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Optimization of PCL Polymeric Films as Potential Matrices for the Loading of Alpha-Tocopherol by a Combination of Innovative Green Processes

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Abstract: Active food packaging represents an innovative way to conceive food packages. The innovation lies in using natural-based and biodegradable materials to produce a system intended to interact with the food product to preserve its quality and shelf-life. Compared to traditional plastics, active packaging is designed and regulated to release substances in a controlled manner, mainly antimicrobial and antioxidant compounds. Conventional technologies are not suitable for treating these natural substances; therefore, the research for innovative and green techniques represents a challenge in this field. The aim of this work is to compare two different polymeric structures: nanofibrous films obtained by electrospinning and continuous films obtained by solvent casting, to identify the best solution and process conditions for subjecting the samples to the supercritical fluids impregnation process (SFI). The supports optimized were functionalized by impregnating alpha-tocopherol using the SFI process. In particular, the different morphologies of the samples both before and after the supercritical impregnation process were initially studied, identifying the limits and possible solutions to obtain an optimization of the constructs to be impregnated with this innovative green technology in the packaging field.

Keywords: supercritical fluid impregnation; electrospinning; solvent casting; antioxidant packaging; materials optimization

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1. Introduction

In recent years, the food packaging sector has been subject to an important re-evaluation derived by the current environmental needs to find alternatives to traditional packaging. Materials of petrochemical derivation have dominated this field for decades due to their numerous advantages in terms of low cost and ease of production. It facilitates the marketing of a wide range of food products through lightweight, highly flexible, elastic, and performing packaging systems [1]. All these advantages have led to a constant increase, over the years, in the production of mainly disposable packaging, which, given their nonbiodegradability and disposal difficulties, have inexorably accumulated not only in landfills but also in the environment, bringing to a global environmental pollution problem [2,3]. For this reason, the scientific community is increasingly aiming at finding new biodegradable materials that can gradually replace plastics. This research seems to have found a solution in using biopolymers synthesized from natural sources, such as biomass and microorganisms [4–7], or even extracted from agri-food wastes, such as polysaccharides and proteins [8–10].

Polycaprolactone (PCL) is a biopolymer of fossil origin, but it is biodegradable. This polyester is attractive because of its excellent properties of biocompatibility, nontoxicity, and thermal stability. For these reasons, it has already found wide use in the biomedical field, also as a drug delivery system approved by the Food and Drug Administration

(FDA) [11–14]. This polymer has been used in the field of food packaging through the production of active packaging [15,16], which are systems capable of interacting with packaged food products by releasing or absorbing controlled and regulated substances [17], in order to preserve the quality and shelf-life of the products [18]. The use of natural substances, such as essential oils, natural extracts, vitamins, etc., for the fabrication of active packaging with mainly antimicrobial and antioxidant action has been reported [19–22]. However, traditional packaging production techniques are no longer an obvious choice when working with biopolymers and natural substances, as they have several drawbacks. For example, in extrusion [23], high process temperatures are required for the melting of polymers, large quantities of often toxic and polluting organic solvents are necessary, and the incorporation of bioactive substances into the polymers themselves is difficult, as they can be degraded by the high process temperatures. In some cases, the natural ingredients are deposited as external coatings of the packaging film; in this case, a low penetration into the polymer structure and significant degradation of the active compounds by external agents have been observed [24].

In order to try to overcome these drawbacks, innovative green techniques that are more suitable for the processing of biopolymers and bioactive molecules have been recently proposed in the literature. In particular, electrospinning is a technique capturing more and more attention, as it allows to work at low temperatures, with the use of green solvents, and it can provide micro and nanostructured polymer matrix [25,26]. It is a technique that uses only the electric field as a driving force to produce fibers arranged in a random way that gives rise to a porous structure with a large surface-to-volume ratio. This characteristic makes electrospun mats suitable for drug delivery systems or active packaging films [27]. Another method, already used on an industrial scale, is solvent casting, a low-cost, versatile, and green technique, which consists of the solubilization of the polymer of interest in an appropriate solvent. Specifically, the solution is poured into a mold, and the evaporation of the solvent leads to the production of thin, isotropic, and transparent films [28]. These techniques have been extensively investigated in the literature for biopolymers processing [29,30]. The impregnation process assisted by supercritical fluids (SFI) is an interesting method for loading active ingredients inside polymeric preformed structures [31]. SFI works by exploiting the high solvent power of CO_2 in supercritical conditions ($scCO_2$) and its high diffusivity to solubilize the active ingredient of interest and diffuse it within the polymer matrix, without the need to use other solvents or high temperatures. Indeed, carbon dioxide reaches the supercritical state in mild conditions (T_c = 31.1 °C, p_c = 7.38 MPa) [32,33]. It is a process that allows high penetration of the compound within the polymeric structure [34].

