Chemical Engineering Journal 204–206 (2012) 210–216

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Preparation and antimicrobial activity of polyethylene composite films with silver exchanged zeolite-Y

Daiane Lúcia Boschetto [a,1], Lindomar Lerin [a,1], Rogério Cansian [a], Sibele Berenice Castellã Pergher [b], Marco Di Luccio [a,*]

[a] Department of Food Engineering, URI – Campus de Erechim, Av. Sete de Setembro, 1621, 99700-000 Erechim, RS, Brazil
[b] Institute of Chemistry, Universidade Federal de Natal, Av. Senador Salgado Filho, 3000, Lagoa Nova, Campus Universitário, 59078-970 Natal, RN, Brazil

HIGHLIGHTS

- Silver exchanged zeolite Y was successfully impregnated in polyethylene films.
- Impregnation of Ag–zeolite in the films did not change the film properties.
- The films showed antimicrobial activity against *Escherichia coli*.

ARTICLE INFO

Article history:
Received 9 April 2012
Received in revised form 5 July 2012
Accepted 16 July 2012
Available online 3 August 2012

Keywords:
Zeolite
Silver
Antimicrobial packaging
Active packaging
Polymer film

ABSTRACT

This study aimed at the preparation of antimicrobial films based on silver (Ag) exchanged zeolite Y. The zeolite was exchanged to a final concentration of 5% silver and was characterized by different methods. The inclusion of silver in the zeolite did not change its structure. The antimicrobial activity of the Ag-exchanged zeolite was assessed on *Escherichia coli*, by the minimum inhibitory concentration method (MIC). The zeolite with 5% Ag showed effective antimicrobial activity. The MIC was 0.5 mg zeolite/mL, which corresponds to 25 μg Ag/mL. The leaching of Ag ions to the medium was assessed by AAS, which showed that 56% of the silver ions was leached from the zeolite to the medium. The polyethylene films with the Ag–zeolite were prepared by the methods of wet-casting and thermal pressing of polyethylene beads mixed with Ag–zeolite, varying the zeolite content from 1 to 10 wt%. The inclusion of the Ag–zeolite in the film did not change the film thermal degradation. The films that showed antimicrobial activity on *E. coli* were those prepared with 5% zeolite containing 5% silver, showing the potential application of such films in food preservation and safety.

1. Introduction

The food package is an important factor on food preservation and quality. The importance of packaging has been increasingly receiving much importance due to the new consumeŕs behavior (internet shopping, consumption of fast meals, frozen meals, demands for frozen meals packed in individual portions, etc.), which arises a new market for food. These new markets demand distribution for longer distances, and thus require increased food shelf life [1–3].

Microbial growth has been motivating the development of innovations for inhibition of microbial contaminants in foods. Active packaging can be used with the purpose to extend producťs shelf life. Examples of active packaging are the antimicrobial packaging that is able to control microbial growth in a food product. This concept includes the packaging material and edible films that contains the antimicrobial agents, and also techniques that modify the atmosphere inside the packaging [4].

The use of an active packaging can increase safety and quality of the food, by interaction of the active principle contained in the packaging material with the food or the microorganisms. These technologies may increase the shelf life and reduce the risk of contamination by pathogens [5,6].

The inclusion of antimicrobial substances in plastic films has the purpose of their gradual release on the surface of the food, inhibiting the growth of microorganisms, increasing the shelf life and safety of the product [7]. The antimicrobial agent interacts with the product or with the headspace between the package film

* Corresponding author. Present address: Departamento de Engenharia Química e Engenharia de Alimentos, Universidade Federal de Santa Catarina, Caixa Postal 476, 88040-900 Florianópolis, SC, Brazil. Tel.: +55 48 3721 2529; fax: +55 48 3721 9687.
E-mail address: diluccio@enq.ufsc.br (M. Di Luccio).
[1] Present address: Departamento de Engenharia Química e Engenharia de Alimentos, Universidade Federal de Santa Catarina, Caixa Postal 476, 88040-900 Florianópolis, SC, Brazil. Tel.: +55 48 3721 2529; fax: +55 48 3721 9687.

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http://dx.doi.org/10.1016/j.cej.2012.07.111

and the food, decreasing the growth of microorganisms present on the food or package surface [5,8,9].

Silver is a metal with well-known antimicrobial properties. At low concentrations, it does not cause toxicity and its use can reduce the resistance problems due to resistant bacteria [10–12,13].

The bactericidal activity of silver is well known. It is used in a wide variety of compounds as topic agents for treatment of burns and ocular infections, as well as additive in dental materials and polymers for food packages [12–16]. The silver ions act on a wide range of bacteria, yeasts and molds, by altering their metabolism. The silver ions inactivate the membrane proteins resulting in DNA damage. Also, they help in generating chemical species reactive to oxygen, form complexes with sulfur, nitrogen and oxygen, damaging cell division mechanism [9,14,17,18].

The antimicrobial properties of silver are often related with the amount of silver and the rate of silver ions release from the materials. In its metallic state (Ag^0) it is inert, but metallic silver can react with skin or food moisture forming active silver ions (Ag^+) [10,19,20].

The direct deposition of metallic silver onto the surface of a substrate by vapor deposition, sputtering, ion beam coating and electrochemical deposition from solution has been studied elsewhere [4,21–25]. These techniques generally suffer from poor adhesion onto surface and poor coating uniformity. Therefore, special and time consuming processing conditions or special techniques for the surface preparation are needed [12,16].

