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Supercritical CO₂ Impregnation of Clove Extract in Polycarbonate: Effects of Operational Conditions on the Loading and Composition

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Abstract: The development of active packaging for food storage containers is possible through impregnation of natural extracts by supercritical CO_2 -assisted impregnation processes. The challenge of $scCO_2$ -impregnation of natural extracts is to control the total loading and to ensure that the composition of the loaded extract may preserve the properties of the crude extract. This study aimed at investigating the $scCO_2$ -impregnation of clove extract (CE) in polycarbonate (PC) to develop antibacterial packaging. A design of experiments was applied to evaluate the influences of temperature (35–60 °C) and pressure (10–30 MPa) on the clove loading (CL%) and on the composition of the loaded extract. The CL% ranged from 6.8 to 18.5%, and the highest CL% was reached at 60 °C and 10 MPa. The composition of the impregnated extract was dependent on the impregnation conditions, and it differed from the crude extract, being richer in eugenol (81.31–86.28% compared to 70.06 in the crude extract). Differential scanning calorimetry showed a high plasticizing effect of CE on PC, and high CL% led to the cracking of the PC surface. Due to the high loading of eugenol, which is responsible for the antibacterial properties of the CE, the impregnated PC is promising for producing antibacterial food containers.

Keywords: Eugenia caryophyllus; eugenol; multicompound systems; active packaging

1. Introduction

Natural extracts have appeared as potential antimicrobial and antioxidant agents for use in food, cosmetic and pharmaceutical applications. They are especially attractive because they are obtained from natural sources and are environmentally friendly [1–3]. For instance, many natural extracts are already classified by the Food and Drug Administration (FDA) as Generally Recognized as Safe (GRAS), including clove, oregano, peppermint, thyme, basil, tea tree, and cinnamon essential oils [4], allowing their application for human consumption in food. Recently, natural extracts have been loaded into polymeric matrices to develop active food packaging [5–7], drug release systems [8,9], and repellent and antioxidant fabrics [10,11]. By loading natural extracts into polymers, some shortcomings related to their high volatility and hydrophobicity are overcome while their properties are maintained [12,13].

Among the natural extracts, clove extract (CE) is known for its antibacterial, antifungal, and insecticidal properties, similar to those of synthetic preservatives [14–18]. CE is mainly obtained from flower buds, rich in eugenol, and contains eugenyl acetate, β -caryophyllene, and α -humulene. CE, or its majoritarian component eugenol, has been impregnated



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). in LLDPE films [19–21], polyamide fibers [22,23], pectin films [24], bacterial cellulose membranes [25], and gelatin–chitosan films [26].

The most common techniques to load polymeric matrices with natural extracts are casting [27-30], extrusion [31,32], and supercritical carbon dioxide (scCO₂) impregnation [33,34]. The advantage of using scCO₂ impregnation compared to the more conventional processes is that it does not require high temperatures or organic solvents, which could promote extract degradation or require a solvent removal step, respectively. In this technique, supercritical CO₂ (above 31 °C and 7.4 MPa) solubilizes the natural extract compounds, and then the solution of $\{CO_2 + compounds\}$ diffuses into the polymeric matrix. After a determined contact time, the CO_2 is easily removed by decreasing the system's pressure, whereas the extract remains impregnated into the matrix. The variables of this process are pressure, temperature, depressurization rate, and time. Pressure and temperature directly affect the solubility of the extract in scCO₂ and the diffusivity of the solution $\{CO_2 + compounds\}$ into the polymeric matrix. Depressurization rate and temperature must be controlled to avoid compounds being dragged out with the CO_2 and the foaming of the matrix. Finally, the supercritical impregnation is also a kinetic process; thus, the time impacts the final loading. Moreover, the interaction between the matrix and the compounds will also affect the partition of the compounds between the polymer and the CO_2 phase [35–38].

