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Review

In situ sonochemical synthesis of ZnO particles embedded in a thermoplastic matrix for biomedical applications



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ABSTRACT

Zinc oxide particles were synthesized and dispersed in situ in a polystyrene (PS) matrix using ultrasound. PS ultrasonic degradation was investigated at different polymer concentrations in organic solvent in contact with aqueous media prior to the particle synthesis. Decrease in weight-average molecular weight (Mw) was strongly dependent on polymer concentration in organic solvent and sonication time: degradation occurred less at higher polymer concentration, yet increased with longer times of more than 30 min. The ZnO particles with a 800 nm flower-like morphology were dispersed in the polystyrene matrix in situ; the composite presented both a lower average molecular weight (M_w) and lower number average molecular weight M_n when compared to pristine polystyrene, however thermal degradation temperature and Young's modulus were similar to the pristine polystyrene. The composite prepared in situ presented lower particle aggregation in comparison with ZnO commercially dispersed with ultrasound under the same conditions. Antibacterial activity of the ZnO/PS coating was tested against Escherichia coli (Gram-negative bacteria; DMS No. 10290) by evaluating bacterial growth inhibition after 20 h on contact with the film surface. The results indicated that bacterial growth was inhibited in the medium in contact with the composite prepared in situ compared to the film of composite prepared by mixing and the pristine PS. This study showed the potential use of ZnO/PS composite prepared in situ as antibacterial coatings.

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1. Introduction

The use of coatings made up of polymers and inorganic particles such as ZnO has recently been studied as a strategy to reduce the bacterial growth on such interfaces that could be applied to medical devices, medical implants and wound dressings [1–4]. The bioapplications of ZnO are usually associated with nontoxic effects in low concentrations and being environmentally friendly [5], making ZnO a good substitute for other filler materials such as Ag [6]. In general, the mechanisms responsible for ZnO antibacterial activity are not fully understood; its antimicrobial properties have been associated with the release of Zn^{2+} which can interact with the microbial membrane causing structural changes and permeability and also with microbial nucleic acids to prevent microbial replication. In addition there is the production of radicals which can disrupt the bacterial membrane [7].

ZnO polymer composite materials have been prepared using techniques such as simple mixing, sol cast method and blending using polymers such as poly(N-isopropylacrylamide) [5], chitosan [6] and polyurethane and polyamide coatings [7,2] as a matrix. The properties of these materials are certainly affected by many factors, including filler size, aspect ratio, orientation in the matrix, adhesion at the filler-matrix interface and degree of dispersion [8].

The use of ultrasound irradiation has been shown to be a good method of dispersing particles [9] and it has recently been employed for the in situ preparation of different polymer nanocomposites [2] such as: amorphous magnetite nanoparticles embedded in polyvinyl alcohol. where the particles are synthesized in aqueous media [10]: synthesis of silver nanowires and polymerization of aniline for the preparation of silver nanowire/polyaniline nanocomposite [11]; and polymerization of methylacrylate with various amounts of amorphous cobalt [12] and amorphous iron nanoparticles [13]. Therefore, fibers and fabrics have previously been coated by the synthesis of particles in situ. Moosavi et al. studied the growth of silver bromide nanoparticles on polyester fibers by sequential dipping steps in alternating baths of potassium bromide and silver nitrate under ultrasound irradiation without using high temperatures during the reactions [14]. Perelshtein et al. synthesized ZnO nanoparticles and deposited them on the surface of cotton fabrics to improve antibacterial properties, irradiating the yarns in the presence of reagent solution for 30 min without significant damage to the structure of the yarns [15].

The use of ultrasound has the advantage of achieving good particle dispersion on the polymer matrix, however it can induce the cleavage of the polymer molecules [9]. Theoretical models and experimental data have been generated to explain the ways in which frequency [9], type of solvent, temperature [16], dissolved gases, intensity, external pressure, solution concentration and solvent vapor pressure [17,18], pH [16], polymer–solvent interaction, initial molecular weight and distribution influence the resultant molecular weight of the polymer. In this contribution the degradation conditions which could decrease polymer degradation are studied.

In addition, mechanical, rheological and structural properties of the composite material are discussed.