SFI has been applied in the literature for active compound impregnation into PCL [35]. Most of the time, these impregnation studies have been conducted using PCL granules [36,37]. PCL films have been rarely processed with SFI due to the foaming activity of CO_2 against this polymer; indeed, the most used polymers matrix for the SFI process are poly(lactic acid) (PLA) [38], acrylic-based hydrogels [39], cellulose acetate [40], and poly(methyl methacrylate) (PMMA) [41]. In some cases, the use of polymeric blend with PCL was demonstrated to improve the structure resistance to the CO_2 foaming effect [42]. Process conditions are particularly important to allow good impregnation without significantly modifying the polymeric structures. For these reasons, PCL was generally processed at low temperatures from 35 to 40 °C and moderate pressure from 110 to 200 bar [35,43].

Therefore, the first part of this paper concerns the optimization of SFI of different polymeric PCL-based structures produced by both electrospinning and solvent casting methods. PCL blended with polyethylene glycol (PEG) has been also studied. PEG was selected to improve the handling of the films produced, especially by solvent casting [28], and for its antifogging properties reported in the literature due to its hydrophilic nature [44]. Then, in the second part of this work, SFI of alpha-tocopherol, selected as a model natural active compound, has been performed [45,46]. The best combination of process conditions has been researched to provide a possible process layout for PCL-loaded alpha-tocopherol films production that allowed good loading of the active compounds, avoiding their degradation, high penetration inside the polymeric film, and preservation of the polymeric structure and functionality.

2. Materials, Equipment, and Methods

2.1. Materials

Polycaprolactone (PCL, Mn 80,000), alpha-tocopherol (purity > 97%), and polyethylene glycol (PEG 400) were purchased by Sigma-Aldrich, Milan, Italy; acetone and acetic acid glacial (extra pure) were provided by Carlo Erba Reagents S.A.S, Val-de-Reuil, France; carbon dioxide (CO_2, purity 99%) was purchased by Morlando Group S.R.L., Sant'Antimo, Naples, Italy.

2.2. Production of PCL-Based Matrices

The polymeric matrices were produced both by electrospinning and solvent casting following the scheme reported in Figure 1. The electrospinning used (Spinbow, Bologna, Italy) is composed of a high voltage generator (PCM, Spellman, New York, NY, USA), a syringe pump (KDS-100, KD Scientific, Holliston, MA, USA) which feeds an 18 Gauge injector needle with a blunt tip to which the anode is connected, while the cathode consists of a flat plate collector discharged to the ground where the fibers are deposited. The solutions to be processed were prepared by dissolving the PCL with a fixed concentration of 20% *w*/*w* with respect to the solvent consisting of a mixture of acetone and acetic acid in a ratio of 3:7 *v*/*v*. PEG was added to the same solution as a plasticizer at different concentrations (from 0% to 10% *w*/*w* with respect to the polymer content). The solutions were stirred at 60 °C for about 1 h, until the complete solubilization of the polymer, after which, once cooled to room temperature, different quantities of solution were processed to obtain films of different thicknesses, with a voltage of 19 kV, a flow rate of 1.7 mL/h, and a needle-collector distance of 16.5 cm.

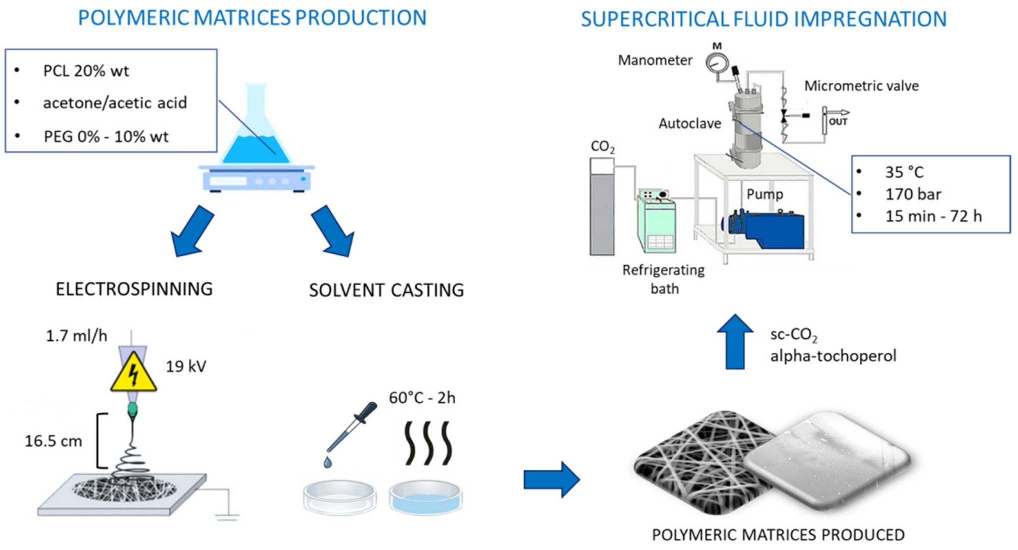


Figure 1. Scheme of the experimental steps based on different combinations of green processes: production of the polymeric matrices by electrospinning and solvent casting (left); supercritical impregnation of the supports (right).