Polycarbonates (PC) are a group of polymers with a carbonate group in their structure. Overall, PCs are transparent, rigid, and have high impact strength, ductility, and impact resistance, in addition to a high glass transition temperature (Tg above 140 °C) [39,40]. The combination of these properties allows them to be applied as engineering thermoplastic in many areas, including rigid food packaging, construction, and automotive [39,41–43]. PC has been impregnated with compounds using scCO₂ in order to develop antimicrobial systems [44], for dyeing [45,46], and to make composites [47,48]. Herein, we aimed to impregnate CE in PC to produce food containers with antibacterial properties.

The bioactivity of a natural extract may be attributed to a specific compound or group of compounds. In some cases, the activity of natural extracts is based on the synergy between their several compounds [49–51]. Furthermore, their complex composition allows natural extracts to act in multiple sites [52,53]. Therefore, the challenge of scCO₂ impregnation of natural extracts is not limited to controlling the total loading. It is also essential to ensure that the loaded extract's composition may preserve the crude extract's bioactivity. This can be ensured by impregnating the compound or the group of compounds responsible for the desired bioactivity. Thus, it is crucial to evaluate the influence of the operational conditions on the composition of the impregnated extract, in addition to the total loading. According to the literature, only a few studies focused on quantifying the relative amounts of the impregnated compounds and explaining why these differ in composition from the crude extract [8,11,54]. Since CE is composed of only four compounds, it can be used as a model to understand the influences of operational conditions on the extract [8,11,54].

Thus, the present study aimed to impregnate CE into PC using scCO₂, to develop food containers with antibacterial properties, and to rationalize the effects of temperature (35–60 °C) and pressure (10–30 MPa) on the clove loading (CL%) and on the composition of the loaded extract. For this, a face-centered design was applied to determine the optimized pressure and temperature for CL%, and to evaluate the effects on the relative amounts of the four compounds of CE (i.e., eugenol, eugenyl acetate, β -caryophyllene, and α -humulene). The differences in proportions of the compounds in the crude extract and in the impregnated one were explained by taking into account the Hansen-type solubility parameters and the polymer–compounds interactions. The impact of the impregnation on the morphological and thermal properties was also studied.

2. Materials and Methods

2.1. Materials

Pellets of bisphenol-A polycarbonate (LEXAN HP1R grade for healthcare products) were supplied by SABIC Innovative Plastics (São Paulo, Brazil). Carbon dioxide (purity 99.985%) was purchased from Oxilumen (São Paulo, Brazil). Silicone oil (Synth, 350 cps) was used for thermostated baths. Ethyl acetate (purity 100%) was obtained from Synth (São Paulo, Brazil) and used as received. Deuterated chloroform (CDCl3, 99.8%) containing 0.05% v/v tetramethylsilane (TMS) as the internal reference was purchased from Cambridge Isotope Laboratories and used in the NMR analysis. Helium (99.9% purity) for gas chromatography analyses was purchased from White Martins (Campinas, Brazil). The analytic standards of eugenol, eugenyl acetate, β -caryophyllene, and α -humulene were bought from Sigma-Aldrich (Barueri, Brazil).

2.2. Supercritical CO₂ Extraction

The clove (*Eugenia caryophyllus*) extract was obtained from grounded raw material via supercritical fluid extraction (SFE) using carbon dioxide as the solvent. The extraction equipment utilized in this study was a pilot-scale SFE (Thar Technologies, Pittsburgh, PA, USA). The extraction was performed using a 5 L extractor. The solvent flow rate was 50 gCO₂/min. The extraction process conditions were 15 MPa and 40 °C. The temperature and pressure conditions were optimized according to Prado and Meireles [55] and Prado et al. [56]. The structures of the four main compounds of clove extract obtained by SFE are presented in Figure 1.



Figure 1. Structures of the four main compounds of clove extract (obtained by scCO₂): (**a**) eugenol, (**b**) eugenyl acetate, (**c**) β -caryophyllene, and (**d**) α -humulene.

