ANTIBACTERIAL EFFECT OF SILVER INCORPORATED POLYETHYLENE BLOWN FILM FOR ACTIVE PACKAGING USE

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Abstract - Food packaging is used to maintain the quality and safety of food products during storage and transportation, and to extend the shelf-life of food products. This is done by preventing unfavourable factors or conditions such as oxygen, light, moisture, spoilage microorganisms, chemical contaminants, mechanical resistance, etc. To be able to do so, packaging materials provide physical protection and also create the proper physicochemical conditions for each product necessary to obtain adequate shelf life and maintain food quality and safety. We report the preparation of polyethylene blown films containing silver nanoparticles by using the ultrasound technique. The silver nitrate was mixed with the surfactant oleic acid (AO) and sonicated for 30 minutes. This solution was mixed with polyethylene using a rotary mixer for 12 hours. Nanocomposites of low density polyethylene (LDPE) with linear low density polyethylene (LLDPE) blends and silver nanoparticles were prepared under melt in a twin screw extruder, using PE-g-MA as compatibilizer agent, ethylene graft maleic anhydride copolymer. The films were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX), field emission scanning electron microscopy (FESEM), differential scanning calorimetry (DSC), percentage reduction of colony-forming units (CFU). The bacterial effect of *Escherichia coli* and *Staphylococcus aureus* were assessed in detail.

Keywords: *polyethylene, silver nanoparticles, oleic acid, antibacterial*

Introduction

Polyethylene is a general purpose thermoplastic resin with good processing used especially for packaging and construction applications because of the acceptable flexibility, transparency, thermal stability, environmental recyclability, as well as relative low price [1,2].

The incorporation of AgNPs in polymers such as plastics [e.g., polyethylene (PE) [3], polypropylene (PP) [4], polystyrene (PS) [5], (PU) [6] and TPE [7]] to form nanocomposites is always interesting because of their possible antibacterial activity in combination with the mechanical properties of conventional plastics.

Thermal processing such as melt blending, extrusion, and injection molding has been applied for incorporating antimicrobials into polymers, but it should be considered the heat stability and chemical compatibility of antimicrobials in polymer matrix, in order to evenly distribute antimicrobial chemicals [8].

In recent work [9] the low-density polyethylene (LDPE) nanocomposite films containing different concentrations of silver nanoparticles (AgNPs) (0.5 and 1% of polymer weight, w/w) were manufactured via extrusion. The results indicated that LDPE nanocomposite films containing AgNPs could potentially be used as antimicrobial packaging for food applications.

The ultrasound radiation is a tool important and was used to Ag nanoparticles chemical reduction for addition in polyethylene fibers. The effect of reducing reagent, power of ultrasound radiation,

reaction time and temperature in growth of the AgNPs were studied. Results show a decrease in the particles size as increasing power of ultrasound irradiation [10].
Several polymeric materials with different molecular weight such as polyethylene glycol (PEG), polyvinyl alcohol (PVA), poly(N-vinyl-2-pyrrolidone) (PVP), and others, mainly water soluble, have been used as coatings of silver nanoparticles to enable particle dispersion [11], and silver nanoparticles stabilized with oleic acid (AO) [12] showed clear advantages in antibacterial activity, penetration bacteria cells, cytotoxicity, time effectiveness, efficiency, and stability against light [13].
In the present research work, LDPE/LLDPE has been employed as matrix for films nanocomposites. The compounds have been altered by the addition silver nitrate and oleic acid with the use of ultrasound. Such materials can be very valuable in films for biocide activity applications.

Experimental

Materials and Methods

Materials

LDPE with a melt flow index – MFI (190/2.16) of 0.27 dg min^{-1} and density: 0.922 g mL^{-1}, LLDPE with a melt flow index – MFI (190/2.16) of 0.80 dg min^{-1} and density: 0.920 g mL^{-1}, Braskem (Brazil) was provided in the form of pellets. The silver nitrate ($AgNO_3$) and oleic acid (AO) were supplied by Labsynth. The commercial clay Cloisite 20 was provided by BYK Additives Company and antioxidant (BASF Irganox B 225 ED) was added in small quantities, 2.0 wt%, to prevent the polyethylene from oxidizing and thermally cross-linking at elevated temperatures. The compatibilizer agent, ethylene graft maleic anhydride copolymer (PE-g-MA) was supplied by Chemtura (Polybond 3029). Three different formulations containing the LDPE/LLDPE were prepared and are represented in Table 1.

