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

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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.

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.

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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 consumers' 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 products 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...
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 (Ag⁰) 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* (ATCC 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 S800, Jeol Ltd., Japan), BET surface area analysis (Auto- sorb 1MP, Quantachrome, FL, USA) and inductively coupled plasma optical emission spectroscopy (ICP-OES, Spectro Ciroc 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 Ag⁰ 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 (AA555, Varian, USA) using a hollow-cathode lamp (λ = 328 nm) and a mixture of air and acetylene.
2.6. Polymer film preparation

The LDPE films were prepared by two different methods: hot casting and wet casting. For hot casting method, the samples were pressed from 80 to 130 °C in a hydraulic press (3710-ASTM, Carver Inc., USA), from 5 to 10 ton, obtaining homogeneous films with 200–300 μm, after cooling at room temperature.

For wet casting method, the polymer (1 g) was solubilized in 1,2-dichlorobenzene (30 mL) under reflux at 120 °C. After solubilization, the solution was cast onto a Petri dish, and the solvent evaporated at room temperature in a hood chamber, until complete solidification of the film.

The films containing zeolite were prepared by dispersing 1–10% (w/w) of zeolite in the polymer solution after polymer solubilization.

2.7. Antimicrobial activity of composite films

The determination of antimicrobial activity of the polymer films was carried out by plate diffusion method. 100 μL of a previously prepared microbial culture was spread over a Petri dish containing Müller–Hinton agar. The polymer films were cut into disks of 7 mm diameter. Four disks were placed on the agar in each plate. The Petri dishes were incubated at 37 °C for 48 h. A control run was carried out with the polymer without any zeolite. Samples were run in triplicates. The inhibition halos were measured with a paquimeter.

3. Results and discussion

3.1. Characterization of zeolite Y impregnated with silver

Fig. 1 shows zeolite Y diffractograms, before and after the impregnation of silver concentration. The diffractograms are typical in Faujasite (IZA) structure. Comparing the diffractograms, it can be noted that the zeolitic structure is maintained after the incorporation of Ag⁺. Only a small decrease in crystallinity occurs, evidenced by the small decrease in the peak intensity. Garza et al. [11] infused up to 10% of silver in the clinoptilolite zeolite. They also found that there was no change in the zeolite diffractograms after impregnation. Only in very high concentrations of silver, the structure could show some significant changes.

According to the EDX analyses results (data not shown), the molar ratio Si/Al of the material does not change significantly with Ag exchange and remains around 3.4 (see Fig. 2).

Table 1 shows the crystallinity of the materials and the values in the specific area BET, using the commercial zeolite Y as standard (100%). It is proved that the incorporation of Ag leads to a loss of crystallinity and specific area, probably due to a small destruction of the structure and to the blockage of the pores impregnated with Ag. This table also shows the levels of Ag obtained by EDX and ICP-OES. The overall content of Ag approaches 5%, as observed by ICP. However, higher content of Ag were obtained by EDX, probably due to a higher Ag concentration in the outer surface, what explains the large amount of silver leached out of the zeolite in the leaching tests of free zeolite in aqueous medium.

The evaluation of zeolite impregnated with different concentrations of silver by the micrographs allowed observing the morphology of the zeolitic structures. Fig. 3 shows the morphology of pure commercial zeolite Y (a); and zeolite Y with 5% of silver (b). It is observed that the process of incorporation of Ag in the structure does not change its morphology, which is consistent with the previous results.

Awuah et al. [17] incorporated 5.8% of silver in the zeolite X, which has the Faujasite structure like the zeolite Y, and studied
possible changes in the zeolite structures due to this incorporation. Through scanning electron microscopy analyses, the authors found that zeolites with or without silver had a very similar particle size and appearance, confirming that there was no change in the zeolite structure with the presence of silver, which is consistent with the results obtained in our work.

