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Zein-Based Ultrathin Fibers Containing Ceramic Nanofillers Obtained by Electrospinning. II. Mechanical Properties, Gas Barrier, and Sustained Release Capacity of Biocide Thymol in Multilayer Polylactide Films

Sergio Torres-Giner, Antonio Martinez-Abad, Jose Maria Lagaron
Novel Materials and Nanotechnology Group, IATA, CSIC, 46980 Paterna, Spain
Correspondence to: J. M. Lagaron (E-mail: lagaron@iata.csic.es)

ABSTRACT: The combination of electrospinning technology and nanomaterials such as nanoclays can synergistically lead to novel materials with enhanced properties and functionalities for their usage in passive and active packaging applications. Part I of this work was focused on the development of ultrathin zein fibers containing nanoclays, which were oriented along the fiber axis and increased the thermal properties. Part II presents the use of the hybrid fibers as passive and active components in multilayer packaging structures. The hybrid fibers are incorporated in poly(lactic acid) films via a two-step process: Electrospinning and compression molding. The composites thus produced presented improved mechanical and barrier properties than the unfilled material. The natural biocide extract thymol is then incorporated in the coating, and its sustained release properties are shown. The antimicrobial capacity of the hybrid fibers was also determined against foodborne bacteria. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40768.

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INTRODUCTION

Electrospinning is a well-known platform technology to generate nanofibers, among other ultrathin structures, from diverse polymer and biopolymer solutions when subjected to high electric fields.[1] Unlike bottom-up methods, electrospun fibers are produced through a top-down process which results in continuous and low-cost mats of ultra-lightweight yet strong fibers that are also relatively easy to align, assemble, and process into multidisciplinary devices and applications.[2] In this regard, highest potential role that the electrospinning technology most likely can play is the construction and reproduction of multilayer materials and novel passive and active designs.[3]

Referring to the packaging area, electrospun fibers can be incorporated either as internal reinforcements or external coatings on plastic and bioplastic matrices to form multifunctional, highly hierarchically organized composites.[4,5] For instance, electrospun polyvinyl alcohol (PVA) fibers have been coffined *in situ* into polystyrene in order to enhance the mechanical properties of the resultant composites.[6] In other original research study,[7] the mechanical stress at yield and Young's modulus was improved in soybean protein isolate films by means of electrospun cellulose fibers. Core-shell nanofibers with PA-6 (Nylon-6), as core, and poly(methyl methacrylate) (PMMA), as shell, were fabricated by a coaxial electrospinning method, and afterward incorporated as reinforcing fillers in transparent composites through a hot press treatment.[8]

Under the influence of the high electric field, the electrospinning process is also able to self-assemble into the fibers some fillers such as nanoclays and nanoparticles, which should be previously properly dispersed in the polymer solution.[9] These polymer/nanoclays fibers, so-called hybrid fibers, can be later incorporated into a polymer matrix to generate novel polymer nanocomposites with the extra functional advantage of increasing the dispersion of the nanoclays in the whole polymer structure. Such polymer/nanoparticles combinations may represent a novel strategy in the development of advanced packaging materials that provides an extra mechanical and barrier performance as well as, for instance, functional protection. As an example, bio-based fibers, intended to be used as a food-packaging component, were recently electrospun from polymer blends of cellulose acetate and poly(ethylene oxide) (PEO).[10] In particular, zinc oxide nanoparticles were incorporated at 2–20 wt % into the blended fibers leading to significant improvement in the elongation at break in combination to tensile strength. In other research work,[11] dielectric boron nitride nanotubes (<5 vol %

nanotubes) were spontaneously oriented along the casting direction of PVA fibers by electrospinning. As a result of this, several fibers, thick sheets composed of parallel fibers, became the basic constituent for further making multilayer bulky polymer films with enhanced thermal conductivity. Novel nanostructured polymer/metal composite films with a thickness of ~100 μm were also manufactured using the electrospinning process.[12] Resultant films attained necessary thermal performance to be applied on thermal interface materials to microelectronics packaging applications, since they successfully provided continuous all-metal thermally conductive pathways.