Table 1. Composition of constituents of polyethylene nanocomposites (wt%).

Samples	Matrix	Irganox	Cloisite	PE-g-MA	$AgNO_3$
PE	LDPE/LLDPE	2	-	-	-
PENC1	LDPE/LLDPE	2	1	2	1
PENC2	LDPE/LLDPE	2	-	2	1

The ultrasound equipment model USC-1400, with a working frequency of 40 kHz and maximum intensity output of 135 Watts RMS was used to synthesis of silver nanoparticles in oleic acid solution. The silver nitrate with AO solution was sonicated for approximately 30 minutes.

Preparation of the Nanocomposites Films

The LDPE/LLDPE (90/10) pellet were mixed with Irganox B 215 ED in a rotary mixer and maintained under this condition for 12 hours. Then the mixture was processed with the addition of clay (MMT 1% by weight) and silver nitrate ($AgNO_3$ 1% by weight) in a twin-screw extruder Haake co-rotating, model Rheomex PTW 16/25, Fig.1, with the following processing conditions: the temperature profile (feed to die) was 145-170 °C, with a speed of 100 rpm. After processed, the nanocomposites were granulated in a granulator Primotécnica W-702-3. The PENC films were produced in planar sheet extruder and the material was placed directly into the hopper of the extruder with a temperature profile (feed to die) of 150-175 ºC, screw speed of 50 rpm and torque of 33-45 Nm. The films were produced with a thickness of ~ 0.05 mm.

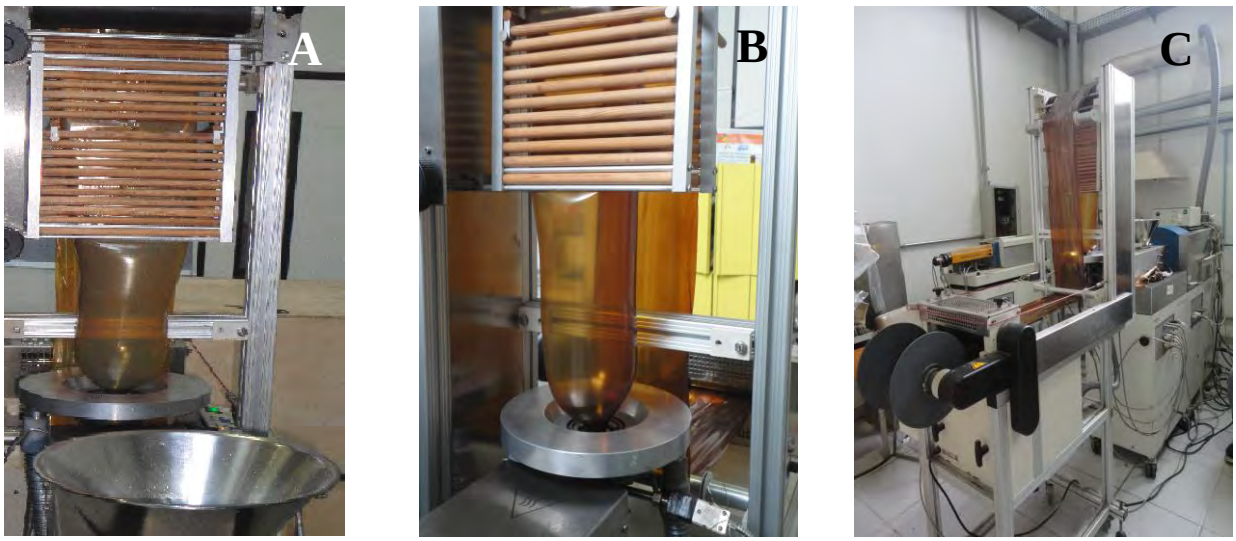

Figure 1. Haake film blowing unit used to prepare the blown films (A). The blown film take-off transports the extruded film in an upward direction (B). The film is guided up to the nip rolls where the tube is flattened to create a 'lay-flat' tube of film (C).

Methods

Scanning electron microscopy and Energy dispersive spectroscopy

Specimens were examined with a Hitachi TM 3000, coupled with a Bruker Quantax 70 for the collection of EDS data. SEM coupled with backscattered electron detector (BSE) and energy dispersive X-ray spectroscopy (EDS). Sample sections for the EDS analysis were taken at 15 keV, and the acquisition period was 120 s.

Field emission scanning electron microscopy

The samples were analyzed by scanning electron microscopy with field emission, JEOL FESEM, JSM-6701F, Japan, using the accelerating voltage of 5.0 kVA which allows the observation with more resolution than conventional SEM.

