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EFFECTIVE ANTIMICROBIAL MATERIALS BASED ON LOW-DENSITY POLYETHYLENE (LDPE) WITH ZINC OXIDE (ZNO) NANOPARTICLES

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Abstract

Effective antimicrobial polymeric nanocomposites were prepared with low density polyethylene (LDPE) and zinc oxide nanoparticles by melt compounding. These nanoparticles (~17 nm) obtained by the sol–gel method, were used both as-synthesized and modified organically with oleic acid (Mod-ZnO). Young's modulus increased ~15 and 18% for LDPE/ZnO and LDPE/Mod-ZnO, respectively, compared to neat LDPE. When these composites were irradiated with white light, they showed an increase with nanoparticle incorporation, and the antimicrobial properties against *E.coli* were ~96-99%. The release of the Zn cations was related to the antimicrobial properties. These nanocomposites are attractive for use as food packaging without external irradiation.

Keywords

Antimicrobial packaging, polyethylene, zinc oxide nanoparticles, mechanical properties

1. Introduction

Polyethylene (PE) is among the polymers used in food packaging due to their low cost, high impact strength and reasonable chemical resistance. The combination of nanoparticles and polymers is of great interest, giving an improvement of thermal and mechanical properties at low loading levels (<10 wt.%). The preparation of nanocomposites using small amounts of nanoparticles (<100 nm) may keep the easy processability of polymer matrices by the traditional processing methods [1].

Some authors have studied metal nanoparticle incorporation into PE in order to produce nanocomposites with antimicrobial properties for use in the packaging industry or in the medicine field by inhibiting the growth of microorganisms [2]. Along this line, nanoparticles such as silver, copper, and titanium oxide have been considered for the preparation of PE-based nancomposites [1,3]. The limitations of the above-mentioned metal/oxide nanoparticles are related to their toxicity and external irradiation.

Zinc oxide (ZnO) nanoparticles are good and inexpensive semiconductors with good biocompatibility, chemical stability, and biocidal activities both *in vitro* and *in vivo*. ZnO has a band gap of 3.37 eV at room temperature and a large free-exciting binding energy of 60 meV. It also revealed antimicrobial properties against food borne pathogens and spoilage bacteria. Additionally, the ZnO is usually recognized as safe by the FDA under the conditions of its intended use, under prescribed limit properties [4–7].

In the literature there are several studies dealing with the influence of the ZnO nanoparticles with diameters between 50 nm and 100 nm in polyethylene on the final polymer properties. In our case we incorporated ZnO nanoparticles with diameters smaller than 20 nm.

Li *et al.* [6] successfully prepared high density polyethylene (HDPE)/nano-ZnO (50 nm) composite films and studied the influence of the modification and proportion (0.2, 0.5, 1

and 2 wt%) of γ-aminopropyltriethoxy silane (ZnO-APS) nanoparticles on the antibacterial and mechanical characteristics of the films. As ZnO content increased, the antibacterial rate was improved against *Escherichia coli* (*E. coli)* and *Staphylococcus aureus* (*S. aureus*) Also, the tensile strength of the HDPE/ZnO-APS composite films was enhanced compared to the original HDPE/ZnO composite due to the better dispersion of ZnO modified nanoparticles. The tensile strength and toughness reached their maximum values at 0.5wt% ZnO loading. At loadings greater than 0.5 wt%, nanoparticle addition led to decreased mechanical properties.

Along this line, linear low-density polyethylene (LLDPE) and ZnO (0–10% w/w) (d<100 nm) nanocomposite films were produced by a melt-mixing extrusion process. The prepared nanocomposite films of LLDPE/ZnO revealed improved oxygen and UV barrier properties as well as better thermal properties compared to neat LLDPE films. The tensile strength of the nanocomposites increased with the ZnO concentration. Although the antimicrobial properties were not assessed, the authors concluded that the LLDPE/ZnO nanocomposite films are good candidates for being exploited as food packaging material, since they protect food from oxygen- and UV-induced lipid oxidation [2].

On the other hand, Emamifar *et al.* [8,9] assessed the antimicrobial activity of nanocomposites of low-density polyethylene (LDPE) and Ag/ZnO nanoparticles (70 nm-10 wt.%) against *Lactobacillus plantarum* (*L. plantarum*) .They found that the ZnO-based nanocomposites extended the shelf life of fresh orange juice at -4 ºC by 28 days without causing adverse effects on the sensory properties. However, although the active packaging materials containing Ag nanoparticles had greater activity in increasing orange juice shelf life, they promoted undesirable effects on the sensory quality of fresh juice.