Additional merit related to electrospinning technology is the functionalization of the fibers by means of encapsulation of exogenous biocides. Antibiotics and silver nanoparticles are the most preferred biocides to generate ultrathin fibers with induced antimicrobial properties.[13] The method habitually involves solubilizing the biocide substance into the polymer solution prior to electrospinning. After fiber formation, the biocide remains embedded within the electrospun nanofibers in droplets of liquid or solid particles. Later, depending on the biocide nature and according to the desired application, the biocide could remain either on the surface or in the interior in order to be properly delivered from the electrospun matrices. Indeed, through the right selection of the electrospun carrier, the release profile of the biocide can be adjusted to accomplish the specific need. For instance, encapsulation of gentamicin antibiotic in PLA fibers and PLA blended with collagen fibers resulted in electrospun fibers with adjustable release capacity for high potential uses in biomedical applications.[14] In general, for antibacterial applications, with a greater emphasis in their functional capability, the biocide-loaded fibers are preferably exposed as electrospun coatings. This definitively represents a straightforward methodology and novel strategy to design plastic surfaces that display protection against bacteria.

The current research work describes passive and active uses for previously produced electrospun ultrathin hybrid fibers.[9] Hybrid fibers were first assembled as an inner layer in multilayer films of poly(lactic acid) or polylactide (PLA) to generate passive packaging plastics with enhanced mechanical and gas barrier properties. In a second part of the work, the sustained release capacity and biocide activity of an electrospun coating on PLA films of the hybrid fibers containing natural antibacterial thymol is also presented.

MATERIALS AND METHODS

Materials

Zein from corn (grade Z3625) was purchased from Sigma-Aldrich (Spain). Ethanol of 96% vol/vol purity and trichloromethane (TCM) were supplied by Panreac Quimica S.A. (Spain). An organomodified mica, commercially marketed as Nanobioter® AC11, was provided in powder form by Nanobiomatters S.L. (Spain). The semicrystalline PLA used was a film extrusion grade produced by Natureworks (USA) with a D-isomer content of ~2%, a number-average molecular weight (M_n) of about 130,000 g/mol and a weight-average molecular weight (M_w) of about 150,000 g/mol. Thymol (grade 89330) was purchased from Fluka Chemie (Switzerland) in powder form. The purity of this material was $\geq$ 99.0% and the molecular weight was 150.22 g/mol. All materials were used as received without further purification.

Electrospinning

Prior to electrospinning, a composite solution of 35 wt % zein/nanoclays of 9 : 1 (wt/wt) was fully dissolved at room temperature in a solution of ethanol/water 85/15 (wt/wt). This polymer solution was selected as the most efficient.[9] For the hybrid antimicrobial fibers, thymol was added to the same solution in a ratio 1 : 2 (wt/wt) of thymol to zein. A pure thymol solution without zein was prepared using the same concentration and solvent mixture than those used in the polymer solution for electrospinning.

Previously described electrospinning equipment using a variable high voltage 0–30 kV power supply and a horizontal flat collector was used.[9] All electrospinning experiences were done under the following conditions: 0.30 mL/h of flow-rate, 15 kV of voltage, and 10 cm of tip-to-collector distance. Environmental conditions were maintained stable at 24°C and 60% RH by having the equipment enclosed in a specific chamber with temperature and humidity control.

Compression Molding

Round 10-cm PLA films were obtained by solvent evaporation from 20 g of a 5 wt % PLA solution in TCM. Resultant PLA cast films were horizontally attached to the electrospinning collector and zein hybrid fibers were electrospun for 10 min on the films surface. After this, one electrospun-coated film and one uncoated film were molded, with the mat between the two films, into 20-μm films by compression molding (20 tons for 3 min) at 150°C. Same process was carried out using electrospun zein fibers without nanoclays from our previous work.[9] Same PLA films without fibers were also made as control.

Morphology

The morphology of the electrospun fibers and the transversal section of the composite films were examined using scanning electron microscopy (SEM; Hitachi S-4100) after having been sputtered with a gold–palladium mixture in vacuum. All SEM experiments were carried out at 8.0 kV. Sizes were measured by means of the Adobe Photoshop 7.0 software from the microscopic micrographs in their original magnification.

Attenuated Total Reflection–Fourier Transform Infrared Spectroscopy

Attenuated total reflection–Fourier transform infrared (ATR-FTIR) spectra were collected at 24°C and 40% RH coupling the ATR accessory GoldenGate of Specac Ltd. (UK) to a Bruker (Germany) FTIR Tensor 37 equipment. The spectra were collected in the materials by averaging 10 scans at 4 cm^{-1} resolutions.