Similarly, for the solvent casting process, the PCL concentration was set at 20% *w*/*w* while the amount of PEG was always varied from 0 to 10% in weight with respect to the PCL content. A variable amount of the solutions was poured into Petri dishes with a diameter of 9 cm, placed in an oven at 60 °C for two days, and then left in the desiccator for at least 30 min before being removed from the plates.

2.3. Supercritical Fluid Impregnation

The feasibility tests of supercritical impregnation and the effective loading of alpha-tocopherol into the polymeric supports were performed in a homemade lab-scale plant. It consists of a 100 mL stainless steel autoclave (NWA GmbH, Ahlen, Germany) into which the CO_2, first cooled and then compressed, is fed by a piston pump (Milton Roy, model Milroyal B, Pont-Saint-Pierre, France). An internal impeller, axially mounted, ensures homogeneous mixing. The operating pressure inside the autoclave is monitored by a digital manometer (Parker, Minneapolis, MN, USA), while the thermal control is performed by a PID controller (Watlow, mod. 93, St. Louis, MO, USA). Finally, the CO_2 is returned in gaseous form in atmospheric conditions by depressurization through a micrometric valve (Hoke, mod. 1315G4Y, Spartanburg, SC, USA).

Before proceeding with the supercritical impregnation, a feasibility study was conducted on films of PCL and PCL + PEG at different concentrations, obtained by electrospinning and solvent casting, placed in contact with $scCO_2$. In particular, a fixed surface (about 2 cm^2) of each sample at different thicknesses was weighed and placed inside the autoclave. The tests were carried out at a temperature of 35 °C and a pressure of 170 bar, testing different contact times up to 72 h. At the end of each test, the CO_2 was depressurized to environmental conditions, and the surface and weight of each sample were re-measured. Once the best combinations of the PEG percentage, thickness, and contact times were identified, the supercritical fluid impregnation experiments were performed; the process was carried out by placing a quantity of alpha-tocopherol inside a container mounted axially on the impeller to let it enter in contact with CO_2 once the process has started, keeping the pressure and temperature conditions, reported above, fixed, and varying the impregnation times. Figure 1 reassumed each step of the work, starting from the production of polymeric matrices through electrospinning and solvent casting, followed by the supercritical impregnation of alpha-tocopherol on the supports fabricated.

2.4. Analytical Methods

The morphology of the samples was observed both before and after the supercritical process through Field Emission Scanning Electron Microscopy (FESEM, LEO 1525, Carl Zeiss SMT AG, Jena, Germany) coating the samples with a gold–palladium layer. The mean diameter of the fibers was evaluated using the image processing software ImageJ, analyzing no less than 300 fibers per sample.

The effective loading of alpha-tocopherol on the supports was evaluated by gravimetric method carried out on all samples for each impregnation time. In detail, the initial weight of the samples before the supercritical process and the final weight of the impregnated samples were evaluated. The effective loading was then calculated as the difference between the final and the initial weight.

The migration tests of alpha-tocopherol were carried out on the samples produced both by electrospinning and by solvent casting after the supercritical impregnation process. The samples with known weight were immersed, in static, in a defined volume of EtOH 50% to simulate the behavior of food products with lipidic content. The samples were placed under accelerated mass transfer conditions at 40 °C, analyzing the release fluid by UV-vis at 295 nm at fixed time intervals until a constant value was reached. Migration kinetic was expressed as the mg of alpha-tocopherol released with respect to the mg of alpha-tocopherol loaded by impregnation.

3. Results

3.1. Feasibility Study of the SFI Process and PCL Supports Optimization

Electrospinning and solvent casting techniques were used to produce different polymeric films, as shown in Figure 2, to support the supercritical impregnation of alpha-tocopherol. To prepare the films, different amounts of polymeric solution were processed by both techniques to obtain supports of different thicknesses, according to the method described in Section 2.2. In particular, nanofibrous samples (fiber mean diameter of 850 nm) with a thickness of 30 to 300 μm were obtained by electrospinning, processing from 5 to 10 mL of a 20% *w*/*w* solution of PCL. Samples with a continuous structure, with a thickness of 50 to 200 μm, were produced by solvent casting, pouring on the casting mold from 5 to 10 mL of the 20% PCL solution. The percentage of PEG, in the case of both techniques, was varied. The presence of PEG was instrumental in the case of solvent casting, as it facilitates the removal of the samples from the mold.