The growth mechanism of ZnO particles prepared with ultrasound using zinc nitrate hexahydrate $(Zn(NO_3)_2 \cdot 6H_2O)$ as a precursor and

hexamethylenetetramine (HMT) was previously studied by [19]. The symbol))) denotes ultrasonic irradiation:

 $\begin{array}{l} (CH_2)_6N_4 + 6H_2O {\rightarrow} 4NH_3 + 6HCHO \\ 4NH_3 + 6H_2O {\rightarrow} NH_4^+ + OH^- \\ Zn^{2+} + 4OH^- {\rightarrow} Zn(OH)_4^{2-} \\ Zn(OH)_4^{2-} {\rightarrow} ZnO + H_2O + 4OH^- \\ Zn^{2+} + 2 \cdot O_2^{-} \overset{)))}{\longrightarrow} ZnO + \frac{3}{2}O_2. \end{array}$

The objective of this study is the in situ synthesis and dispersion of ZnO particles for application as antimicrobial coating.

2. Materials and methods

2.1. Materials

Styrene (Aldrich, 99%) was rinsed with 10% NaOH to remove 4-tertbutylcatechol; the monomer was polymerized using benzoyl peroxide (Fluka, 97%) as an initiator at 90 °C. The polymer was dissolved in toluene and precipitated using cold methanol under stirring three times. Subsequently the precipitate was collected and dried under vacuum at 40 °C.

2.2. Ultrasonic polystyrene degradation study

Solutions of 0.14, 0.28 and 0.40 g/mL PS (Mw = 90,000, polydispersity = 5.4) were prepared in toluene. A half-inch titanium tip was used in the sonochemistry apparatus; the tip was immersed directly in the reaction vessel; 200 mL of distilled water was added, and samples were withdrawn at certain irradiation times (30, 45 and 60 min). The frequency used was 20 kHz and the amplitude was 40%; a constant level of the solution was maintained by adding solvent (if necessary) to account for vaporization. The application of ultrasound was initiated by subjecting the samples to continuous sonication cycles of 5 min and 2 min of rest with 6, 9 or 12 sonication cycles depending on the length of the study period. A cold water bath was used to maintain the temperature at 40–50 °C. The aqueous phase and the organic phase were separated by placing the sample in a cold water bath and decanting the upper organic phase. Next, the polymer was precipitated and washed free of the organic phase with cold methanol under stirring.

2.3. Procedure for ZnO/polystyrene composite synthesis

All chemical reagents, of chemical grade (Aldrich), were used without further purification. Zinc nitrate hexahydrate $(Zn(NO_3)_2 \cdot 6H_2O, 98\%,$ Aldrich) and hexamethylenetetramine (HMT, $(CH_2)_6N_4$, 99%, Junsei) were used as zinc cation and hydroxide anion precursors, respectively, for the synthesis of ZnO particles. A solution containing $Zn(NO_3)_2$ (0.05 M) and HMT (0.05 M) in deionized water was prepared at room temperature. A solution of 0.40 g/mL PS in toluene was added to the reaction vessel, and the reaction mixture was then irradiated for 30 min; 6 sonication cycles. The application of ultrasound was initiated by subjecting the samples to continuous sonication cycles of 5 min of sonication and 2 min of rest; a cold water bath was used to maintain the temperature at 40-50 °C. The organic phase was separated and washed with water and ethanol to remove traces of precursors.

2.4. Coating preparation for antibacterial test

Glass substrates were dip coated in the composite or polystyrene solution and left to dry for 7 days under normal environmental conditions, avoiding fast drying as this could precipitate a breakdown of the film. After this time the samples were put into a vacuum oven (Heraeus Instruments Vacutherm, Thermoscientific) at 70 °C for 2 h.

2.5. Material measurement techniques

2.5.1. Molecular weight determination

The M_n and M_w were determined by size exclusion chromatography (SEC) using a HT-GPCModule 350 A at 150 °C, equipped with a refractive-index detector. The samples were solubilized in 1,2,4-trichlorobenzene, stabilized with 0.05 g/mL 2,6-bis(1,1-dimethylethyl)-4-methylphenol to reduce thermo-oxidative degradation, and the flow rate was 1 mL/min. The molecular weight distribution (MWD) curves, M_w and M_n were calculated using the software Omni SEC 4.7.0. The columns were calibrated using polystyrene standards from 1000 to 4 million g/mol (UCS-200 polycal HT-UCS_PS standards).

2.5.2. Viscosity measurements

The intrinsic viscosity measurements were performed using a Brookfield DV-III Ultra rheometer; the temperature was maintained at 25 °C \pm 0.1 °C. The specific viscosity (η_{sp}) and intrinsic viscosity (η_r) were calculated using Eqs. (1) and (2) respectively:

$$\eta_{\rm sp} = \frac{\eta - \eta_0}{\eta_0} \tag{1}$$

$$\eta_{\rm r} = \lim_{c \to 0} \frac{\eta_{\rm sp}}{c} \tag{2}$$

where c is the concentration of the polymer in the solvent, η_0 is the solvent viscosity, and η is the viscosity of the polymeric solution [20].

