC (i.e., the weight ratio of AA/(PHMG + HEC)), and the theoretical solid content. The nanoparticles prepared in a medium of pH 3, at a weight ratio of AA/(PHMG + HEC) of 1, at a HEC amount of 10% (based on the total weight of PHMG and HEC), at a theoretical solid content of 20 g/L were used for various