Differential scanning calorimetry

Thermal properties of specimens were analyzed using a differential scanning calorimeter DSC 822, Mettler Toledo. The thermal behavior of films was obtained by: (1) heating from -50 to 280 ^{o}C at a heating rate of 10 ^{o}C min^{-1} under nitrogen atmosphere; (2) holding for 5 min at 280 ^{o}C, and (3) cooling to -50 °C and reheating to 280 °C at 10 °C min^{-1}. The crystallinity was calculated according to the Eq.1.

$$X_C = P\ x\ \frac{\Delta H_f\ x\ 100}{\Delta H_0} \qquad (1)$$

Where: ΔH_f is melting enthalpy of the sample, ΔH_0 is melting enthalpy of the 100% crystalline PE which is assumed to be 280 kJ kg $^{-1}$ [14, 15], and P was the fraction content of PE in the sample.

Percentage reduction of colony forming units

The adapted standard JIS Z 2801 [16] was used for the tests. The cell suspension for the inoculum was 900 x 10^{6} mL^{-1} CFU for each tested step. The following procedure was performed separately for each microorganism: samples of the films of PE–AgNPs were placed in a sterile Petri dish and inoculated on the surface of 50 mL of suspension of each organism in an area of 40 x 40 mm^{2}. All of them were incubated for 24 h at 37ºC.

Results and Discussion

The images of Fig.2 and 3 are related to the PE film with AgNPs.

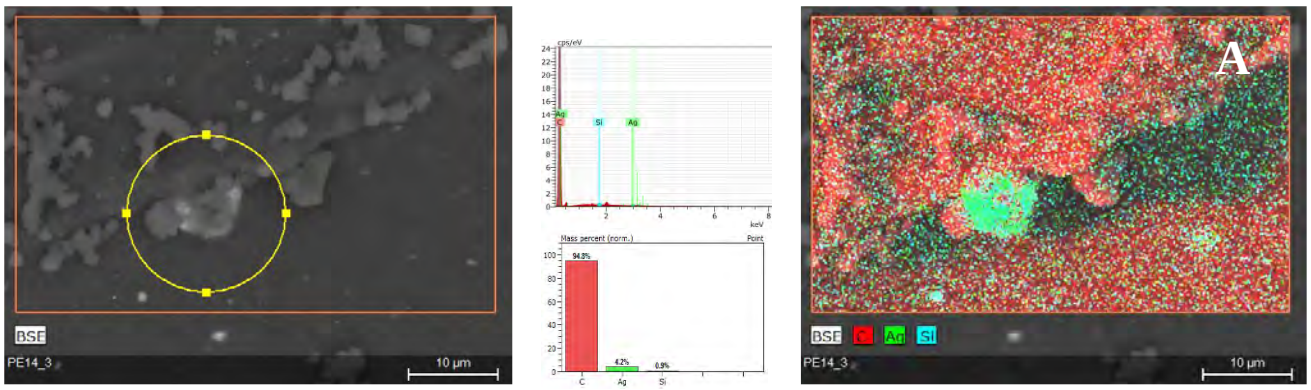

Figure 2. Elemental maps, magnification 3000X (scale=10µm) from SEM-EDX of (A) The surface of the PENC1 nanocomposite film showing the distribution of silicon (blue) and silver (green) atoms.