In this work we studied the preparation of the PE/ZnO-based nanocomposites via melt compounding. The ZnO (~17 nm) nanoparticles were obtained by the sol-gel method and

were additionally surface-organic modified with oleic acid (Mod-ZnO). In this sense, the effect of the presence of ZnO and Mod-ZnO on the thermal, mechanical, and antimicrobial properties of the nanocomposites was assessed in order to evaluate its processing conditions, its final properties, and its antimicrobial properties without the need for ultraviolet treatment after processing.

2. Experimental section

2.1 Materials

For the synthesis of the nanoparticles, sodium hydroxide (Merck KGaA, reagent grade, 99%), zinc chloride (Merck, reagent grade 80-100%) distilled water, and 2-propanol (Equilab, reagent grade 99.8%) were used. The reagents used for organic nanoparticle modifications were oleic acid (Sigma-Aldrich, 90%) and hexane as solvent (J.T. Baker 99.8%). Low density polyethylene (LDPE), purchased from B.O. packaging, was used as matrix.

2.2 Synthesis of ZnO nanoparticles

The ZnO nanoparticles were obtained by the sol–gel method reported by Becheri *et al*. [10]. The precursor solution was obtained by adding 5.5 g of $ZnCl_2$ (to 200 mL of distilled water) at 90 °C in an oil bath. The second solution was prepared with 5 M NaOH in distilled water and it was added dropwise to the first solution, stirring during 10 minutes at 90 °C. The suspension was washed with distilled water to reduce the NaCl concentration below 10^{-6} M, as verified with a silver nitrate ($AgNO_3$) solution. The particles were mixed with 2-propanol in an ultrasonic bath during 10 minutes at 20 ºC. Next, the particles were centrifuged at 5000 RPM for 15 min and they were then washed three times with 2-propanol at 60 °C. Finally, the particles were calcined at 250 °C during

5 h in order to obtain ZnO. The organic modification method for the ZnO nanoparticles (Mod-ZnO) was described by our research group in a previous report [3].

2.3 Preparation of LDPE nanocomposites with incorporation of nanoparticles of ZnO and modified ZnO

For the preparation of the composites a Brabender Plasti-Corder internal mixer was considered. In particular, 3, 5 and 8 wt.% ZnO nanoparticles were mixed with LDPE in an inert atmosphere (nitrogen) at 170 °C and a mixing speed of 110 rpm during 10 min. The materials were moulded during 3 minutes in a hydraulic press (HP Industrial Instruments) at 50 bar and 170 °C, and then cooled to room temperature under pressure with water circulation.

2.4 Characterisation of ZnO nanoparticles and LDPE/ZnO nanocomposites

2.4.1 ZnO nanoparticles and their organic modification characterisation

The morphology and size of the nanoparticles was studied under a Philips (The Netherlands) Tecnai 12 microscope at 80 kV. The X-ray diffraction patterns of the ZnO nanopartilces were analysed on a Siemens D5000 diffractometer using Ni-filtered Cu Kα radiation (λ = 0.154 nm). Fourier transform infrared (FTIR) studies of the ZnO and Mod-ZnO nanoparticles were made in a Bruker Vector 22 FTIR spectrometer. The IR spectra were recorded in the 4000 to 500 cm^{-1} range at room temperature.

2.5 LDPE/ZnO and LDPE/Mod-ZnO nanocomposite characterisation

The thermal properties in terms of melting temperature and enthalpy of fusion of the LDPE and LDPE/ZnO nanocomposites were measured by differential scanning calorimetry (DSC) (Mettler Toledo Modelo DSC1/500). For this purpose, a first heating

segment from 25 °C to 180 °C was applied at a rate of 10 °C/min to remove the thermal history. Then, a cooling segment to 25 °C at the same rate was applied. Finally, a second heating segment from 25 to 180 °C was applied, and the values of this segment were considered as representative. The crystallinity degree (X_c) was calculated according to **Equation 1**, where ΔH^o_f is the enthalpy of fusion of an ideal polyethylene with 100% crystallinity (289 $J \cdot g^{-1}$ [11]) and ΔH_f is the melting enthalpy ($J \cdot g^{-1}$) of the polymer nanocomposite. The values were normalized to the weight fraction of the matrix in the nanocomposite [3].

$$X_c = \frac{\Delta H_f * 100}{\Delta H_f^0 \, (1-x)} \quad \textbf{(Equation 1)}$$

The thermal stability of the nanocomposites was studied on a Mettler-Toledo TGA 851 thermogravimetric analyser (TGA). About 4 mg of samples were placed in 70 μL capacity perforated alumina crucibles. The samples were analysed from 25 to 600 °C at 10 $°C \cdot min^{-1}$ under an inert argon atmosphere at a flow rate of 50 $mL \cdot min^{-1}$. All the experiments were ran twice to verify the reproducibility of the results.