For the viscosity measurements the PS (after the ultrasound treatment time) was dried in a vacuum oven at 70 °C; the PS was redissolved in toluene at the studied concentration. The intrinsic viscosity of the solutions was calculated by extrapolating the η_{sp} as a function of concentration to zero concentration; a minimum of five concentration levels was measured (linear regression with $R^2 \ge 0$, 98, data not shown).

2.5.3. Dynamic mechanical analysis (DMA)

The temperature dependence of the Young modulus (E) was evaluated using a DMA 25 (Metravib-01-dB). The samples were heated at a rate of 2 °C/min from room temperature to 75 °C in compression mode at 1 Hz frequency and E was calculated (compression testing is used more for pure polymers in general, while tension tests are more characteristic of flawed materials) [21]. Three samples of each specimen were tested and the average values were plotted. The dimensions of test specimens were: 10 mm long, 9 mm wide and about 3 mm thick.

2.5.4. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX)

The samples were coated with gold at approximately 10 nm thickness prior to SEM and EDX studies. The morphology and dispersion of the particles in the polymer matrix were investigated by SEM using an XL30 FEG, an ultra-high-vacuum system with a base pressure of 1×10^{-5} Pa and an acceleration voltage of 25 kV and 20 kV for SEM and EDX respectively.

2.5.5. X-ray diffraction (XRD)

The XRD patterns were recorded in a Rigaku D/MAX 2100PC diffractometer using Cu-K α radiation in the range of 5–90° (2 θ) in steps of 0.02°.

2.5.6. Fourier transform infrared spectroscopy

Fourier transform infrared spectra were obtained with a Bruker spectrometer. Attenuated total reflection (ATR) FTIR spectra were taken in the range of 4000–400 cm⁻¹ wavenumbers. Each scan was an average of 32 scans obtained at a resolution of 4 cm⁻¹.

2.5.7. Thermal analysis

Thermogravimetric analysis of the composite and pristine polymer films was conducted in a NETZSCH STA 409C/CD instrument at up to 750 °C, using a scan rate of 10 °C/min under nitrogen gas (N_2).

2.5.8. Antibacterial activity

The antibacterial activity of ZnO/PS coatings against Escherichia coli was investigated. Substrates coated with PS and composite with a size of 2 cm² were used. The bacteria were grown in 5 mL of Luria Bertani (LB) broth overnight at 37 °C, to stationary phase (10⁹ colony-forming) units (CFU)/mL). Next, the overnight culture was centrifuged and the supernatant was discarded. The pellet was suspended in minimal medium (1 mL LB broth in 99 mL of sterile phosphate-buffered saline (PBS)). This step was repeated 3 times. Finally, the bacteria were diluted in minimal medium to a concentration of 10⁶ CFU/mL. The substrates were placed in sterile petri dishes, and 200 µL of bacterial suspension (106 CFU/mL) was dropped on the films. The suspension was covered with a sterile coverslip (18×18 mm), and sterile water was pipetted onto the edges of the petri dishes to avoid evaporation. The carrier films were incubated at 30 °C for 20 h, and the coverslips were removed from the samples. The bacteria were removed from the surface by rinsing the samples with 200 µL of PBS with pipetting up and down. The resuspended bacteria were transferred to a 96-well microplate, and 50 µL of LB broth was added to the wells. The microplate was covered with a sealing membrane and placed in a microplate reader (Mithras LB 940, Berthold Technologies, Germany). Bacterial growth was followed online for 24 h by optical density measurements at 620 nm using the kinetic detection mode.



Fig. 1. Relationship between intrinsic viscosity and sonication time at different PS concentrations (frequency 20 kHz, power 50 W, temperature 40–50 °C, organic phase:aqueous phase ratio 1:10, solvent: toluene).



Fig. 2. Average molecular weight distribution as a function of sonication time, for 0.40 g/mL sample (frequency 20 kHz, power 50 W, temperature 40–50 °C). a. Organic phase: aqueous phase ratio 1:10. b. Organic phase:aqueous phase ratio 2:10.