The incorporation of silver into molten polymers is another conventional approach to obtain antimicrobial polymer composites. Consequently, silver ions become available on both inner and outer surfaces of composites that could experience contact with microorganisms like the food packages [12,15,16].

There are many studies related with the application of antimicrobial agents in polymer films and their effect on pathogens. The antimicrobial activity of silver containing zeolites on different microorganisms has been studied elsewhere, drawing commercial and industrial interest, mainly on health and food applications [3,12,15,25,26–31]. Some reports on the production of polymer films impregnated with silver containing zeolites can also be found in literature [15,30–32], but they are often focused on health applications.

There are some advantages of loading silver into the zeolite and then loading the Ag–zeolite into the polymer matrix. The antimicrobial potential is increased since both sides of the films are active [31], and also the diffusion rate of Ag out of the material is slower, when contrasted to loading the silver ions directly into the polymer matrix. This may increase the potential application in long-term antimicrobial behavior and safety for food applications, since smaller amounts of silver are released in the food that is in contact with the package [33].

Although studies could be found, concerning the application of silver containing zeolites on polymer films, like polypropylene [15], polyurethane [30] and polylactide [31], at the authors' best knowledge, the impregnation of polyethylene films with such antimicrobial agent is still scarce in the scientific literature. In this context, the aim of this work was to study the preparation of polyethylene films containing silver exchanged zeolite-Y, and characterization of antimicrobial activity and color of the films.

2. Experimental

2.1. Materials

A commercial zeolite Y was used in the tests (CBV100). The model microorganism tested in antimicrobial activity study was a strain of *Escherichia coli* (ATTC 25922). For microbiological analyses two different media were tested. Luria Bertani (LB) was used in the tests for determination of minimum inhibitory concentration (MIC) and contained tryptone 10 g/L (Vetec, Rio de Janeiro, Brazil), yeast extract 5 g/L (Vetec), sodium chloride 5 g/L (Reagen, São Paulo, Brazil). Müller–Hinton agar (Merck, São Paulo, Brazil) 34 g/L was used for plate diffusion method. Commercial low-density polyethylene (LDPE) in pellet form was used as base polymer for the preparation of the films.

The silver ions were obtained with silver nitrate (Merck, 99%). For wet casting film preparation, 1,2 dichlorobenzene was used for LDPE solubilization.

2.2. Silver exchange in zeolite Y

The incorporation of silver in zeolite Y was accomplished by ionic exchange. Three grams of zeolite Y and 50 mL of an aqueous solution of silver nitrate 0.47% (w/v) was kept under reflux at 80 °C for 16 h with magnetic stirring. After separation from the solution, the zeolite was dried at 100 °C and stored in well-closed flasks.

2.3. Characterization of materials

The characterization of silver exchanged zeolite Y was carried out by X-ray diffraction spectroscopy (XRD, Diffraktometer D5000, Siemens, WI, USA), scanning electron microscopy (SEM, SSZ550, Shimadzu, Japan), energy-dispersive X-ray spectroscopy (EDX, JSM 5800, Jeol Ltd., Japan), BET surface area analysis (Autosorb 1MP, Quantachrome, FL, USA) and inductively coupled plasma optical emission spectroscopy (ICP-OES, Spectro Ciros CCD, Spectro Analytical Instruments GmbH, Germany).

The polymeric material was characterized by thermogravimetric analysis (TGA Q50, TA Instruments, DE, USA), differential scanning calorimetry (DSC-2100, TA Instruments) and instrumental color (CR400, Konica Minolta, NJ, USA).

2.4. Antimicrobial activity of silver exchanged zeolite

The antimicrobial analysis of Ag–zeolite was carried out by minimum inhibitory concentration (MIC) technique, using *E. coli* ATCC 25922. The MIC was determined by indirect method based on estimation of bacterial growth by optical density in liquid culture medium. The selected microorganism was cultivated in LB medium at 37 °C for 24 h. After growth, 40 μL of pre-inoculum was transferred to 4 mL of sterile LB broth containing different amounts of Ag–zeolite. The test tubes were incubated at 32 °C for 24 h in a reciprocating shaker at 120 rpm.

Samples of 120 μL were taken at 0 and 24 h of incubation and analyzed in a microplate reader at 490 nm (EL800, Bio-Tek Instruments Inc, Winooski, USA). Triplicates were carried out for each run. The amount of zeolite tested ranged from 0.025 to 25 mg zeolite/mL.

2.5. Silver leaching to the medium

For determining the amount of silver leached from the zeolite to the liquid medium, 4 mL of the LB medium was placed in test tubes with different amounts of Ag–zeolite or polymer containing Ag–zeolite, and incubated at 32 °C for 24 h in a reciprocating shaker at 120 rpm. The LB medium was used for leaching tests instead of water, since other studies show that the Ag^+ release can be increased due to the presence of other cations that can exchange the Ag^+ sites [20].

After separation of the solid sample from the liquid by centrifugation or settling, the amount of silver in the supernatant was determined by atomic absorption spectroscopy (AAS55, Varian, USA) using a hollow-cathode lamp (λ = 328 nm) and a mixture of air and acethylene.