Tensile Tests

Mechanical tests were carried out on the PLA composites at 24°C and 50% RH by means of an Instron 4400 Universal Tester. Dumb-bell shaped specimens with initial gauge length and width of 25 mm and 5 mm respectively, were die-stamped from the sheets in the machine direction according to ASTM D638.

The thickness of all specimens was about 20 μm. A fixed cross-head rate of 10 mm/min was utilized in all cases and results were taken as the average of four tests. The yield point was considered when the zero slope was reached. The samples were preconditioned at 54% RH before testing and were assayed within 2 weeks after preparation of the films.

Oxygen Transmission Rate Measurements

The oxygen permeability (P) was derived from oxygen transmission rate (OTR) measurements recorded using an Oxtran 100 equipment of Modern Control (USA). Conditions were kept at 24°C and 0% RH and experiments were done in duplicate. The samples were purged with nitrogen for a minimum of 20 h, prior to exposure to a 100% oxygen flow of 10 mL/min, and a sample area of 5 cm^2 was measured by using an in-house developed mask. The diffusion coefficient (D) was estimated from fitting the OTR-time curve to the first six sum terms of the following solution of the Fick's second law[15]:

$$\mathrm{OTR}\,(t)=\frac{P_p}{l}\left[1+2\sum_{n=1}^{\infty}(-1)^n\exp\left(-\frac{D\pi^2n^2t}{l^2}\right)\right] \quad (1)$$

In eq. (1), P_p is the oxygen partial pressure and l is the film thickness. The solubility coefficient (S) was calculated by solving for S in the following equation[16]:

$$P=D\times S \quad (2)$$

Release Kinetics

Thymol release kinetics were determined by ATR-FTIR spectroscopy during desorption of the antimicrobial substance, as in previously described methodology.[17] In order to do so, about 5-μm mats of both zein and hybrid zein fibers containing thymol were electrospun on the surface of the ATR accessory of the spectroscopy equipment. For the kinetics of release of the free substance, a drop of the thymol solution without zein was cast in the same experimental conditions.

Experimental curves and diffusion coefficients of thymol were determined by ATR-FTIR spectra during desorption of the antimicrobial substance. To obtain D values from the desorption curves, an approach based on an observed initial "lag" time (normalized to path length L), during which little desorption occurs within the evanescent field, followed by a pseudo-Fickian behavior at short times, was used[18]:

$$\frac{A_t}{A_\infty}=\frac{2}{L}\left(\frac{D}{\pi}\right)^n t^n \quad (3)$$
$$n=0.5$$

In eq. (3), L is the thickness of electrospun mat whereas A_t and A_∞ are the absorbances (of the thymol ring vibration band at 807 cm^{-1}) at a given time t and at saturation or equilibrium sorption conditions, respectively.

Antibacterial Assay

For antimicrobial assays, *Listeria monocytogenes* CECT 5672 (Spanish Type Culture Collection, Spain) was selected as model food-borne pathogen bacterium for the susceptibility tests. The strain was stored in phosphate buffer saline with 10 wt % tryptic soy broth (TSB) and 10 wt % glycerol at −85°C until needed. Previous to each study, an aliquot from the culture was refreshed overnight, transferred to TSB, and grown at 37°C to the mid-exponential phase of growth. A bacterial suspension of this culture was spread on tryptic soy agar (TSA) plates as to achieve bacterial counts of about 5 × 10^5 colony forming units (CFU).