3.2. Antimicrobial activity of zeolite Y impregnated with silver

The antimicrobial activity of zeolite Y impregnated with silver was determined by the minimum inhibitory concentration (MIC) evaluated by optical density at a wavelength of 490 nm in microplates. The MIC was defined as the lowest concentration of the Ag–zeolite, in which there was no growth detected after 24 h of incubation. The analysis was performed by testing the zeolite impregnated with 5% of silver in amounts ranging from 0.025 to 25 mg of zeolite/mL. A control test was performed with the commercial zeolite Y without the impregnation with silver, and other control was carried out only with the bacteria, for comparison of antibacterial activity (Table 2). Assays with higher amounts of zeolite could not be performed, since the zeolite particles interfered with the spectrophotometric reading, due to the large amount of solids present in the liquid.

Table 2 shows that a concentration of 0.5 mg/mL of the zeolite containing 5% of silver inhibited bacterial growth. The tests performed with zeolite Y without the presence of silver showed no antimicrobial activity, and a fast growth of the bacteria was observed, confirming that the antimicrobial activity was due to the presence of silver ions in the zeolitic structure that was gradually delivered to the medium.

Other authors performed tests of the antimicrobial activity of zeolite A and X impregnated with 5.8% of silver, proving that they also showed antimicrobial activity against *E. coli*, *Pseudomonas aeruginosa* and *Staphylococcus aureus* [17].

Fig. 4 shows the antimicrobial activity of silver in the zeolite. The concentration of 5% of silver inhibited the growth of bacteria within 24 h of testing, proving to be an effective antimicrobial agent. The minimum inhibitory concentration found to this zeolite was 0.5 mg zeolite/mL corresponding to 0.025 mg Ag/mL.

Awuah et al. [17] and Kawahara et al. [34] found that the zeolite is responsible for the slow and sustained release of silver ions from the structure to the medium containing the microorganisms. According to Matsumura et al. [14], Feng et al. [35] and Yamanaka et al. [36], the mechanism of bactericidal action occurs in the first place by the contact between the bacteria and zeolite containing silver. The microorganisms absorb the silver ions, which inhibit its essential enzymes that are necessary for ATP production. This action also includes plasmolysis and partial rupture of the cytoplasmic membrane and of the outer membrane. Yamanaka et al.
states that the silver ions interact with the cell cytoplasm, causing the plasmolysis.

3.3. Leaching tests for silver in water

In antimicrobial packaging, it is necessary to know the conditions and characteristics of migration of substances added to the packaging material. It is important that these substances migrate to the food surface for an effective antimicrobial action and, at the same time, it is necessary to identify the amount of substance that is present in the foodstuff at the moment of consumption, so that the content of silver is below the maximum allowed for food. The results showed that 56% of the silver present in zeolite was leached to the medium, in the test conditions, for zeolites containing 5% of silver in the structure. When these zeolites with silver are added to the polymer, the leaching amount drops considerably to about 5%. This result shows that the impregnation of the zeolite in the polymer can decrease the releasing rate of silver to the medium. The release of Ag from the zeolite in the free form is expected to be much higher than from the zeolite trapped into a polymeric matrix. When the zeolite is immobilized, the release rate is lower due to increased resistance for diffusion of the ions from the zeolite cross the polymeric matrix to the bulk medium [33].

The levels of Ag released in the medium by the film are in accordance to EU regulations. The European Food Safe Authority (EFSA) has published a restriction regarding silver migration into food matrices, which was based on toxicological data. The maximum silver migration is limited to 0.05 mg Ag+/kg of food, and maximum content in polymer is limited to 10% (w/w) of silver zeolite A, with less than or equal to 5% silver [13].

Radheshukumar and Munstedt [16] impregnated 8% of silver in polypropylene films and assessed the amount of silver that was released from the polymer in water by voltammetry. Another test was carried out by the preparation of composite films to verify if the leaching of silver was only superficial. It was observed that, even in composite films, there was a release of silver to the medium, but to a lesser extent, proving that not only the superficial silver is released to the surrounding medium.