The distribution of the nanoparticles into the polymer matrix was studied in a Zeiss Ultra 55 Field-Emission Scanning Electron Microscope (FE-SEM). The film nanocomposites were placed on the conductive tape and mounted on metal studs. Electron microscope images were taken at 22 ºC and 20 kV.

The tensile properties were determined on an HP model D-500 dynamometer. Dumbbell-shaped samples with a length of 30 mm and a width of 5 mm were cut from the compression-moulded films. The samples were evaluated at a rate of 50 mm/min at 20 ºC. The experiments were run in quadruplicate to ensure representativity.

The antimicrobial effect was analysed by a plate count method referred to ISO 20143 with *E. coli ATCC 25922* as bacterial agent. The method used in this analysis was reported in a previous paper [1]. The percent reduction of the colonies was calculated

byth **Equation 2**, which relates the number of colonies from the neat LDPE to the number of colonies from the LDPE/ZnO nanocomposites.

$$\%\text{Reduction} = \frac{\text{CFU}_{\text{neat polymer}} - \text{CFU}_{\text{nanocomposite}}}{\text{CFU}_{\text{neat polymer}}} * 100 \quad (\textbf{Equation 2})$$

The release of zinc ions (Zn^{2+}) from the nanocomposites was analysed by means of inductively coupled plasma (ICP) spectrometry. The nanocomposite samples (1×2×0.01 cm) were soaked in 10 mL of deionized water with continuous stirring. The measurements were studied after immersion for 1, 4, 8, 12, 15, and 28 days.

3. Results and discussion

3.1. ZnO nanoparticle characterisation

The yield of the reactions of ZnO nanoparticles was 88.9%. The ZnO nanoparticles show irregular spherical shapes with an average size of ca. 17 ± 3.2 nm, as determined from the TEM images shown in **Figure 1**.

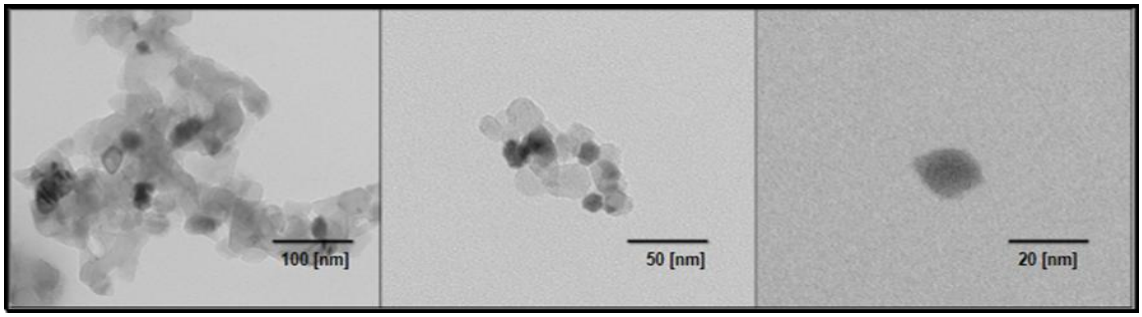

Figure 1. Image of TEM analysis of zinc oxide nanoparticles.

The crystalline phase of the ZnO nanoparticles was studied by X-ray diffraction (XRD), whose resultant spectra are displayed in **Figure 2**. Several peaks are seen in a 30° to 80° range, and the crystallographic planes coincide with those reported by other authors. ZnO NPs exhibited strong diffraction peaks at 32° (100), 34° (002), 36° (101), 47° (102), 57°

(110), 63° (103), 66° (200), 68° (112), and 69° (201), associated with the hexagonal wurtzite structure of ZnO [12–14].