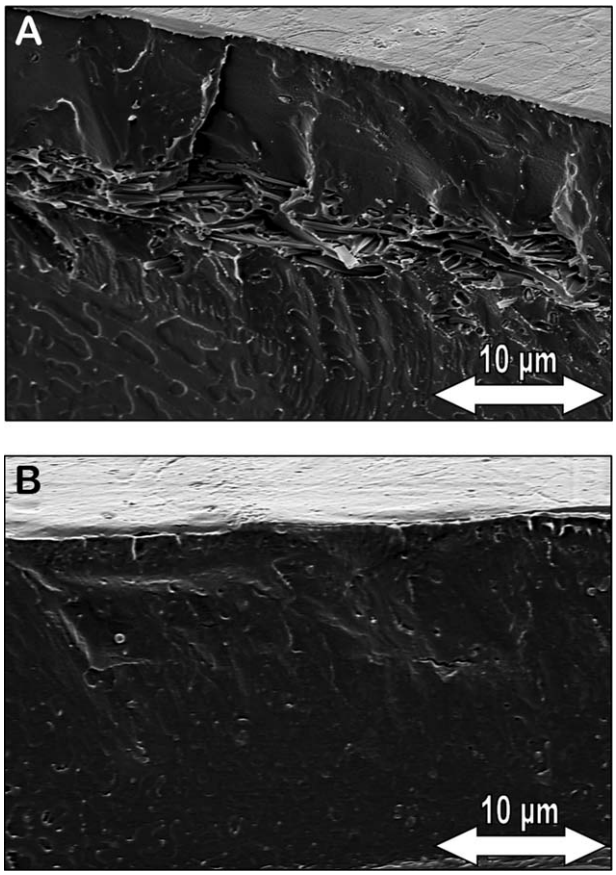

Figure 1. SEM photographs of the transversal sections of: (A) PLA/zein hybrid fibers/PLA multilayer film and (B) PLA monolayer film. Scale markers of 10 μm in both cases.

The antimicrobial potential of the hybrid fibers was performed by incubating *L. monocytogenes* for 72 h in a closed atmosphere in desiccators of 3200 cm^3 at 43% RH and 22°C containing increasing weights of the thymol-loaded fibers electrospun on the PLA films. Antibacterial properties of same zein fibers without thymol were also checked to evaluate the effect of the residual ethanol solvent that may be attained in the fibers after the electrospinning and could affect bacterial growth. All antibacterial experiments were carried out in triplicate.

RESULTS AND DISCUSSION

Multilayer Films

The PLA multilayer film, i.e. the PLA film containing the electrospun zein hybrid fibers as an inner layer, is presented in Figure 1(A). As a result of the compression molding process, the ultrathin fibers were incorporated as a core layer of about 5 μm of thickness sandwiched in two PLA layers. Weight measures carried out on the PLA films, before and after electrospinning, and previous to the compression molding process, determined that the fibers represented about 1.45 wt % to the whole mass.

Table I. Thickness and Mechanical Values of the PLA Films

Sample	d (μm)	E (GPa)	σ_{yield} (MPa)	ε_{break} (%)
PLA film	21.03 ± 1.01	1.24 ± 0.38	29.50 ± 1.27	8.06 ± 0.14
PLA film with zein fibers	19.95 ± 0.98	1.25 ± 0.29	29.01 ± 0.87	9.01 ± 0.21
PLA film with hybrid zein fibers	20.52 ± 1.06	1.51 ± 0.77	31.80 ± 1.00	5.58 ± 0.12

Table II. Oxygen Permeability, Oxygen Diffusion Coefficient, and Solubility Coefficient of the PLA Films at 0% RH and 24°C

Sample	P (m^3 m/s m^2 Pa)	D (m^2/s)	S (g/g Pa)
Literature value PLA[19]	$2.25e^{-18}$		
PLA film	$2.27 \pm 0.02e^{-18}$	$1.60e^{-12}$	$14.19e^{-7}$
PLA film with pure zein fibers	$1.34 \pm 0.06e^{-18}$	$0.86e^{-12}$	$15.53e^{-7}$
PLA film with hybrid zein fibers	$1.19 \pm 0.06e^{-18}$	$0.78e^{-12}$	$15.37e^{-7}$
Literature value zein[21]	$1.60e^{-19}$		
Literature value PP[22]	$8.60e^{-18}$		
Literature value PET[19]	$2.15e^{-19}$		

This implies that the bulk density of the zein fibers introduced in the PLA matrix was only about 58.6 kg/m^3. Additionally, the attained multilayer films did not noticeably show the presence of voided regions or phase separation between the zein fibers and the PLA matrix. As a result of this, a good interfacial adhesion between the biopolymer and fibers can be expected. Figure 1(B) presents the PLA film transversal section without fibers used for the control.