2.3. Characterization of PC Chemical Structure by ¹H NMR

Approximately 50 mg of PC was dissolved in 0.6 mL of CDCl₃, and the spectrum was recorded in a Varian VNMRS 500 MHz at 27 °C, using 30,000 transients. ¹*H* NMR (CDCl₃-d¹) d (ppm): 1.68 (s, -C-(CH₃)₂, 6H), 7.17 (d, -CH-CH-C-O-, 4H), 7.25 (d, -CH-CH-C-C(CH₃)₂-, 4H), corresponding to poly(bisphenol A carbonate) with high purity [57]. The ¹*H* NMR spectrum is presented in Supplementary Materials. The chemical structure of poly(bisphenol A carbonate) is represented in Figure 2.



Figure 2. Structure of poly(bisphenol A carbonate).

2.4. Preparation of PC Films

PC pellets were used as received. The polymeric films used in the impregnation process were obtained by hot pressing on a hydraulic press with heating (model SL-11, Solab). For this process, the pressure was increased from 0 ton to 6 ton in 10 min, and the temperature was kept constant at 280 °C. Teflon sheets were used for contact between the

press and the samples. The thickness of the films was 0.4 mm. The films were cut into squares of approximately 1 cm², corresponding to approximately 50 mg per sample.

2.5. scCO₂ Impregnation Method

The scCO₂ impregnations were carried out in a batch process, and the scheme of the experimental set-up is presented in Figure 3. Approximately 1 mL of clove extract was placed at the bottom of a 10 mL stainless steel high-pressure cell. The amount permitted the saturation of the CO₂ phase. A stirrer bar was also added to the cell to ensure the homogeneity of the CO₂ phase. Finally, for all batches, around 300 mg of polymer was placed above the compound(s) in a single glass container to physically separate the films from the natural extract. All these films were carefully placed so they did not touch each other. The high-pressure cell was closed and immersed in a thermostated water bath. Then, a high-pressure pump (pneumatic pump) introduced CO₂. Once the desired pressure was achieved, the magnetic stirring was turned on (100 rpm), and the temperature and pressure were kept constant for the impregnation time, which was set to 3 h after preliminary tests. After the impregnation time, the high-pressure cell was dipped in dry ice (-78 °C) to freeze the scCO₂ and avoid the extract's removal during depressurization. Once system pressure decreased to values between 0.7 and 1 MPa due to the temperature decrease and dry-ice formation, the cell was opened to carry on the depressurization (2 s).



Figure 3. Scheme of the experimental set-up.

2.6. Design of Experiment

The design of experiments methodology was used to evaluate the influences of pressure (10–30 MPa) and temperature (35–60 °C) on scCO₂ impregnation of CE in PC. Therefore, for two factors (pressure and temperature), the experimental design consisted of factorial assays (22 = 4 assays at levels of -1 and +1), including four axial points (at levels of -1 and +1) and three replicates at the central points (at level 0). Thus, a face-centered design (FCD) was developed using 11 tests (Table 1). The maximum and minimum levels of pressure and temperature were defined according to data published in the literature for scCO₂ impregnation to enhance loading and to avoid the extract thermodegradation [36,37]. The impregnation time (3 h) was defined after preliminary tests (Supplementary material).

Assay	Pressure (MPa) ¹	Temperature (°C) ¹	scCO ₂ Density (kg/m ³)	CL (%)
1	10 (-1)	35 (-1)	712.8	15.8
2	30 (+1)	35 (-1)	929.1	9.5
3	10(-1)	60 (+1)	289.9	18.5
4	30 (+1)	60 (+1)	829.7	9.4
5	10(-1)	47.5 (0)	432.7	18.0
6	30 (+1)	47.5 (0)	880.4	6.8
7	20(0)	35 (-1)	865.7	9.4
8	20 (0)	60 (+1)	723.7	13.9
9	20 (0)	47.5 (0)	798.6	11.2
10	20 (0)	47.5 (0)	798.6	9.8
11	20 (0)	47.5 (0)	798.6	10.2

Table 1. Supercritical impregnation experiments and their clove extract loading (CL%) in PC.

¹ Coded values in parentheses.