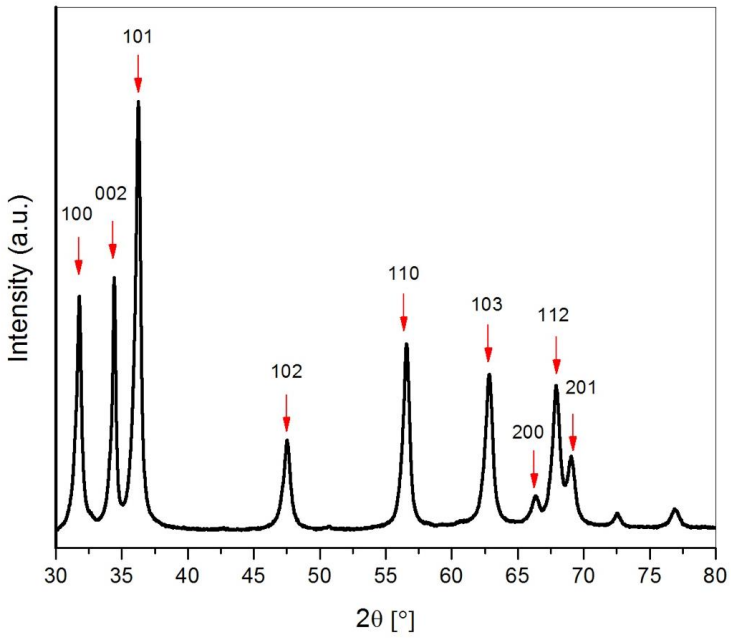

Figure 2. XRD pattern spectrum of zinc oxide nanoparticles.

The chemical structure of the nanoparticles was further assessed by FTIR, with the characteristic spectra of ZnO, oleic acid, and Mod-ZnO displayed in **Figure 3**. The modification of the nanoparticles will improve the interaction between the matrix and ZnO nanoparticles. ZnO shows a signal from 450 cm^{-1} to 600 cm^{-1}, correlating to the vibrations of the Zn–O bond of the nanoparticle. The second signal, between 719 cm^{-1} and 899 cm^{-1}, corresponds to the stretching and deformation vibrations of Zn–O. Finally, the band from 3452 cm^{-1} to 3493 cm^{-1} corresponds to the vibration of the O–H bond [15].

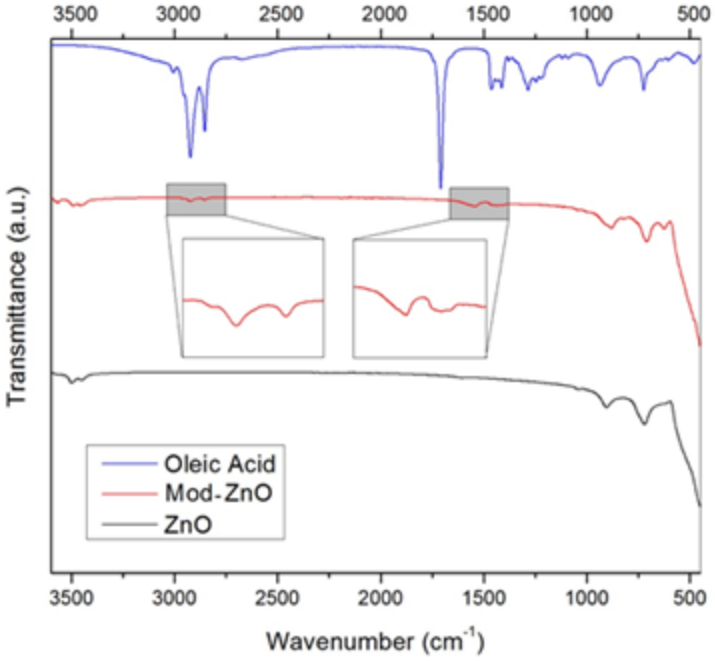

Figure 3. Infrared spectrum of oleic acid, ZnO, and ZnO nanoparticles modified with oleic acid (Mod-ZnO).

The spectrum of the Mod-ZnO shows that the nanoparticles were modified after the treatment with oleic acid as suggested by the signals associated with the vibration at 2854 and 2925 cm^{-1} of CH_2 from the alkyl carbon chain of oleic acid. The peak at 1590 cm^{-1} is due to the presence of carboxylate groups, and the peaks at 1550 cm^{-1} and 1430 cm^{-1} correspond to the presence of COO^- [3], caused by the carboxylic acid group of oleic acid reacting with surface hydroxyl groups from the ZnO nanoparticles.