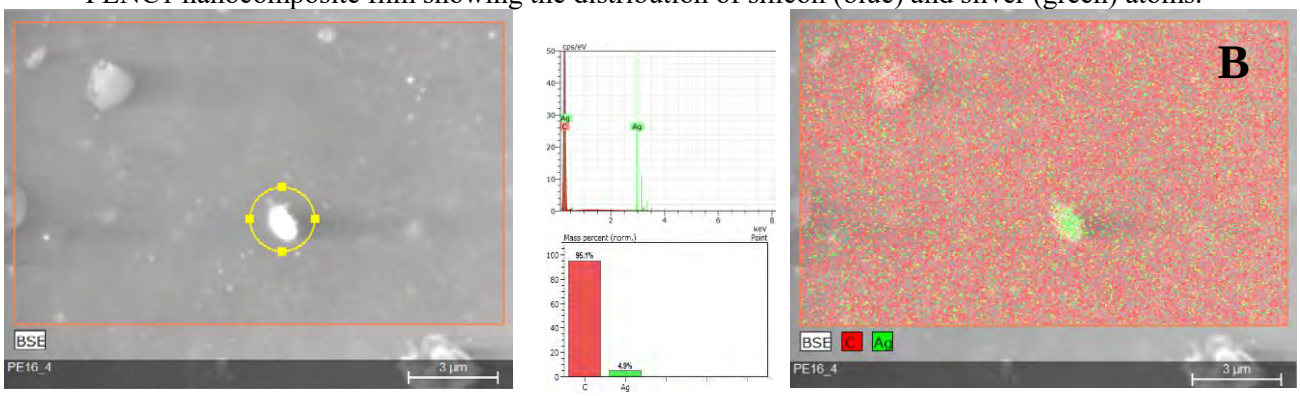

Figure 3. Elemental maps, magnification 10000X (scale=3µm) from SEM-EDX of (A) The surface of the PENC2 nanocomposite film showing the distribution of carbon (red) and silver (green) atoms.

The degree of dispersion of nanofillers plays an important role in influencing the properties of the resulting nanocomposites and energy dispersive X-ray spectroscopy (EDX), combined with scanning electron microscopy. EDS on the virgin surface of both nanocomposites of PE matrix, comprising carbon, the presence of silver and silicon in Fig.2 and in Fig.3 silver. The evidence of the elemental analysis suggests that the nanofillers were well dispersed into the bulk of PE matrix and just to the PENC1 film shows agglomerates. The FESEM-EDX results are shown in Fig.4.

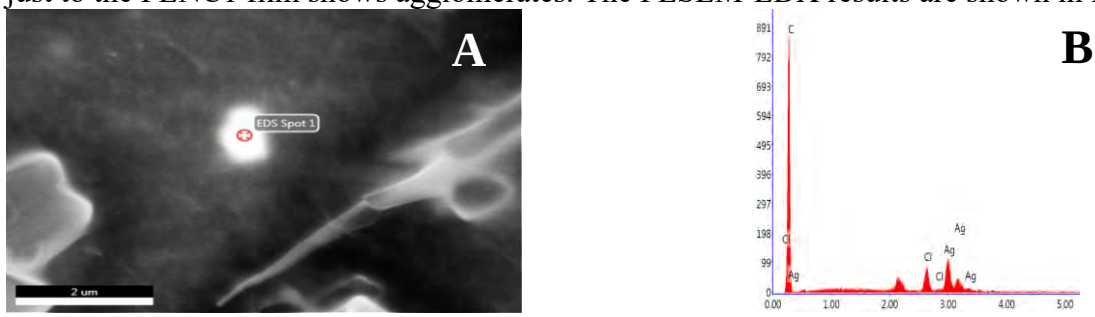

Figure 4. FESEM image of polyethylene film with silver nanoparticles (PECN2), magnification 20000X (scale=2µm) (A) and EDX (B).

The DSC results are shown in Table 2.

Table 2. DSC parameters for various polyethylene: PE, PENC1 and PENC2.

Samples	Melting peak temperature, T_{m1} /°C (±0.1%)	Crystallization peak temperature, T_C /°C (±0.1%)	Melting peak temperature, T_{m2}/°C (±0.1%)	Degree of crystallinity, X_C/% (±0.5%)
PE	113.1	97.9	112.1	32.0
PENC1	112.6	96.9	110.4	38.4
PENC2	109.8	96.6	111.0	32.8

The incorporation of the MMT-AgNPs increased the degree of crystallinity (%) of PE from 32.0% to 38.4% in sample PENC1. This fact suggests that the AgNPs impart a high efficiency to the heterogeneous nucleation of PE. A research work which corroborates with the idea of this work was published by Benchacine et al. [17] the silver incorporation in MMT plays an important role in the crystallinity degree X_C of PE that increases when Ag–MMT is added.
The results show that good dispersion and antimicrobial properties were obtained with AO as a surfactant against *S. aureus* and *E.coli*. The addition of coated AgNPs to the PE matrix represented na interesting solution for increasing protection against *S. aureus* and *E.coli*. The percentage reduction for the CFU assay showed positive 100% biocidal results for *S. aureus* and *E.coli* in film PENC2.

Conclusion

The addition of coated AgNPs to a PE matrix during the extrusion process represents an interesting solution for increasing the protection against *S. aureus* and *E. coli*. AgNPs in PE film properly hindered the bacterial activity in the bulk, and when appropriated surfactant (AO) was used, the overall effect was a high antibacterial efficiency on the surface film PENC2.

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