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ScienceDirect
European Polymer Journal 43 (2007) 3621–3628
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

Preparation and antibacterial activity of hybrid materials containing quaternary ammonium salts via sol–gel process

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Received 18 October 2006; received in revised form 27 March 2007; accepted 1 June 2007
Available online 15 June 2007

Abstract

Organic–inorganic hybrid coatings containing quaternary ammonium salts (QAS) bonded to the organic–inorganic network were prepared from tetraethoxysilane and triethoxysilane terminated poly(ethylene glycol)-block-poly(ethylene) using a sol–gel process. They were applied as a thin layer (0.6–1 μm) to PE films and the antibacterial activity of the coated films was tested against both Gram-negative (*Escherichia coli* ATCC 25922) and Gram-positive (*Staphylococcus aureus* ATCC 6538) bacteria. Measurements at different contact times showed a rapid decrease of the viable count for both the tested strains. In particular, after 48 h of contact, a decrease of 96.4% and 99.1% of *E. coli* and *S. aureus,* respectively, was observed. The permanence of the antibacterial activity of the coated films was demonstrated through repeated washings and prolonged immersion in physiological saline solutions at 37 °C. Indeed, due to the removal of QAS moieties by the nucleophilic attack of water, the antibacterial activity after 24 h was strongly reduced when measured on samples submitted to several washings. However, a quite good antibacterial activity was observed even on the same samples after 96 h, probably due to a spontaneous partial restoring of the QAS on the surface. Very good transparency, quite good adhesion and high wettability are further features of these hybrid coatings.

Keywords: Organic–inorganic hybrid materials; Sol–gel process; Quaternary ammonium salt; Antibacterial activity; Polyethylene

1. Introduction

Plastics, combining low cost with good mechanical properties and easy processability, are widely used to prepare biomedical devices and food packaging; however, typically they do not present antibacterial activity, an important feature desirable for both biomedical and food packaging applications to prevent human beings to be infected by microorganisms like bacteria, moulds, yeasts, viruses, etc., present in the living environment.

Novel plastic materials with antibacterial properties can be prepared for this purpose either by polymerization or copolymerization of new monomers [1] and/or blending of polymers [2]. However, the development of new materials using new monomers

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0014-3057/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2007.06.002

often leads to unacceptable high costs and changes in the bulk properties, and sometimes the obtained materials suffer from poor thermal stability which limits their processability.

When specific surface properties are required, another more attractive strategy is the use of functional coatings, which allows one to modify the surface properties of a given substrate leaving unchanged the bulk properties. Of course in order to meet the required functionality and durability, good mechanical properties of the coating and good adhesion to the substrate are critical points.

Among the various existing approaches to coat plastics, the preparation of organic–inorganic hybrid coatings by a sol–gel process seems particularly attractive because it presents several advantages such as high purity of the reactants and of the resulting products, mild processing conditions (low temperature, atmospheric pressure), possibility of controlling connectivity and morphology by a suitable choice of reactants, catalyst and reaction conditions, easy application to any kind of substrate geometry, transparency due to the nanosized organic and inorganic domains, good balance of mechanical properties, barrier properties, wettability and, particularly interesting for this study, the possibility to include in the starting solution reactive organic products containing functional moieties. Therefore, the organic–inorganic hybrid materials that can be prepared by the sol–gel process have a huge of potential applications as they can behave as multifunctional coatings when suitable reactants and reaction conditions are used. In fact, it seems possible to prepare coatings that show antibacterial activity in addition to other properties such as good scratch resistance [3], controlled wettability [4], flame resistance [5] and improved barrier against leaching of the additives included in coated plastics [6].

Indeed the possibility of preparing bioactive materials by using the sol–gel approach has been recently proposed [7–10].

Antibacterial plastics are frequently obtained by including various organic and inorganic substances, such as tea extraction, chitosan, copper, silver, zinc, etc. [11–24], in various polymer matrices.

Biocides incorporated in film-forming polymers are generally active by diffusion in the environment and may have some negative effects. For instance, the use of tin derivatives has been the object of severe restrictions for this reason. Since a long time, quaternary ammonium salts (QAS) have been known to be active moieties against microorganisms by interaction with the cell membrane and therefore offer an interesting alternative to heavy-metal additives because one may expect coatings be active by contact without liberation of toxic compounds, and therefore QAS-containing polymers have been prepared and were the object of several investigations [25–28]. However, when QAS are included in polymer matrices they present two main drawbacks: (i) they can be easily removed by diffusion when in contact with liquids, leading to a fast loosing of the antibacterial activity, and (ii) QAS are known to be not stable at high temperature when in contact with good nucleophiles, as "QA are good outgoing groups which are transformed into tertiary amines when in contact with water or nucleophilic compounds" [29].

In order to overcome the diffusion of antibacterial additives from a plastic matrix, extensive researches have been carried out in the last decades to prepare plastics containing antibacterial moieties covalently bonded to the polymer [1,2,7–25], the challenge being to obtain good biocidal activity with permanency after washing.

In this context we decided to investigate the preparation of antibacterial hybrid coatings containing a quaternary ammonium salt covalently bonded to the organic–inorganic network. A novel trialkoxysilane quaternary ammonium salt was synthesized for this purpose and was added to other reactants to obtain a coating by sol–gel reactions. The main goal of this study was to demonstrate that the application of sol–gel coatings to plastics is a possible approach to develop new multifunctional biomaterials (as it was recently reported for the nitric oxide release [30]) that combine good and permanent antibacterial activity with other properties typical of hybrid materials such as good scratch resistance and barrier against leaching of plastics additives. In particular, in this paper we describe the preparation and the characterization of QA-containing hybrid materials, and their antibacterial effect when used as coating for plastics.

2. Experimental section

2.1. Materials

Bubble extruded LDPE thin films (50 μm thick, supplied by Polimeri Europa S.P.A.) was used, as received without any surface pre-treatment, as polymer substrates for hybrid coatings.