Colloids and Surfaces B: Biointerfaces 114 (2014) 60–66

Contents lists available at ScienceDirect

Colloids and Surfaces B: Biointerfaces

journal homepage: www.elsevier.com/locate/colsurfb

Plasma treated polyethylene terephthalate/polypropylene films assembled with chitosan and various preservatives for antimicrobial food packaging

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ARTICLE INFO

Article history:
Received 19 August 2013
Received in revised form
23 September 2013
Accepted 26 September 2013
Available online xxx

Keywords:
Plasma treatment
Chitosan
Preservatives
Antimicrobial activity
Release speed

ABSTRACT

In this study, polyethylene terephthalate/polypropylene (PET/PP) films were treated via atmospheric pressure plasma, assembled with chitosan and various preservatives and applied for antimicrobial food packaging. Surface properties of these obtained films were studied by contact angle measurement, atomic force microscopy (ATM), X-ray photoelectron spectroscopy (XPS), Fourier transformed infrared spectroscopy (FT-IR) and dynamic laser scattering (DLS). The above results showed that the surface hydrophilicity and roughness of the films increased after the plasma treatment. Besides, chitosan and the preservatives were successfully assembled onto the surface of the films. In addition, the antimicrobial activities of the films against three kinds of microorganisms (*Staphylococcus aureus*, *Bacillus subtilis* and *Escherichia coli*) were investigated and the results indicated that the inhibition ratios against *B. subtilis* and *E. coli* reached almost 100% while the inhibition ratios against *S. aureus* were lower than 85%. Moreover, the accumulative release profiles of the antimicrobial substances migrating from the assembled films into the release solutions revealed that their release speed increased with the increment of temperature and acidity, but decreased with enhancing the ionic strength regulated by sodium chloride or with lowering the ionic mobility regulated by sucrose.

1. Introduction

Nowadays, there have been considerable interests in antimicrobial and environmentally friendly food packaging due to the grim situation of food safety and environmental safety [1,2]. Herein, more and more researchers focused on fabricating antimicrobial food packaging films which are edible and/or biodegradable [3]. However, the poor mechanical and water vapor barrier properties of most degradable and edible materials make them not suitable for food packaging films, so the traditional polyolefin membranes are still used extensively, because of their good chemical resistance, high impact resistance, plentiful supply and low cost [4]. In spite of their outstanding characteristics, the polyolefin membranes possess little inherent antimicrobial activity and are susceptible to bacterial contamination [5]. Therefore, various methods have been developed to modify the polyolefin membranes such as incorporating antimicrobial agents into them [6,7], or assembling antimicrobial agents onto their surface [8].

Generally, polyolefin materials such as polyethylene, polypropylene and polyethylene terephthalate have poor surface adhesion properties [9]. Surface modifications including corona discharge, chemical etching and plasma modification are widely used to improve their surface adhesion abilities [10]. Plasma modification is much superior to others because it is more environmentally friendly and has lower destructive effects on the films [11]. Plasma treatment is mainly applied for the cleaning, sterilization and surface etching of the films in food packaging production. In fact, surface hydrophilicity and adhesion ability of the films increase dramatically after plasma treatment because polar groups are formed on film surfaces [5,11]. Therefore, further modification is possible such as assembling hydrophilic substances with antimicrobial abilities onto the surface of the treated films.

As the assembled substances on the polyolefin films would migrate from the films into foodstuff, the antimicrobial substances selected to be coated on the surface of the films should

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http://dx.doi.org/10.1016/j.colsurfb.2013.09.052