3.2 Characterisation of LDPE nanocomposites with ZnO incorporation

3.2.1 Dispersion and thermal analysis of LDPE/ZnO nanocomposites

The dispersion of the ZnO nanoparticles into the LDPE matrix was assessed by means of field-emission scanning electron microscopy (FE-SEM), from the study of the surface of the film with a high accelerating voltage. The FE-SEM micrographs of the LDPE/ZnO and LDPE/Mod-ZnO nanocomposites are displayed in **Figures 4** and **5**, respectively. In

general, the ZnO nanoparticles in the LDPE matrix were homogeneously distributed, except for some zones with agglomeration, which increased with the amount of nanoparticles. A better dispersion was found when Mod-ZnO nanoparticles were incorporated into LDPE, because the surface modification is an efficient route for improving nanoparticle dispersion in the matrix. The better dispersion of Mod-ZnO is due to the presence of the oleic acid cues. Therefore, the nanoparticle modification could increase the interaction between the modified nanoparticles and the polymer, therefore improving the distribution of ZnO.

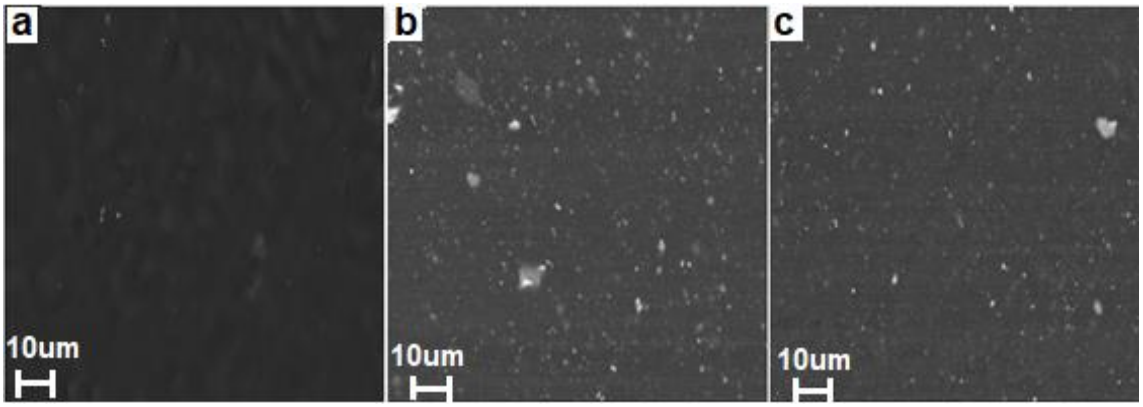

Figure 4. Scanning electron microscopy images of a) LDPE; b) LDPE/ZnO; and c) LDPE/ZnO-Mod nanocomposites with 5 wt.% nanoparticle incorporation.

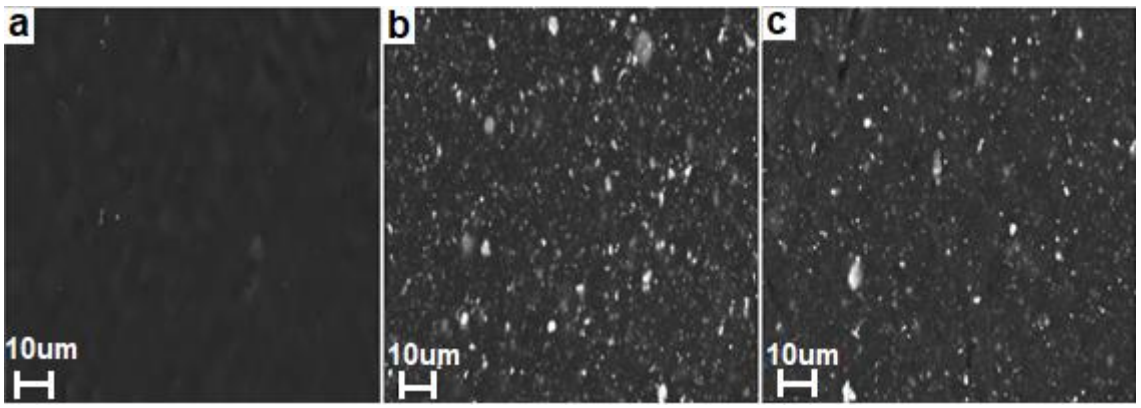

Figure 5. Scanning electron micrographs of a) LDPE, b) LDPE/ZnO, and c) LDPE/Mod-ZnO nanocomposites with 8 wt.% nanoparticle incorporation.