The experimental design allowed the study of a wide range of scCO₂ densities (289.9 to 929.1 kg/m³). All assays were performed in triplicate and in random order. Data were analyzed using the Protimiza Experimental Design software, with a significance level of 5%. Initially, the effects of pressure and temperature were calculated, and the results were used to determine the regression coefficients (β_0 , β_1 , β_{11} , β_2 , β_{22} , and β_{12}) of the coded model (Equation (1)).

$$CL\% = \beta_0 + \beta_1 x_1 + \beta_{11} x_1^2 + \beta_2 x_2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 \tag{1}$$

Equation (1) is a quadratic polynomial equation that relates the total clove extract loading (*CL*%) to the coded values (Table 1) of pressure (x_1) and temperature (x_2). Analysis of variance (ANOVA) was used to verify the fitting quality of the model. Response surfaces (three-dimensional (3D) plots) and their respective contour plots were obtained based on the validated models and were later used to define the optimal conditions for scCO₂ impregnation.

2.7. Clove Extract Loading

The clove extract loading (*CL*%) was defined as the mass of CE impregnated in the polymeric matrix per mass of polymer and was measured gravimetrically using a balance (precision 10^{-4} g, model AY-220, Marte, Shimadzu) and calculated using Equation (2).

$$CL\% = \frac{m_{after \ impregnation} - m_{before \ impregnation}}{m_{before \ impregnation}} \times 100$$
(2)

where $m_{after impregnation}$ is the mass of the film after the impregnation and $m_{before impregnation}$ is the mass of the film before the impregnation.

For each operational condition, the impregnation was performed by placing at least three PC films in the high-pressure cell. The results presented are the average loadings of all the samples. The samples were weighed 48 h after impregnation to ensure that the CO_2 was removed from the polymer. The impregnated samples were stored at -20 °C until further analysis.

In order to confirm that the measured mass corresponded to the compounds impregnated in the polymer bulk, some samples were weighted, and their surfaces were cleaned with tissue paper soaked with ethanol and weighted again. No mass variation was observed, confirming that all the extract was impregnated in the polymer bulk and not deposited on the polymer surface.

2.8. Composition of the Impregnated Extract

The loading of each of the four majoritarian compounds of CE was obtained by extracting the impregnated extract from the polymeric films and quantifying it using gas chromatography (GC). For the extraction, one film was immersed in 5 mL of ethyl acetate in a closed flask. This flask was sonicated in an ultrasound bath (Unique, model 750 A, 25 kHz) for 1 h every day for one week, at room temperature. Preliminary tests confirmed that this procedure permitted the complete extraction of the impregnated extract. All compounds are soluble in ethyl acetate.

The crude CE composition and the composition of the impregnated extract (i.e., recovered from the impregnated films by extraction) were determined using a gas chromatograph with a flame ionization detector. A chromatograph GC-FID (Shimadzu, CG17A, Kyoto, Japan) equipped with a capillary column of fused silica DB-5 (J&W Scientific, 30 m imes $0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$, Folsom, CA, USA) was used. For each sample, 1 μL of the ethyl acetate/extract solution was injected into the chromatograph using a split ratio of 1:20. Helium was used as carrier gas and flowed at 1.1 mL/min. The injector and the detector temperatures were 220 and 240 °C, respectively. The column was heated from 60 °C to 246 °C at 3 °C/min. Eugenol ($C_{10}H_{12}O$ –CAS 97-53-0), eugenyl acetate ($C_{12}H_{12}O_3$ –CAS 93-28-7), β -caryophyllene (C₁₅H₂₄–CAS 87-44-5), and α -humulene (C₁₅H₂₄–CAS 116-04-1) were identified by comparing the retention indices with chemical standards (25.440, 28.266, 29.710, and 32.656 min, respectively). Their quantification was performed using external standard calibration curves, so the mass $m_{GC,X}$ of each compound was determined. For the quantification of compounds, calibration curves for all compounds were analyzed in the range 0.04–1.0 mg/mL. The proportion of each compound present in the impregnated extract (P_X %) was calculated using Equation (3).

$$(P_x\%) = \frac{m_{GC,X}}{m_{impregnation}} \times 100$$
(3)

where *X* represents the compound, $m_{GC,X}$ is the mass of the impregnated compound obtained by GC, and $m_{impregnation}$ is the mass of the impregnated extract. The reported value for the proportion of each compound is the average of two samples prepared in two different impregnation batches. The central point of the DoE was performed in triplicate

The crude extract was analyzed right after its extraction from clove buds and again when the impregnations were performed. No composition variation was observed over time when storing the crude extract at 8 $^{\circ}$ C and in the dark.