3. Results and discussion

3.1. Ultrasonic degradation of polystyrene

Intrinsic viscosity was calculated to correlate the changes in molecular weight due to the ultrasonic irradiation. According to Mark– Houwink–Sakurada the changes to viscosity average molecular weight are proportional to the intrinsic viscosity; the relation is shown in Eq. (3); whereby K and a are constants which are dependent on the temperature, polymer and solvent [22,23].

$$\eta_r = K M_v^a. \tag{3}$$

Fig. 1 shows the variation in intrinsic viscosity at different sonication times for different polymer concentrations in the organic solvent. The results indicate that intrinsic viscosity decreased with longer sonication

times and was lower in the samples that had a higher concentration of polystyrene. Increasing the solution concentration increases the viscosity of the solution which decreases the mobility of polymer molecules, reducing the shear gradients around the collapsing bubbles and thus increasing the energy required for cavitation to occur. Furthermore, the entanglements at high concentrations could influence the energy transfer processes between solvent and polymer, reducing the rate of degradation [24,16]. The results also indicated that the extent of degradation was more pronounced after 30 min for different solution concentrations. There is no evidence of direct interaction between sound waves and the polymer chains because the acoustic wavelengths are much larger than the molecular dimensions. The cleavage of the polymer is associated with the frictional and impact forces that arise during bubble cavity collapse and the release of shock wave energy [20].

Fig. 2a shows the changes in the MWD curve of the sample with higher concentration (0.40 g/mL) in toluene after different sonication times (Table 1). The MWD curve shifts to the high molecular weight side at 30 min, showing the presence of a high molecular weight fraction. However, after 45 min a downward shift occurs. If there are monomer molecules present, the extreme conditions produced by ultrasound are believed to act as an initiator, resulting in the breakdown of covalent bond and the production of radicals, which could enhance polymerization [24]. Biggs and Grieser studied the polymerization of a styrene in water (o/w) emulsion at 30 °C under ultrasonic irradiation in the absence of any added chemical initiator, and found that radical polymerization of styrene monomers occurred as a consequence of cavitation [25] with or without a chemical initiator [26]. Nevertheless, PS was purified after polymerization and consequently there was a lack of high concentrations of residual monomer for chain initiation to occur. In general, when degradation is predominantly through chain scission, the shift of the MWD curve to higher molecular weights is due to grafting, branching and crosslinking of the polymer chains [27–30]. Moreover, the ultrasonic degradation process is distinguished from other techniques such as thermal, photochemical and radiation by the tendency of larger molecules to degrade faster, and at a certain limiting molecular weight no significant degradation occurs [24]. The shifting of the curve to higher molecular weights after 30 min was associated with the cleavage of polymer chains generating macroradicals that could recombine to produce larger molecules [29], but with longer sonication, chain scission caused by the frictional and impact forces have a greater influence on molecular weight.

The toluene to water volume ratio was increased from 1:10 to 2:10, keeping the total volume in the reaction vessel constant. The results are shown in Table 1. Fig. 2b shows a more pronounced degradation when the organic phase proportion was increased with respect to the aqueous phase. This effect could be associated with the absorption and dissipation of ultrasonic waves by water, limiting the degradation of the polystyrene molecules [18]. In a "good solvent" the polymer can present in an extended open coil structure [24], but the presence of water causes the collapse of polymer chains, resulting in a coiled conformation, reducing the polymer scission rate of the polymer chains.

According to the results showed in Fig. 2, a reaction time of 30 min, polystyrene in toluene concentration of 0.40 g/mL and an organic solvent to water ratio of 1:10 were chosen as optimal conditions in which the degradation effect of ultrasound can be reduced.

Table 1

Average molecular weight, number average molecular weight and polydispersity depending of sonication time, for a 0.40 g/mL polystyrene solution in toluene (frequency 20 kHz, power 50 W, temperature 40–50 °C, organic phase:aqueous phase ratio 1:10 and 2:10).

Sonication time (min)	M _v (g/mol) Ratio 1:10	M _v (g/mol) Ratio 2:10	M _n Ratio 1:10	M _n Ratio 2:10	Polydispersity Ratio 1:10	Polydispersity Ratio 2:10
0	90,000	90,000	16,648	16,648	5.4	5.4
30	101,000	75,000	36,000	21,000	2.8	3.6
45	70,000	58,000	18,000	20,000	3.9	2.9
60	69,000	75,200	28,000	24,000	2.5	3.1



Fig. 3. SEM micrographs of ZnO particles synthesized in situ.