Mechanical Properties

Table I summarizes the mechanical values of the PLA multilayer films obtained from the tensile test. From the table, it can be seen that PLA biopolymer is, as expected, a brittle and elastic material. This may replace packaging applications of conventional rigid plastics such as those of amorphous general purpose polystyrene (GPPS). In relation to the fiber incorporation, on one hand, it was found that the introduction of the electrospun zein fibers without clays did not exert a significant effect on the tensile properties of the PLA film. On the other hand, the mechanical resistance of the multilayer PLA films with the electrospun hybrid fibers was found to increase. This resulted in a more elastic and slightly rigid material. In particular, the Young's modulus and the tensile strength at yield increased about 22% and about 8%, respectively, while the elongation at break decreased about 31%. This demonstrates that the hybrid fibers effectively reinforced the PLA film, even though the clay content for the whole multilayer structure was relatively low, about 0.15 wt %.

Gas Barrier

In Table II are presented the experimental oxygen permeability values for the PLA multilayer film. The table also gathers values for other commercial polymers and biopolymers at dry conditions. Experimental values for pure PLA biopolymer is similar to that found in literature.[19] Results also indicated that the PLA multilayer films containing the electrospun zein-based fibers have lower oxygen permeability compared to the unfilled PLA films obtained at same process conditions. In particular, diffusion decreased to about 41% and about 47% for films with pure zein and hybrid zein fibers, respectively. Reduction of oxygen permeability was not as high as that recently obtained using zein electrospun fibers for a PLA/polyethylene glycol (PEG) blends (ca. 71%).[20] However, in our previous work, reduction was higher because the PLA matrix was definitely plasticized by PEG. Interestingly, the table also indicates that permeability reduction was achieved in spite of the fact that oxygen solubility was higher, certainly due to the presence of rich zein regions in the PLA matrix. A reason for this is that, as it can be seen in the table, the electrospun fibers produced a severe decrease in the gas diffusivity. In fact, corn zein is a high barrier polymer to oxygen at dry conditions.[21] The electrospun zein mesh, presented as an inner layer in the PLA films, succeeded to reduce the oxygen diffusion of the biopolymer by creating a tortuous

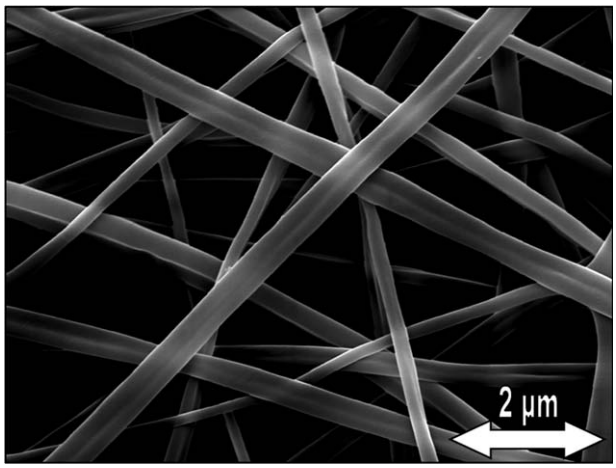

Figure 2. SEM micrograph of the electrospun fibers of zein/nanoclays of 9 : 1 (wt/wt) containing thymol. Scale marker of 2 μm.