Regarding the thermal analysis, the characteristic melting temperature (T_m) and degree of crystallinity (X_c) of LDPE and LDPE/ZnO nanocomposites are gathered in **Table 1**. The assessment of the T_m and X_c results showed that the thermal behaviour remained almost constant with the ZnO incorporation into the LDPE matrix. Similar results have been reported when different nanoparticles like clay, silica, silver, or TiO_2 were incorporated into LDPE. This behaviour may be correlated with the minimum volume fraction of the nanoparticles incorporated into the composite [1,2,16]. Also, the similar thermal properties of the matrix and composites would suggest analogous processing conditions as that of LDPE at a hypothetical industrial-scale production of these nanocomposites.

Table 1. Thermal properties of the LDPE and LDPE/ZnO nanocomposites

Sample	ZnO wt.%	T_m °C	X_c %	T_{10} °C	T_{max} °C
LDPE	**-**	113	24	450	479
LDPE /ZnO	**3**	112	24	449	480
	5	112	25	455	479
	8	112	24	459	482
LDPE /Mod-ZnO	**3**	113	25	455	480
	5	113	26	452	479
	8	112	25	458	481

T_m: melting temperature; X_c: crystallinity degree, T_{10}: decomposition temperature at 10% weight loss, T_{max}: temperature for maximum weight loss rate.

The effect of the ZnO nanoparticle incorporation on the thermal stability of LDPE/ZnO and LDPE/Mod-ZnO nanocomposites were studied by thermogravimetric analysis (TGA) in an inert atmosphere. The results in terms of the temperature for 10% mass loss (T_{10}) and the peak of each degradation stage obtained from the derivative TGA curve (T_{max}) are given in **Table 1**. All the materials displayed at T_{max} related to the thermal degradation of LDPE at 480 °C. With the nanoparticle incorporation, the nanocomposites

showed analogous T_{max} values. The T_{10} increased 9 ºC for LDPE/ZnO with 8 wt.% of ZnO compared to LDPE, regardless of the nanoparticle modifications. These results suggest that the nanoparticles may provide a better insulator and mass transport barrier for the volatile products generated during their decomposition in the LDPE [2,17–19]. Palza *et al*. [19] described several models related to the increased thermal stability of polymer nanocomposites, which can be caused by either chemical or physical processes. From the chemical point of view, the surface of some nanoparticles can interact with radicals coming from the polymer's degradation, and this mechanism had been explained when spherical nanoparticles were incorporated into the polymer. On the other hand, the physical models established the lower diffusivity due to the presence of nanoparticles, which may decrease the out-diffusion of volatile compounds from the decomposition.

3.2.2 Mechanical properties of the LDPE/ZnO nanocomposites

The mechanical properties of the neat LDPE and the nanocomposites were assessed by tensile tests, whose results are shown in **Table 2**. Young's modulus increased approximately 18% and 15% for the LDPE/ZnO and LDPE/Mod-ZnO nanocomposites, respectively, compared to neat LDPE. The elastic limit of the LDPE/ZnO and LDPE/Mod-ZnO remained constant compared to neat LDPE. The elongation at rupture decreased ~15% and 11% for LDPE/ZnO and LDPE/Mod-ZnO, respectively, compared to neat LDPE.

Table 2. Mechanical properties of neat LDPE and LDPE/ZnO nanocomposites.

Sample	ZnO (wt.%)	E (MPa)	σ_y (MPa)	ε (%)
LDPE	-	220 ± 7	9.1 ± 0.4	59.0 ± 8.0
LDPE /ZnO	3	240 ± 7	9.9 ± 0.3	53.0 ± 2.2
	5	255 ± 5	8.8 ± 0.2	51.0 ± 3.1
	8	261 ± 8	9.2 ± 0.2	50.0 ± 4.1
LDPE /Mod-ZnO	3	230± 3	8.9± 1.0	51.0± 3.0
	5	250± 6	8.9± 0.1	53.6±1.0
	8	256±8	9.3±0.1	52.2±1.2