3.2. Synthesis in situ and film composite characterization

The particles were synthesized in situ from the respective precursors. The liquid (aqueous/organic phase) was irradiated with ultrasound, creating the alternating expansive and compressive acoustic waves which produce bubbles that oscillate and collapse, releasing the concentrated energy stored [31], thus generating free radicals which can participate in the particle synthesis. [19] During ultrasound irradiation the liquid media is also under constant stirring and it is possible to produce an emulsion of the organic phase and liquid phase; the ultrasonic irradiation can promote the migration of formed particles close the interface between the aqueous and organic phase and the formed particles can be stabilized by the polymer which could prevent their aggregation [32,33].



Fig. 4. a) SEM micrographs: dispersion of ZnO particles synthesized in situ. b) EDX analysis on the surface.



Fig. 5. ZnO commercial powder dispersion by ultrasound.

Fig. 3 shows a representative image of the in situ synthesized particles, which has a flower-like morphology with an average size of 800 nm. Fig. 4a shows well-dispersed particles in the polymeric matrix. Fig. 4b shows the EDX spectra of the composite in situ films, indicating that Zn and O elements are present. Fig. 5 shows the dispersion of commercial powder in polystyrene using the same conditions as the synthesis in situ. The particles display a good dispersion in the matrix, but there is the presence of larger-sized agglomerates (around 2.5 µm) compared with the sample prepared in situ.

XRD analysis indicated the formation of ZnO particles, Fig. 6 shows the ZnO crystallographic planes and crystalline peak intensities. Fig. 6 shows a broad noncrystalline peak (10–30) referring to the amorphous polymer. The XDR patterns of the composite showed highly intense peaks corresponding to ZnO. The diffraction peaks corresponded to the hexagonal phase of ZnO (PDF: 89-7102); peaks at (20) 31.74, 34.55, 36.21, 47.64, 56.69, 62.83 and 67.95° were assigned to the (100), (002), (101), (102), (110), (103) and (112) reflection lines of hexagonal ZnO particles, respectively. During the formation of the particles, growing units derived from the precursor $Zn(NH_3)_4^{2+}$ and other complexes could be present as intermediates, indicating the need for more ultrasonic treatment or better purification [19]. No peaks characteristic of any impurities were detected.

The interface affinity between PS and ZnO was evaluated by FTIR. Fig. 7 shows the FITR spectra of pristine polystyrene and the composite. Both spectra showed absorption bands ranging from 3200 to 2900 cm⁻¹, which were assigned to polystyrene aromatic C–H stretching.



Fig. 6. X-ray diffraction analysis: PS film and PS/ZnO film samples.



Fig. 7. FITR spectra of pristine PS and composite samples.

The characteristic vibrational bands of aromatic C=C of styrene units were observed at 1601, 1493, and 1452 cm⁻¹; the bands at 759 and 698 cm⁻¹ indicated that a monosubstituted ring was present. No sharpening or shift differences in the absorption bands of the polymer and the composite were detected.

3.3. Ultrasonic degradation of PS from the composite

Fig. 8 shows the MWD curve of the PS from the composite and the pristine polystyrene. The MWD curve is shifted to the low molecular weight side, showing the presence of a low molecular weight fraction. The degradation is higher than for the PS irradiated for 30 min in similar conditions. This effect could be attributed to the surface particle being a suitable nucleation site for the cavitation, causing an increase [34]. Furthermore it could be related to additional mechanical stress due the interparticle collisions [35] (Table 2).

3.4. Mechanical and thermal properties

One of the parameters that influence the polymer mechanical properties is the molecular weight [36]. The E was measured to determine the effect of ultrasonic degradation on mechanical properties. Fig. 9 shows that after 30 min of ultrasound, there was an increase in E and



Fig. 8. Average molecular weight distribution as a function of sonication time, for 0,40 g/mL sample (frequency 20 kHz, power 50 W, temperature 40–50 °C, organic phase:aqueous phase ratio 1:10).

Table 2

Average molecular weight, number average molecular weight and polydispersity depending of sonication time, for a 0.40 g/mL polystyrene solution in toluene (frequency 20 kHz, power 50 W, temperature 40–50 °C, organic phase:aqueous phase ratio 1:10) and PS pristine.

Sample	M _v (g/mol)	M _n	PD
Pristine PS	90,000	16,648	5.4
Composite	48,200	9,310	5.17

that after 45 min no large difference with respect to the pristine polystyrene is detected. The increase in E could be associated with the increase in M_v and M_n (Table 1). For 30, 45 and 60 min M_n is higher than in the pristine PS which indicates that even with a lower M_{v_1} there is a higher number of molecules with a medium size than the PS. The cleavage was preferential towards the high molecular weight molecules. Fig. 2a shows no pronounced changes to the small size and medium size molecule fraction; thus no pronounced changes are expected on the E.