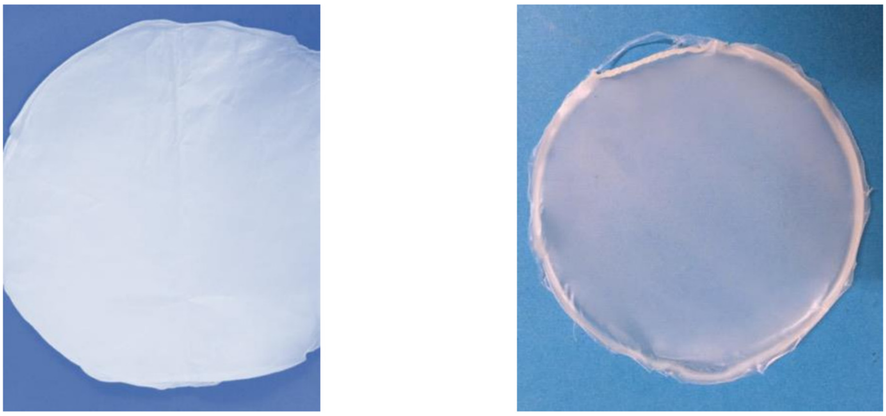

(**a**) (**b**)

Figure 2. PCL 20% wt + PEG 10% wt films produced by (**a**) electrospinning and (**b**) solvent casting.

The feasibility study of supercritical impregnation was conducted by first investigating the behavior of the two different materials placed in contact with supercritical CO_2 (in the absence of alpha-tocopherol). When in contact with $scCO_2$, PCL is subjected to the foaming phenomenon; this causes the formation of pores inside the structure in which the active ingredient can then be impregnated. Unfortunately, however, $scCO_2$ generates a depression of the melting temperature (T_m) in semicrystalline polymers. Campardelli et al. [37] observed that PCL is processable with $scCO_2$ at 40 °C/150 bar or 35 °C/200 bar. For this reason, the first part of the work concerned optimizing the solution composition and operating parameters of film production to obtain a structure that can be maintained after contact with $scCO_2$. In particular, the $scCO_2$ contact tests were conducted on samples with different thicknesses and different PEG content (from 0 to 10% *w*/*w*), at 35 °C, 170 bar, varying the contact times with the $scCO_2$ between 15 min and 72 h.

Table 1 summarizes and schematizes the experimental tests of contact with $scCO_2$, which indicate, for both techniques, the effect obtained and the parameters that most influenced the process.

Table 1. Summarized results of tests conducted on all supports in contact with $scCO_2$ at 35 °C and 170 bar.

Thickness (μm)	**% PEG**	**Contact Time (h)**	**Macroscopic Aspect**	**Formation of Pores**
		ELECTROSPUN SUPPORTS		
<100	0–2.5–5–10	15 min–72 h	Nonintact structure	yes
>100	0–2.5–5	<2 h	Nonintact structure	yes
>100	5–10	<2 h	Intact structure	yes
		SOLVENT CASTING SUPPORTS		
<100	0–2.5–5–10	15 min–72 h	Nonintact structure	yes
>100	0	<24 h	Nonintact structure	yes
>100	2.5–5	<24 h	Semi-intact structure	yes
>100	10	<24 h	Intact structure	no

In particular, for very thin samples, with a thickness lower than 100 µm, placed in contact with $scCO_2$, it was not possible to maintain the structure of the films, neither for those produced by electrospinning nor for those made by solvent casting; indeed, the effect of T_m depression was predominant for each contact time. Furthermore, the presence of PEG has also been found to have an important role in improving the structure of the samples, since, on the one hand, it acts to improve the handling and, on the other hand, it has been shown to act as a protective barrier of the polymer from the action of $scCO_2$. This is especially the case for supports produced by solvent casting, where its effect is particularly evident and allows to work for longer contact times than electrospun supports, for which, instead, the limiting factor is mainly the contact time. In fact, in the case of casted films, for all the PEG contents, the porous structure was maintained, as shown in Figure 3, in which the FESEM images of the samples obtained by casting before and after the contact with $scCO_2$ are reported. Indeed, after the supercritical process, the structure of the supports obtained by casting has holes, which decrease in size as the PEG content increases. The diameters of the holes, measured by image analysis software, are reported in Table 2.