3.4. Polymer characterization

The DSC curves for cooling and second heating are showed in Figs. 5 and 6, respectively, for the polymer film with different amounts of zeolite incorporated (0%, 1%, 2%, 3%, 5% and 10%). The impregnation of zeolite had no significant effect on the melting and crystallization temperatures.

![Fig. 5](image1.png)  
**Fig. 5.** Melting temperatures of LDPE films with different amounts of zeolite Y, determined by DSC (heat flow endo up).

![Fig. 6](image2.png)  
**Fig. 6.** Crystallization temperatures of LDPE films with different amounts of zeolite Y, determined by DSC (heat flow endo up).
The crystallization temperatures \( (T_c) \) and the melting temperatures \( (T_m) \) calculated for all conditions are shown in Table 3, as well as the degree of crystallinity \( (%c) \) of the polymers impregnated with different amounts of zeolite.

The data in Table 3 were examined by analysis of variance (ANOVA), followed by Tukey’s test to check for the difference among the media. No significant difference among the temperatures and the crystallinity values was observed, indicating that there was no change in the polymeric material characteristics with the addition of zeolite. The crystallization and melting temperatures agree with those reported for the LDPE \( (T_c: 78–105 \degree C, T_m: 101–126 \degree C) \) [20]. Pehlivan et al. [15] incorporated zeolite in polypropylene and also found that the impregnation of the polymer films with zeolite did not change the melting and crystallization temperatures of the polymer, suggesting the other characteristics of the polymer might as well not be affected by the addition of zeolite-Y.

TGA tests of the samples containing Ag–zeolite were carried out, but no change in degradation temperature was observed. The mass remained constant until 400 \degree C, where the onset of the polymer degradation was detected. This behavior is consistent with the one reported for the commercial low-density polyethylene [22], and shows that no residual solvent is present in the sample.

The color analyses of the films are shown in Table 4. It is observed that the films prepared by pressing showed lower \( L' \) values than the films with no zeolite and no silver and also lower than the one prepared with zeolite and silver by wet casting. This result shows that, in the films prepared by wet casting, the stability of the silver in the film was higher, with probably less reduction of silver ions in the film. The high temperature and pressure during the preparation of the pressed films may have contributed for the reduction of silver, causing the film to become darker.

The \( a' \) and \( b' \) values were also different among the films containing Ag–zeolite prepared by wet casting and by pressing. Both parameters were higher for the films prepared by pressing, indicating a higher saturation in the colors red \( (a') \) and yellow \( (b') \). This tendency to yellowing can also be related to the reduction of silver contained within the polymer film. It is also observed that the increase in the Ag–zeolite content in the film obtained by pressing

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**Table 3**

| Sample | \( T_m \) (\degree C) | \( T_c \) (\degree C) | \( C(\%c) \) | \( C(T_m) \) (\%c) |
|--------|----------------------|----------------------|-------------|---------------------|
| LDPE   | 124.5 ± 0.7          | 109.0 ± 0.7          | 23.0 ± 1.4  | 25.5 ± 3.5          |
| LDPE 1%| 124.0 ± 0.7          | 111.0 ± 2.8          | 24.5 ± 0.7  | 24.5 ± 0.7          |
| LDPE 2%| 125.5 ± 0.7          | 107.5 ± 0.7          | 26.5 ± 3.5  | 27.0 ± 2.8          |
| LDPE 3%| 124.5 ± 0.7          | 108.0 ± 0.7          | 23.0 ± 0.7  | 25.0 ± 0.7          |
| LDPE 5%| 125.0 ± 0.7          | 107.5 ± 0.7          | 25.0 ± 0.7  | 24.5 ± 0.7          |
| LDPE 10%| 123.5 ± 0.7         | 108.5 ± 0.7          | 25.0 ± 1.4  | 24.0 ± 1.4          |

* Percentages in the sample name stand for the amount of zeolite in the polymer film composition.