The M_v and M_n of the polymer from the composite made in situ decreases but the E increases (average 279 MPa) with respect to pristine polystyrene (average 231 MPa); the enhancement of E is associated with the dispersion of the ZnO particles which act as reinforcement for the polymeric matrix [37].

The TGA curves of PS and PS/ZnO composites are shown in Fig. 10. The presence of the particles slightly increased the degradation temperatures of PS. Both curves first show a loss of weight at 90–235 °C, which could be attributed to the evaporation of residual solvents and trapped water. The second sharp drop in weight was attributed to the decomposition of the polymer beginning at 269 °C and ending at 540 °C for pristine polystyrene and beginning at 280 °C and ending at 533 °C for the composite, to yield carbon and hydrocarbons. The percentage of inorganic phase dispersed in the polymeric matrix was 2.9 wt.%; the volume weight fraction of ZnO is 0.51%.

3.5. Antibacterial coating properties

The antibacterial activity of composite coatings was tested against *E. coli*. The influence of the surface properties on microbial viability was evaluated. The antimicrobial effect was measured by removing the bacteria from the test surface after a certain contact time followed by the evaluation of bacterial growth. Surfaces with antimicrobial properties were expected to display no or reduced bacterial growth in comparison with control surfaces. Fig. 11 shows a time-dependent growth



Fig. 9. Variation in Young's modulus with temperature, for 0.40 g/mL polystyrene in toluene (frequency 20 kHz, power 50 W, temperature 40–50 °C, organic phase:aqueous phase ratio 1:10) after 30, 45 and 60 min of ultrasonic irradiation and composite synthesized in situ.



Fig. 10. Effect of ZnO particles dispersed and synthesized in situ on the thermal stability of PS.

curve of bacteria in the suspensions obtained from the substrates. Three sample substrates coated with PS/ZnO in situ, ZnO/PS mixture by ultrasound in the same conditions and substrates coated with the pristine PS with the same dimensions were tested, and an average of 3 measurements for each sample substrate was calculated and plotted. Absorbance at 620 nm of the bacterial suspensions was measured over 24 h.

The results indicated that bacterial growth was strongly inhibited on contact with the surface of the composite film made in situ (3 sample substrates). The composite film made by mixture using ultrasound under the same conditions does not completely inhibit the bacterial cell growth; a certain number of viable cells of E. coli remain after a period of 20 h in contact with the surface; 2 substrate samples presented a delay of the growth phase. The inhibition of the film prepared with the composite prepared in situ is attributed to the better particle dispersion. The higher surface area can enhance such processes as ion diffusion as well as other properties of the ZnO such as bacteriostatic behavior [38]. In comparison, bacterial growth was detected on the control sample (pristine polystyrene film). To make sure that the detected bacterial growth was not due to contamination, the used solutions (LB, PBS, minimal medium) were tested in the same microtiter plate. For further evaluation of the results, a bacterial culture (10⁶ CFU/mL in minimal medium) with no contact with the samples was included in the test. The resulting growth curve was similar to that of the control samples



Fig. 11. Time-dependent growth of *E. coli* bacteria after 20 h in contact with the surface of PS and PS/ZnO film samples, compared with the growth of *E. coli* suspension of 10⁶ CFU/mL.

(see Fig. 11). These findings revealed that ZnO films made in situ have great potential to be used as antibacterial coatings.

4. Conclusions

The data presented in this paper indicate that it is possible to synthesize and disperse ZnO particles in polystyrene in one simple step using ultrasound. Ultrasonic treatment causes polymeric chain scission, but it is possible to minimize the degradation effect by varying the polymer concentration, the aqueous/organic solvent ratio and the sonication time used. In general, degradation was less at a higher polymer concentration in the organic solvent and increased with sonication time without the presence of the precursors and particles. The cleavage of the polymeric chains was higher, however the mechanical properties were enhanced with the dispersion of ZnO particles. The composite has a higher Young's modulus and similar thermal stability when compared with pristine polystyrene. ZnO/PS composite prepared in situ shows a good dispersion of the particles in the surface and inhibition of E. coli (Gram-negative bacteria) growth after 20 h of contact. A polystyrene film with 2.9 wt.% ZnO prepared in situ has great potential for use as antibacterial coatings.

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