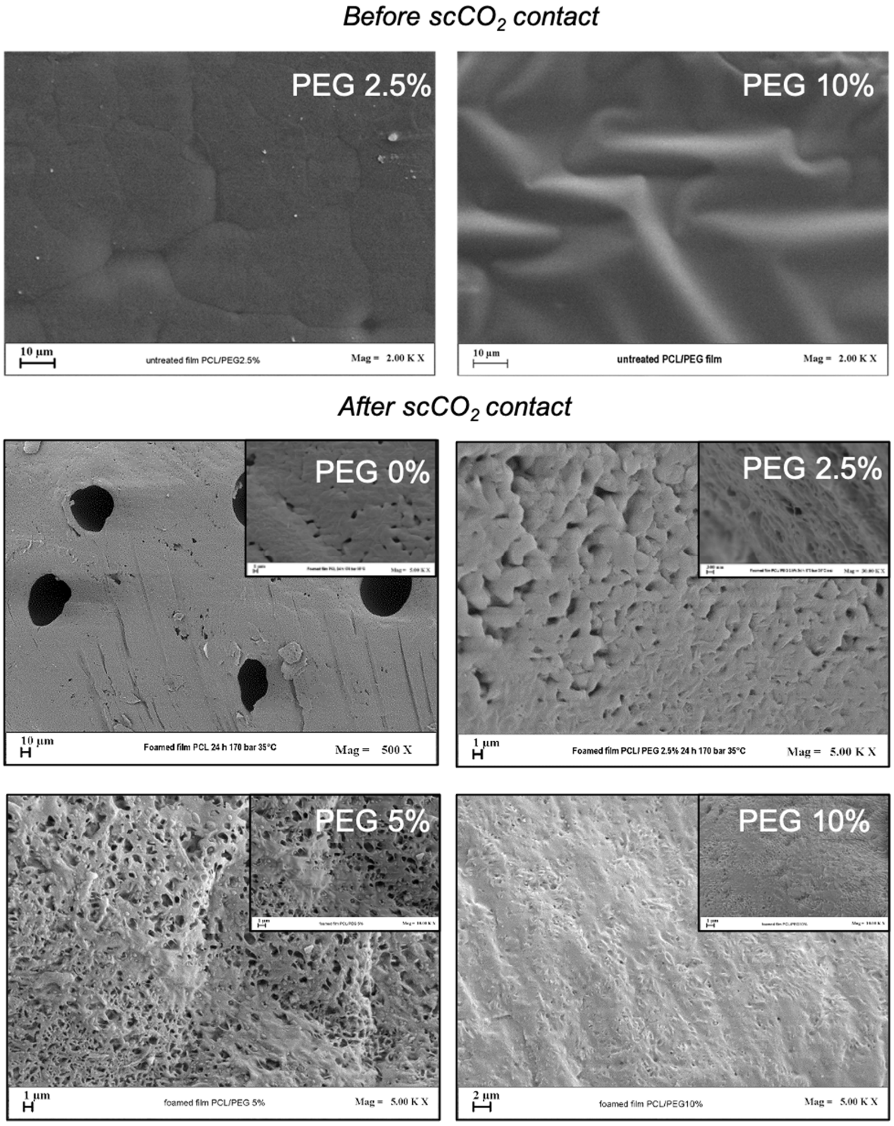
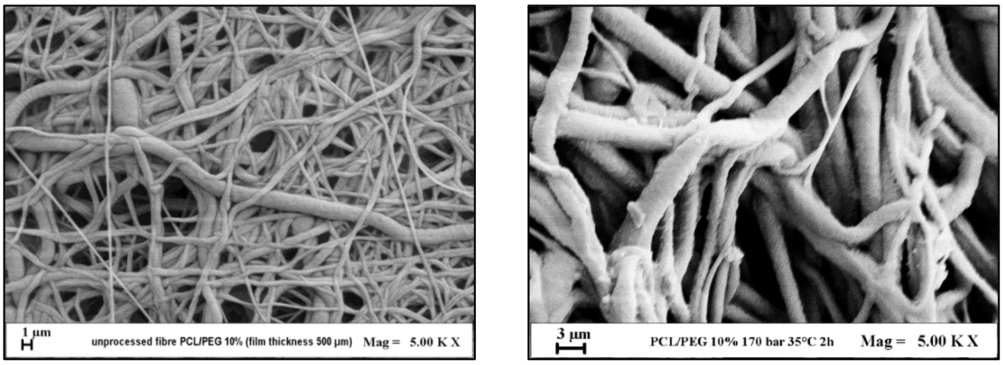


Figure 3. FESEM images of casted film of PCL + PEG 2.5% and PCL + PEG 10% before the $scCO_2$ process; and FESEM images after the contact with $scCO_2$ for 24 h at 170 bar and 35 °C as the PEG percentage varies.

Table 2. The pore size of the casted films after contact with $scCO_2$ for 24 h at 170 bar and 35 °C.

PEG Content (%)	Pore Size (μm)	Standard Deviation (μm)
0	1.22	0.28
2.5	0.85	0.22
5	0.46	0.09
10	0.15	0.04

In Figure 4, the FESEM images of the samples obtained by electrospinning before the contact with $scCO_2$ and after the contact referring to the best conditions investigated are reported.



(**a**) (**b**)

Figure 4. FESEM images of the electrospun films of PCL + PEG 10% with a thickness of 500 μm: (**a**) before the contact with $scCO_2$ and (**b**) after the 2 h of contact.

Considering that the FESEM images reported in Figure 4 are taken at the same magnification, it is evident that the contact of the fibers with $scCO_2$ causes the swelling of the fibers without compromising the structure of the sample. The optimization of the supports, intended as maintaining the macrostructure of the samples, was therefore obtained by working with samples with a thickness greater than 100 μm, with a PEG content equal to 10%, in particular for casting supports, and for contact times with the supercritical fluid not longer than 2 h for the electrospun supports. For lower thicknesses, lower quantities of PEG, and higher contact times, the structure is damaged, as seen in Figure 5, which shows the results before (a) and after (b) optimizing the materials' production.