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**Table 4**

| Sample          | \( L' \) | \( a' \) | \( b' \) |
|-----------------|----------|----------|----------|
| LDPE wet-cast   | 95.98    | 0.50     | 2.69     |
| 1% LDPE-Z-wet-cast | 95.82   | 0.01     | 3.08     |
| 2% LDPE-Z-wet-cast | 95.78   | 0.21     | 2.68     |
| 3% LDPE-Z-wet-cast | 91.71   | 0.05     | 2.2      |
| 4% LDPE-Z-wet-cast | 95.8    | 0.04     | 2.85     |
| 5% LDPE-Z-wet-cast | 80.46   | 2.11     | 5.88     |
| 10% LDPE-Z-wet-cast | 95.38  | 0.17     | 2.32     |
| 10% LDPE-Z-Ag-wet-cast | 76.84  | 4.87     | 9.69     |
| LDPE-pressing   | 90.46    | 0.28     | 5.78     |
| 1% LDPE-Z-Ag-pressing | 86.59  | 1.19     | 13.00    |
| 2% LDPE-Z-Ag-pressing | 82.69  | 1.31     | 21.17    |
| 3% LDPE-Z-Ag-pressing | 77.10  | 2.56     | 16.91    |
| 4% LDPE-Z-Ag-pressing | 73.65  | 2.20     | 20.44    |
| 5% LDPE-Z-Ag-pressing | 77.10  | 2.56     | 16.91    |
| 10% LDPE-Z-Ag-pressing | 73.65  | 2.20     | 20.44    |

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![Fig. 7](image-url) Tests for determination of inhibitory activity (a) of film prepared by wet casting, (b) pressed film with 5% of Ag–zeolite, (c) film obtained by wet casting with 5% of Ag–zeolite and (d) amplification of c.
led to greater discoloration. This behavior was also observed by Pehlivan et al. [15], who analyzed the polypropylene containing Ag–zeolite. However, these authors do not discuss the cause of the film discoloration.

3.5. Antimicrobial activity of the polymer containing zeolite impregnated with silver

The results obtained from the tests of the plate diffusion method showed antimicrobial effectiveness proportional to the concentration of silver in the polymer and to the way it was prepared. Fig. 7 shows the inhibition halos on *E. coli* growth after 24 h of incubation. The halo obtained with the use of the film prepared by pressing was around 3 mm, while for the film prepared by wet casting, the halo was around 7 mm.

The lowest antimicrobial activity of the film prepared by pressing occurs probably due to the high temperatures used for the process, which may affect the stability of silver, causing its reduction. Another reason could be the loss of the antimicrobial agent effectiveness, due to its non-homogeneous distribution in the film and, thus, it is not completely exposed on the surface of the polymer [23]. According to Han [24], another alternative for this case would be to design the package in multilayers and impregnate the antimicrobial agent in a thin layer that remains in contact with the food and has a controlled release. The test performed only with the polymer prepared by wet-casting without Ag–zeolite showed no antimicrobial activity, indicating that the antimicrobial activity is actually due to the release of silver and that the LDPE film is inert to the microorganism. The sizes of inhibition halos were quite small. However, it is known that the antimicrobial activity of a compound depends on its solubility in the medium, which, in this case, does not show great amount of water to allow fast diffusion of the active agent, explaining small halos observed.

4. Conclusions

The results obtained in this work showed that the incorporation of silver in the zeolite in a concentration of 5% did not alter the zeolite structure or its chemical composition, occurring only a slight loss of crystallinity and surface area, probably due to the blockage of the pores impregnated with silver.

The zeolite Y impregnated with silver inhibited the growth of *E. coli* for concentrations higher than 0.025 mg Ag–zeolite/mL, demonstrating the antimicrobial potential of silver and the controlled release of the zeolitic structure.

The LDPE antimicrobial film containing zeolite incorporated with silver showed inhibitory effects against *E. coli*. Thus, the Ag–zeolite-Y-LDPE films show potential for application in food packages, aiming at increasing food safety and shelf-life.

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