E: Young's modulus; σ_y: elastic limit; ε: elongation at rupture

Comparing our results with other literature reports, Ahmed et.al, obtained PE/ZnO nanocomposites with 10 wt.% of ZnO (d<100 nm). They found an increase of only approximately 12% of Young's modulus and a 63% decrease of elongation at break. They explained this behavior as due to ZnO nanoparticles incorporated into the LLDPE matrix having toughening and reinforcing effects, thereby restricting the molecular motion of LLDPE polymer chains [2]. On the other hand, Li et al. prepared HDPE/ZnO nanocomposites by melt-blending. In order to increase the interaction between ZnO (d ≈ 50 nm) and polymer, the nanoparticles were modified with ϒ-aminopropyltriethoxy silane (ZnO-APS). With increased nanoparticle amounts above 1.5 wt.%, the mechanical properties were not significantly enhanced. HDPE/ZnO-APS nanocomposites with 2 wt.% ZnO-APS increased the tensile strength ~12% compared to that of neat HDPE. The authors correlated this observation with the feasible aggregation of nanoparticles, which leads to a decrease in the interaction between the nanoparticles and the HDPE. [6].

The results proposed in the present study revealed improved mechanical properties compared to other literature reports when using nanoparticles, and this may be ascribed to the smaller particle diameter (d ≈ 17 nm), which increased the contact area between the nanoparticle and LDPE for a given weight percentage. Also, the decrease of the

elongation at rupture of the nanocomposites was similar to that found in the literature. These results may be due to the fact that modified nanoparticles increased slightly the interaction between the polymer and the nanoparticles, as shown by FE-SEM images.

3.2.3 Antimicrobial properties of LDPE and LDPE/ZnO nanocomposites

The antimicrobial properties of the polymers against *E. coli* are given in **Table 3**. The polymers were irradiated with UV light and the results were compared to those after white light irradiation.

Table 3. Reduction percentage of *E. coli* by LDPE/ZnO and LDPE/Mod-ZnO nanocomposites under UVA and white light.

Sample	ZnO (wt.%)	Bacterial reduction (%)	
		UV light	White light
LDPE/ZnO	3	99.99	33.87
	5	99.99	91.94
	8	99.99	99.90
LDPE/Mod-ZnO	3	99.99	82.26
	5	99.99	89.03
	8	99.99	99.16

All the LDPE/ZnO nanocomposites after UV irradiation were effective against *E. coli* ~99.99%, regardless of the nanoparticle concentration and surface modification. Given the semiconducting behaviour of ZnO, the incident radiation with photon energy higher than the value of its band gap (~3.3 eV) causes the movement of electrons from the valence band to the conduction band of the nanoparticle, promoting the formation known as an electron hole (h^+) in the valence band and a free electron (e−) in the conduction band. The electron hole (h^+) reacts with H_2O molecules giving •OH and H^+. Furthermore, O_2 molecules are charged generated superoxide radicals (O_2^-), it react with H^+ to

generate ($HO_2^{\bullet}$). These species generating hydrogen peroxide anions (HO_2^-).Thus, the hydrogen peroxide anion reacts with hydrogen ions to produce H_2O_2. It was reported that the H_2O_2 can penetrate the cells, causing their peroxidation and then their death [20].

The antimicrobial properties of the LDPE/ZnO and LDPE/Mod-ZnO nanocomposites irradiated with white light show increased effectiveness with the nanoparticle incorporation, and high antimicrobial properties ~99% against *E.coli* were achieved. At low ZnO incorporation (3 wt.%), the modification of the nanoparticles had an effect on the antimicrobial properties, as revealed by the bacterial reduction of ~82.26%. This behavior may be correlated with the enhanced dispersion of modified ZnO nanoparticles into the LDPE matrix. At higher nanoparticle concentrations (5 and 8 wt.%), the antimicrobial properties were independent of the modification.

The antimicrobial mechanism of ZnO nanoparticles is unclear, and it is being studied in order to understand the behaviour of ZnO. However, the antimicrobial properties of ZnO nanoparticles is attributed to different mechanisms. Based on the experimental evidence, the antimicrobial activity of ZnO nanoparticles has been related to four mechanisms, such as (i) the release of zinc cations from the surface of nanoparticles, (ii) interaction between nanoparticles and microbial cells, (iii) permeation of nanoparticles (ZnO) into the cell membrane, and (iv) the formation of reactive oxygen species (ROS) as explained before [7,14]. Zn^{2+} ions obtained from the hydrolysis of ZnO nanoparticles generate toxicity in the medium containing the microorganisms. The solubility of ZnO depends on concentration and time. With respect to the second mechanism proposed, the interaction electrostatic forces between ZnO and bacterial cell membranes is due to the fact that ZnO nanoparticles have a positive charge, (zeta potential: +24 mV) [21], and the cell has a negative charge due to the excess of carboxylic groups. This causes a strong interaction between the nanoparticles and the bacterial surface, and consequently damage to the cell

membrane of the bacteria. After the contact between ZnO and the bacteria, there is a perturbation of the cell wall, causing the penetration of nanoparticles into the bacterial cells [22].