(**a**) (**b**)

Figure 5. Macroscopic structure of electrospun PCL films after contact with $scCO_2$: (**a**) not optimized and (**b**) optimized.

3.2. Loading of Alpha-Tocopherol and Study of the Supercritical Impregnation Kinetics Performed on the Optimized Supports

Having identified the limits and the best conditions for subjecting both types of polymeric supports to the supercritical process, the systematic study of alpha-tocopherol loading was started. The impregnation process was carried out on the samples (support size of 2 cm^2) at 170 bar and 35 °C at different impregnation times, depending on the support production technique, considering the process optimization performed in Section 3.1.

In particular, concerning the samples produced by casting, it was seen that the concentration of PEG is a determining parameter for the preservation of the macrostructure. It was, therefore, decided to investigate the kinetics of impregnation as the concentration of PEG varies, from 0% to 10%, initially setting an impregnation time equal to 24 h, with time identified as the maximum above which even the samples produced with the maximum concentration of PEG and high thicknesses are damaged. The main results obtained are shown in Table 3.

Table 3. Kinetics of impregnating alpha-tocopherol in PCL films by casting varying % of PEG [set at impregnation time 24 h, at 250 °C and 170 bar].

% PEG	Alpha-Tocopherol Impregnated (mg_{TOC}/mg_{FILM})	Effect
0	1.234	Higher impregnation but a significant modification of the structure
2.5	0.998	Impregnation and foaming
5	0.959	Impregnation and foaming
10	0.828	Lower impregnation but preservation of the structure

Specifically, loading the antioxidant into the supports without PEG, a higher effect of CO_2 was observed: larger pores were formed, a higher amount of alpha-tocopherol was charged into the sample, but the macroscopic structure was damaged. In the samples with PEG values equal to 2.5% and 5%, both the impregnation of the antioxidant compound and the formation of pores were observed, while for PEG values equal to 10%, the impregnation was prevalent with respect to the modification of the structure.

On the other hand, alpha-tocopherol impregnation results showed lower loadings as the percentage of PEG increases, going from 1.234 mg_{TOC}/mg_{FILM} loaded on the sample of only PCL to 0.828 mg_{TOC}/mg_{FILM} loaded on samples of PCL + PEG 10% with the same contact time of 24 h. This trend can be explained by considering the morphology study carried out through FESEM analysis, reported in Figure 6. Indeed, as the concentration of PEG increases, the size of the pores decreases. Considering that the structures formed are closed-cell structures, the larger pores offer a greater exposed surface in which the alpha-tocopherol can be impregnated; therefore, the larger the pores, the higher the amount of alpha-tocopherol charged.

In the case of the samples obtained by electrospinning, the effect of PEG% on alpha-tocopherol impregnation was not evaluated since PCL + PEG 10% was the only condition that allows preserving the structure of the polymeric matrix for a contact time lower than 2 h. The alpha-tocopherol impregnation kinetics was then studied, varying the impregnation time, using PCL + PEG 10% films for both electrospun and casting films. The results are reported in Table 3. For the films obtained by casting, the impregnation kinetics was studied from 2 to 24 h. In the case of electrospun mats, the impregnation time varied in the range from 15 min to 2 h, considering the previous feasibility study reported in Section 3.1. From Table 4, it can be seen that the fibrous supports allow a more effective impregnation of the active compound than those obtained by casting with the same contact time; the alpha-tocopherol amount, which is loaded on the fibers in 2 h, is loaded on the film obtained by casting in 6 h. Therefore, the porous structure of the electrospun sample, once optimized, the composition of the fibers with PEG at 10% *w*/*w* and the impregnation time can produce the same active compound loading in a lower time.