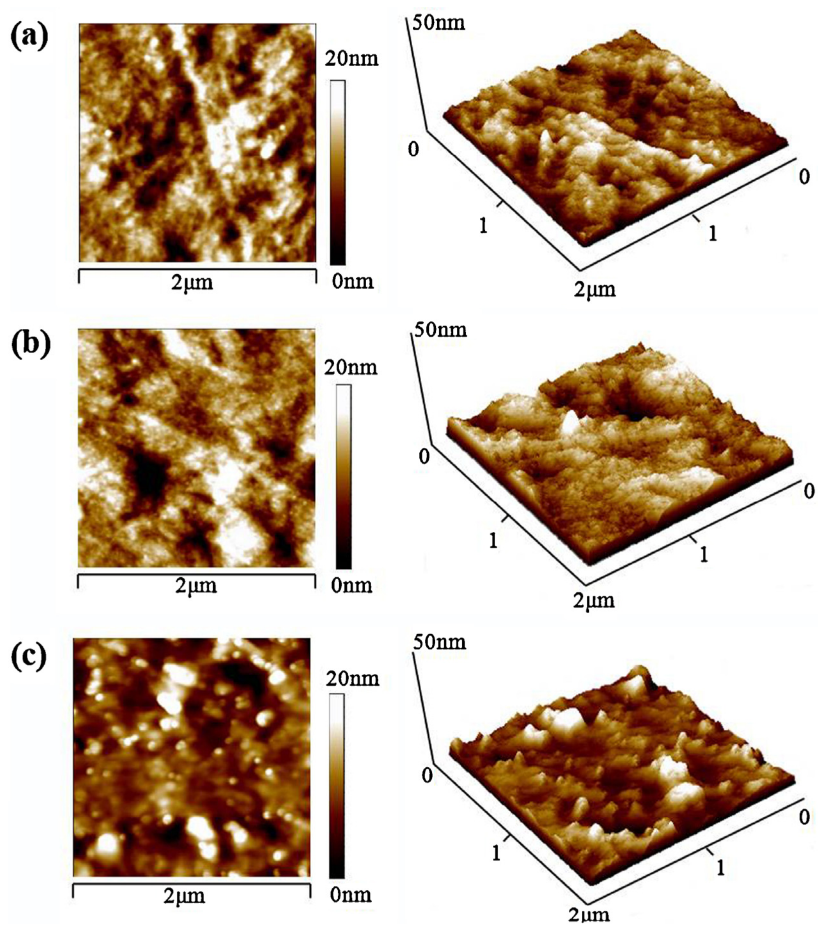

Fig. 1. AFM images of the surface of the films: (a) before plasma treated, (b) treated by plasma and (c) assembled with chitosan and potassium sorbate.

be safe and efficient [12]. Antimicrobial substances approved to be used in food consist of natural antimicrobial substances (chitosan, nisin, lysozyme and so on) and traditional synthetic preservatives (sodium benzoate, potassium sorbate, calcium propionate and so on). Chitosan (CS) is a bio-degradable and nontoxic polysaccharose with excellent biocompatibility, which is composed of β-1, 4 linked glucosamine and N-acetyl-D-glucosamine [13,14]. To the best of our knowledge, chitosan has good fiber and film forming properties [15,16]. Thus investigating its potential application on biomedical materials which could be used in drug delivery system and cell adhesion has aroused the interests of many researchers [16,17]. Besides, chitosan is a good candidate for antimicrobial films because of its superior film-forming property and antimicrobial ability [18]. Previous studies have proved that the combination of CS and other antimicrobial substances such as nisin and Ag^+ had better antimicrobial activities [19,20]. As traditional synthetic preservatives such as sodium benzoate, potassium sorbate and calcium propionate are widely used in keeping food fresh, it is important to investigate the composite antimicrobial effects of the mix of chitosan and each traditional synthetic preservative.

Until now, reports about polyolefin films coated with or compounded with CS, or about edible antimicrobial films fabricated by incorporating CS films with antimicrobial substances are tremendous, but reports about antimicrobial films fabricated by coating CS and traditional preservatives onto the surface of polyolefin films are few [21–24]. The main interests of this research were to fabricate a new type of food packaging by assembling the composite antimicrobial substances (the complexes of chitosan and the traditional synthetic preservatives) onto the plasma treated PET/PP films, and to investigate the surface properties and antimicrobial activities of the assembled films. Release profiles of CS and the preservatives under different conditions were also evaluated.

2. Materials and methods

2.1. Materials

The starting materials were used as follows: transparent PET/PP films (PET/PP with PP adhesive layer on one side, Hubei Liangli packaging Co., China), chitosan (CS, Mw 300 kDa, DD 91.5%, Zhejiang Jingke Biochemical Co., China), ε-poly-L-lysine (Zhejiang Yingxiang Bioengineering Co., Ltd, China). Other chemical reagents used in this research were all of chemical grade without any purification. All aqueous solutions were prepared using purified water with a resistance of 18.2 MΩ·cm. The microorganisms (*Staphylococcus aureus*, *Escherichia coli* and *Bacillus subtilis*) were provided by Huazhong Agriculture University in China.

2.2. Preparation of the assembled films

The 2% (w/w) CS solution was prepared by dissolving CS powder in 2% (v/v) acetic acid aqueous solution. Four kinds of traditional synthetic preservatives were compounded with the CS solution, respectively. The obtained solutions containing various concentrations of the preservatives including sodium benzoate, potassium sorbate, calcium propionate and ε-poly-lysine (the concentrations of ε-poly-lysine were 0.2, 0.4, 0.6, 0.8 and 1.0 wt.% while the concentrations of the other three preservatives were 1, 2, 3, 4 and