Finally, it should be noted that such small nanoparticles have greater surface area leading to a high inhibition of bacteria due to easy penetration into the bacterial cell membrane [23]. In general, the results confirm that the toxicity of ZnO nanoparticles could take place in the dark and it is not just affected by ROS production [24].

3.2.4 Ion release from LDPE matrix

The results of the ICP analysis of zinc cation release in an aqueous environment during 28 days are shown in **Figure 6,** for the LDPE/ZnO and LDPE/Mod-ZnO composites. The cations released increase with the amount of nanoparticles. After 20 days of immersion of the LDPE/ZnO and LDPE/Mod-ZnO nanocomposites, the cation release took place regardless of the nanoparticle modification. The cation release results obtained were related to the antimicrobial properties, but we do not discard the presence of reactive oxygen species (ROS) on the surface.

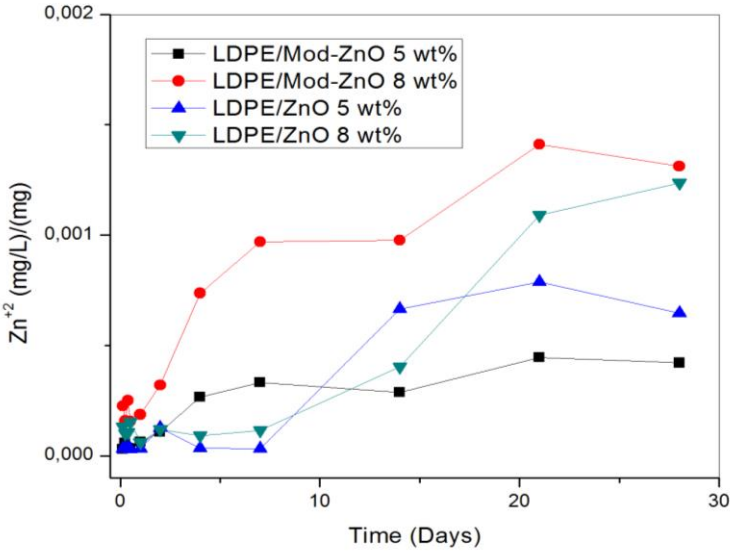

Figure 6. [Zn^{+2}] release from LDPE/ZnO and LDPE/Mod-ZnO with 5 and 8 wt% of as a function of time after 28 days.

In particular, for LDPE/ZnO and LDPE/Mod-ZnO with 8 wt%, on the first 5 days Zinc ion release increased, causing a quick release from the LDPE matrix. After that, the zinc ion release increased slowly. The initial release of zinc ions is due to particles on the specimen's surface. Amorphous layers near the surface are able to accommodate more water molecules, resulting in greater ion release. A similar behaviour was obtained from silver nanoparticles [1].

4. Conclusions

ZnO nanoparticles with diameter of ~17 nm were successfully obtained, modified, and incorporated in a low-density polyethylene (LDPE) matrix by means of industrial machinery, and good dispersion of the nanoparticles was achieved.

The thermal behaviour of nanocomposites scarcely differs from that of pure low density polyethylene, and thermal stability is improved, suggesting similar processing conditions for composites as well as for pure polyethylene.

Young's modulus increased slightly for LDPE/ZnO and LDPE/Mod-ZnO compared to neat LDPE due to the high interfacial area between LDPE and ZnO. Despite the decreased elongation at rupture for the nanocomposites, these values are low compared to those reported in the literature, in view of the good dispersion of the ZnO in LDPE, especially when the nanoparticles were surface modified with oleic acid.

The antimicrobial properties of the UV-irradiated LDPE/ZnO nanocomposites reached 99.99% efficacy against *E.coli*, regardless of the nanoparticle concentration and surface modification. Also, the antimicrobial properties of the nanocomposites irradiated with white light was strictly correlated to the nanoparticle concentration, reaching high antimicrobial properties of 96-99% against *E.coli* for nanocomposites containing 8 wt.% of ZnO and Mod-ZnO. The release of the Zn cations was related to the antimicrobial properties.

Therefore, the proposed LDPE/ZnO nanocomposites with suitable mechanical and biocidal properties may be considered as good candidates for being exploited in the food-packaging sector.

Acknowledgements

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