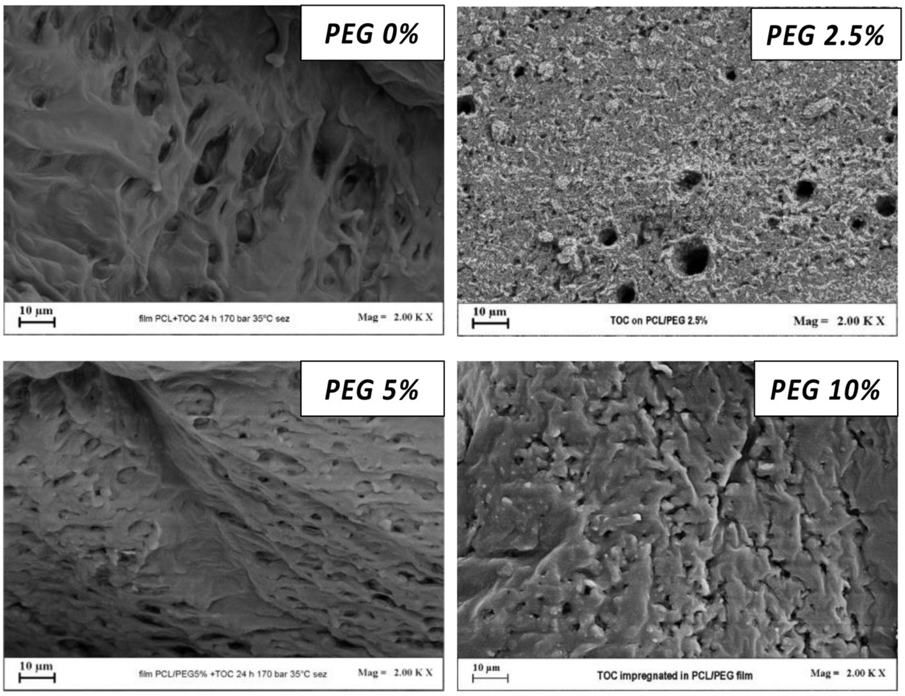


Figure 6. FESEM images of the casted samples at different PEG percentages after an impregnation time of 24 h, at 35 °C and 170 bar.

Table 4. Alpha-tocopherol loading on PCL + 10% PEG films produced by casting and electrospinning technique at different impregnation times, at 35 °C and 170 bar.

Impregnation Time	**Alpha-Tocopherol Impregnated (mg_{TOC}/mg_{FILM})**
PCL + PEG 10% CASTING FILMS	
2 h	0.25
6 h	0.40
15 h	0.67
24 h	0.82
PCL + PEG 10% ELECTROSPUN FILMS	
15 min	0.17
1 h	0.31
2 h	0.64

The morphological aspect of the fibers after the supercritical impregnation can be observed in Figure 7, where FESEM images taken at the same enlargement of samples processed at different impregnation times are reported. In particular, from Figure 7, it is possible to note that the plasticizing effect of the presence of alpha-tocopherol [47,48] contributes to lowering the T_m of the polymer, even more than CO_2 alone can. In fact, the fibers obtained after impregnation with alpha-tocopherol for 2 h have a less regular (and slightly melted) appearance than those obtained by processing the polymer with CO_2 in the absence of an active ingredient. The fibers obtained considering impregnation times equal to 1 h and 15 min have a stable structure. In particular, from the FESEM image related to 15 min impregnation time, it is possible to observe the presence of alpha-tocopherol in the form of nanoparticles on and in the fibers. Indeed, during the depressurization step, the carbon dioxide with the active ingredient solubilized in it returns to the gaseous form; therefore, the solute precipitates.

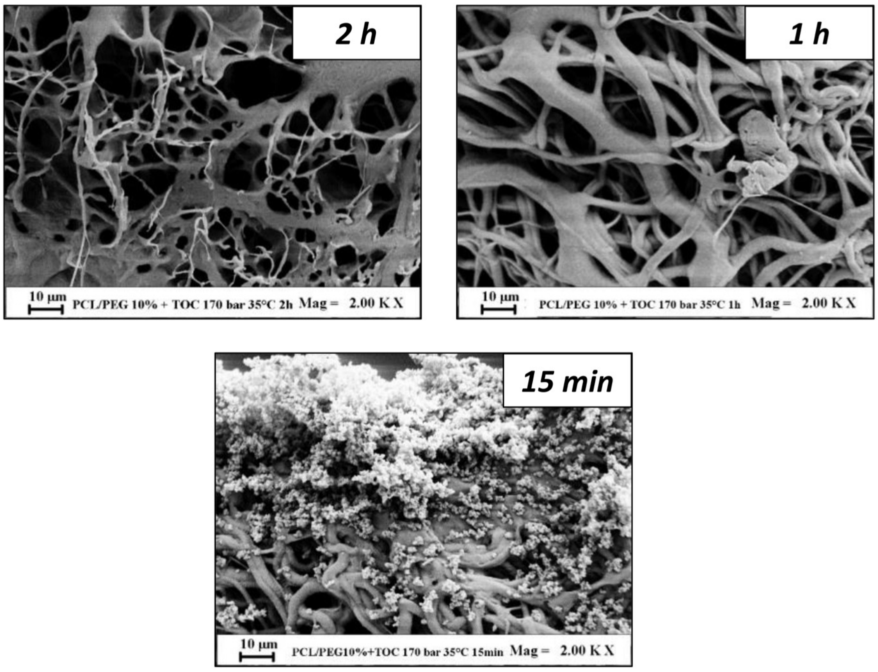


Figure 7. FESEM images of the electrospun fibers impregnated with alpha-tocopherol at 35 °C and 170 bar and different impregnation times: 2 h,1 h, and 15 min.