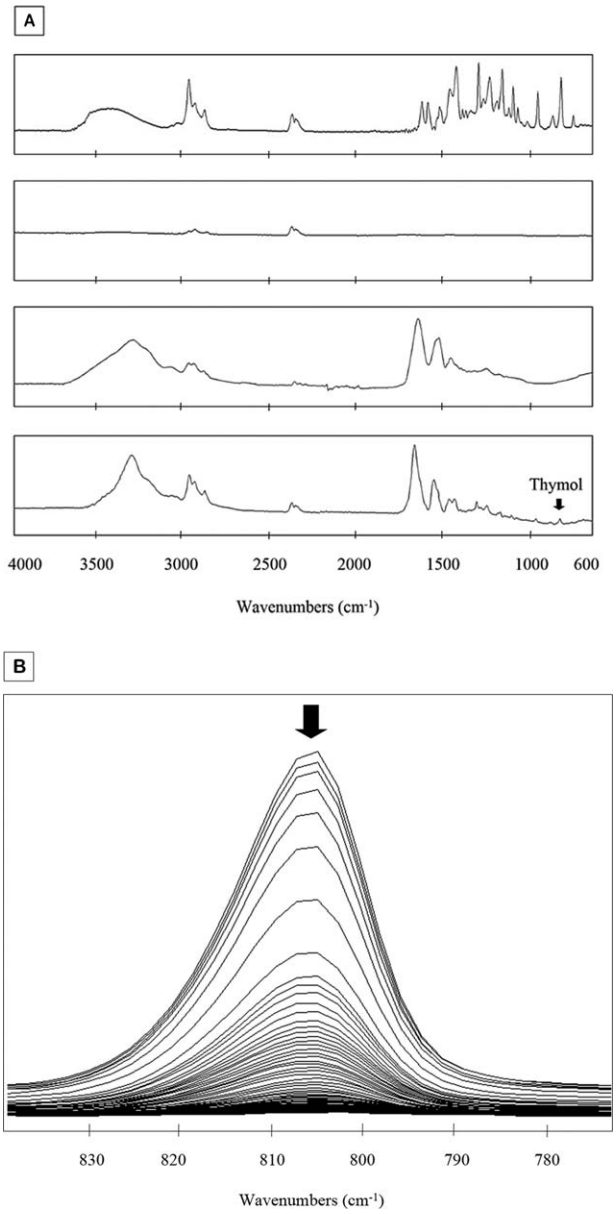

Figure 3. A: ATR-FTIR spectra of, from top to bottom, fresh thymol, released thymol, zein hybrid fibers, and zein hybrid fibers containing thymol; (B) Detail of the evolution of the ATR-FTIR band at 807 cm^{-1} in the spectra of thymol recorded during the *in situ* release for a time span of 5 h. The arrow indicates the presence of the band and the direction of the band evolution over time.

pathway for the gas molecules. In particular, highest barrier was observed for the hybrid fibers, which feasibly acted as a more effective arrangement to block the oxygen molecules route by the additional platelet-like nanoclays presence. In particular, the multilayer PLA films containing the electrospun hybrid fibers resulted about sevenfold more barrier to oxygen than polypropylene (PP)[22] and only fivefold more permeable than PET.[19]

Release Capacity

Figure 2 shows the SEM micrograph of the hybrid zein fibers containing thymol after being electrospun on the PLA films surface. It can be seen from the image that typical tubular-like fibers of 283 nm were obtained. Addition of thymol to the polymer solution did not affect the zein fiber morphology and fibers are similar in shape and size to those of zein hybrid fibers previously obtained at the same processing conditions.[9]

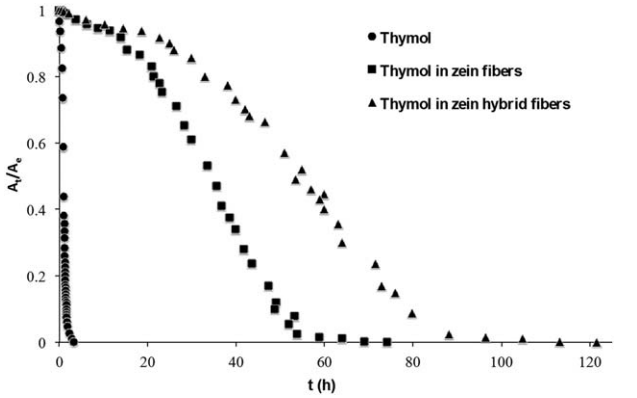

Figure 4. Normalized ATR desorption (A_t, absorbance at any time t during desorption vs. A_e, initial equilibrium absorbance at time zero) kinetics of the thymol release from fresh thymol, zein fibers containing thymol, and zein hybrid fibers containing thymol.

Figure 3(A) gathers the FTIR spectra of the pure thymol solution before and after release, the electrospun hybrid fibers, and the electrospun hybrid fibers containing thymol. From the fresh thymol solution (top spectrum) it can be seen that major absorption bands of thymol are at about 738 and 807 cm^{-1} that correspond to ring vibrations of the thymol chemistry.[23] By comparison between this and the released thymol (2nd spectrum from the top), it is seen that some bands changed intensity and/or shape during the release process. In particular, the major spectral change of thymol can be observed in the band at 807 cm^{-1}. Figure 3(B) shows the decrease over time of the mentioned characteristic band of thymol recorded *in situ* during open-air release at ambient conditions. It is seen that the peak intensity vanished with time, in both free and encapsulated thymol, albeit clearly faster in the free thymol (see later). From the normalized peak intensity drop, release kinetics for thymol could be easily followed.