Electrospun films are more suitable for impregnation than those obtained by casting when the proper impregnation conditions are selected to avoid the denaturation of the structure because of the depression of the melting temperature caused by the interaction with $scCO_2$ and with alpha-tocopherol. Therefore, a good balance between impregnation time and film characteristics should be studied each time.

3.3. Migration Test of Alpha-Tocopherol into Fluid Simulant

Migration tests for the evaluation of alpha-tocopherol release from polymeric supports were carried out on the optimized samples considering, for each, the maximum impregnation time: PCL films produced by electrospinning impregnated for 2 h and PCL + PEG 10% films produced by casting impregnated for 24 h. The tests were carried out in static at 40 °C, using a 50% hydroalcoholic solution of ethanol as a simulant fluid for food products with a lipidic content. The released fluid was analyzed for one week, at predetermined time intervals, by UV-vis analysis at 295 nm through which the release percentage expressed as mg of alpha-tocopherol released/mg of theoretically impregnated alpha-tocopherol was estimated. The quantity of sample placed in contact with the simulant was evaluated to have the same initial theoretical load of impregnated antioxidant, about 9.5 mg per sample, for both techniques.

Figure 8 shows the graph comparing the alpha-tocopherol release kinetics from the impregnated samples produced by electrospinning and solvent casting. The samples produced by casting have, in the first hours, higher release kinetics than those produced by electrospinning, even though the fibers have a greater surface area exposed to the stimulant. After the first two days, the migration kinetics from electrospun samples becomes greater than those produced by casting. This trend is due to the fact that tocopherol, as observed in the SEM images of Figures 6 and 7, penetrates much better into the fibers, for contact times of 2 h, compared to casting films impregnated for 24 h, where instead the impregnation is more superficial, as the pores for PCL + PEG 10% samples are small and offer a smaller surface area exposed to the supercritical process. For this reason, the release from the fibers is more gradual and constant over time. For both techniques, however, about 50% of the impregnated tocopherol was released in 48 h.

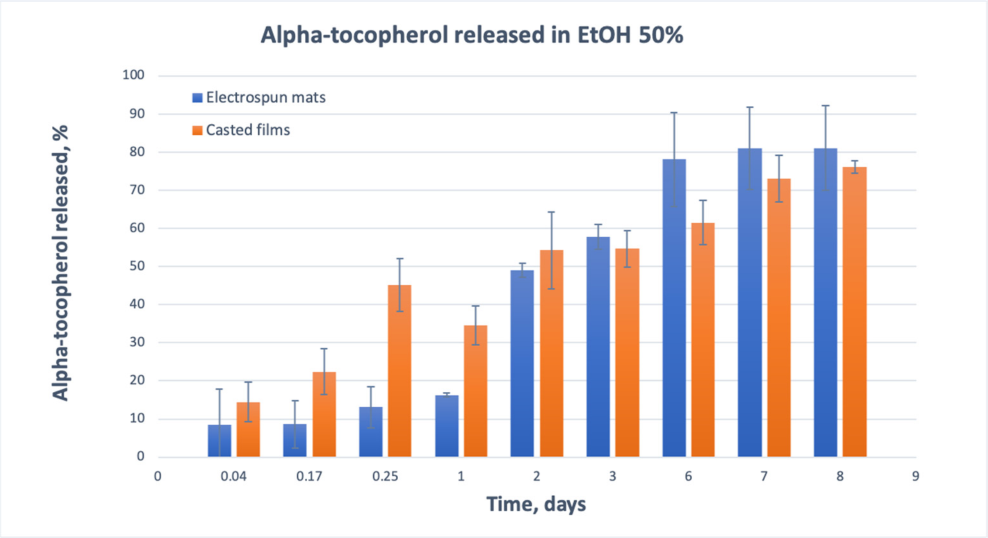


Figure 8. Release of alpha-tocopherol from electrospun sample impregnated for 2 h and from casted sample impregnated for 24 h, in EtOH 50% as a simulant, for a week at 40 °C.

4. Conclusions

This paper focused on the use of alternative green techniques for the preparation of active packaging films. The polymeric support was produced both by electrospinning and by solvent casting, and then it was loaded with alpha-tocopherol by impregnation with $scCO_2$. We demonstrated that the operating conditions have to be suitably selected as PCL has a low melting temperature, which is significantly reduced due to the presence of CO_2 in supercritical conditions. Furthermore, alpha-tocopherol has a plasticizing effect, which contributes to the negative modifying of the polymer structure. Therefore, for both tested green techniques combinations (casting with supercritical fluid impregnation and electrospinning with supercritical fluid impregnation), the optimal operating conditions, summarized in Table 5, were determined to obtain an active packaging.

Table 5. Summary of the optimized set condition for both electrospun and casted PCL films to be impregnated with $scCO_2$.

Conditions	Electrospun Films	Casted Films
Thickness (μm)	>100	>100
PEG content %	10	10
Impregnation time [h]	<2	<24

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