Figure 4 shows the release curves obtained from the FTIR spectra. The curves clearly indicated that there is a decrease in the release kinetics of thymol when this was encapsulated in the zein fibers. Particularly, free pure thymol became completely consumed (taken as the time at which the band at 807 cm^{-1} vanished in the spectra) in 3 h. On the contrary, when thymol was encapsulated in the electrospun zein fibers, complete release was extended for more than 72 h. In the case of the hybrid fibers, release of thymol was additionally sustained up to about 110 h. Table III presents

Table III. Diffusion Coefficients (m^2/s) for the Release of Thymol

Sample	D (m^2/s)
From pure thymol	$5.74 \pm 0.06e^{-15}$
From zein fibers	$1.61 \pm 0.08e^{-16}$
From zein hybrid fibers	$1.03 \pm 0.07e^{-16}$

Table IV. Fiber Weight, Maximum Thymol Concentration Inside the Desiccators (Assuming 100% Release from the Fibers), CFU Counts and Growth Inhibition of the Electrospun Hybrid Fibers Containing Thymol

Fiber weight (mg)	Max. thymol concentration ($\mu g/cm^3$)	Bacterial counts (Log CFU)	Growth inhibition (%)
0	0	5.71 (0.05)[a]	-
200	0	5.69 (0.09)	6.67%
5	0.3	5.67 (0.07)	8.80%
10	0.6	5.56 (0.09)	29.21%
25	1.6	2.69 (0.32)	99.91%
50	3.1	2.58 (0.21)	99.93%
75	4.7	1.56 (0.36)	99.99%
100	6.3	N.G[b]	100%
200	12.5	N.G.	100%
200	12.5	N.G	100%

[a] Standard deviation.
[b] No growth observed.

the diffusion coefficients obtained from the curves. This table shows that thymol is released from the zein hybrid fibers with slower kinetics, with a reduction of about 36% when compared to the neat zein fibers, due to the presence of the nanoclays. This is likely the result of an extra tortuosity effect imposed by the dispersed platelet-like nanoclays for the diffusion of the thymol molecules through the zein fibers.

Antibacterial Activity

Table IV gathers results obtained from the antibacterial tests. The table reveals that zein fibers without thymol did not exert a significant decrease in the bacteria growth as compared to the control. This indicates that the antimicrobial effect of the fibers was not related to any amount of entrapped ethanol from the polymer solution in the electrospun mesh. Therefore, the biocide activity is only attributed to the release of thymol. CFU in samples with 0.3 and 0.6 ppm of thymol is not significantly different to the control without fibers. Remarkably, a concentration as low as 1.6 ppm was able to produce a decrease in CFU of about 3 log units, meaning that the growth of 99.9% of the bacterial population was being inhibited at that concentration. Furthermore, above 6.1 ppm no CFU were detected. This demonstrates the high biocide efficiency of the tested hybrid fibers and their potential use as coatings against selected food-borne model bacteria.

CONCLUSIONS

Passive and active packaging represents, definitely, one of the most accessible and potential industrial application related to the electrospinning technology.[5] The present work demonstrates that electrospun fibers, and particularly hybrid fibers of zein with nanoclays, can play a major role in the design of novel multifunctional materials for food packaging.

For load-bearing applications, the zein hybrid fibers show potential as reinforcing fillers to improve the mechanical performance of bioplastic PLA matrices. When incorporated as inner layers, these can be applied to develop multilayer packaging structures with enhanced gas barrier properties. This is achieved due to the large aspect ratio (length/diameter) of the electrospun fibers, which can successfully establish a tortuous pathway for the diffusion of the oxygen gas molecules. Additionally, electrospun coatings of the hybrid fibers can also help to control the release of natural extract biocide thymol. Uses of such biocide ultrathin fibers may represent an excellent potential for added-value applications in the active packaging field to, for instance, increase protection and extend shelf life for foodstuffs.[13]

The electrospinning technology is, therefore, originally presented here as a novel platform to produce high added-value biopolymer-based multilayer structures with potential uses in food packaging. Since reported hybrid fibers have the advantage of being renewable and biodegradable, they can be regarded as good candidates to improve the physical properties as well as to control the release of biocides in bioplastics.

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