2.9. Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy

The impregnation of the CE was evaluated by comparing the FTIR spectra of the neat PC, the clove extract, and impregnated PC (sample impregnated with CL = 18.5% prepared at 60 °C and 10 MPa). For Fourier-transform infrared spectroscopy (FTIR), a Spectrum Two FTIR spectrometer from PerkinElmer was used in ATR mode (diamond crystal doped with zinc selenide ATR accessory). The analyses were performed at room temperature with resolution of 1 cm⁻¹, in 16 scans from 700 to 4000 cm⁻¹. The surfaces of the impregnated PC samples were first cleaned with ethanol to avoid the interference of any compounds deposited on their surfaces. The sample was stored for two hours to allow the ethanol to evaporate before the measurement.

2.10. Thermal Analysis

Differential scanning calorimetry (DSC) analyses were performed to evaluate the impact of CO₂ treatment and of the impregnation process on the thermal properties and crystallinity of the PC. The instrument Q200 from TA Instruments was used. The neat PC, scCO₂-treated PC, and impregnated PC films were analyzed. The scCO₂-treated PC and impregnated PC were prepared at 60 °C and 10 MPa, but the scCO₂-treated PC was prepared in the absence of extract. Small film pieces with 7 to 8.5 mg were sealed in an aluminum pan, and the thermograms of the first heating cycle were obtained by heating

the pans from 25 to 240 °C at a heating rate of 10 °C·min⁻¹. The second heating cycle was also obtained by cooling the samples to -80 °C at a rate of 20 °C·min⁻¹ and heated again to 240 °C at a rate of 10 °C·min⁻¹. The crystallinity of the samples was obtained using Equation (4).

$$\chi = \frac{\Delta H_f - \Delta H_c}{W \cdot \Delta H_{100f}} \times 100 \tag{4}$$

where ΔH_f (J·g⁻¹) is the experimental fusion enthalpy, ΔH_c (J·g⁻¹) is the experimental crystallization enthalpy, *W* is the polymer mass fraction, and ΔH_{100f} is the fusion enthalpy of 100% crystalline polymer, 109.6 J·g⁻¹ for the PC [58].

2.11. Scanning Electron Microscopy

The films morphology of neat PC, scCO₂-treated PC, and impregnated PC films were evaluated by SEM using a JEOL JSM 6010LA microscope. The cross-section of the samples were analyzed after cryogenic fracture. The samples were sputtered with a 15 nm layer of gold.

3. Results and Discussion

3.1. Influences of the Impregnation Conditions on the Clove Extract Loading

The clove extract loading (CL%) obtained for each experimental condition in PC is reported in Table 1 and Figure 4. High loadings were obtained: CL% ranged from 6.8% (30 MPa and 47.5 °C) to 18.5% (10 MPa and 60 °C), and the standard deviation was 0.7% (calculated with the central-point test). These results indicate that the impregnation yield depends on the pressure and temperature used in the impregnation of CE in PC.



Figure 4. Influences of pressure (10–30 MPa) and temperature (35–60 $^{\circ}$ C) on the clove extract loading (CL%) in PC. Standard deviation of 0.7%.

3.1.1. Effects of Pressure

In isothermal conditions, $scCO_2$ pressure had a negative effect on CL% (Figure 4); i.e., an increase in pressure resulted in a decrease in the extract loading. These negative effects can be explained by the increased density of $scCO_2$ with pressure. Regarding the polymer/CO₂ system, Tang et al. [59] and Zhao et al. [60] reported an increase in the CO₂ sorption in PC with an increase in pressure at a constant temperature of between 40 and 80 °C [60,61], which should favor the impregnation. They found that the CO₂ sorption rises from 7.6 to 12.98 wt% by increasing the pressure from 10 to 30 MPa at 60 °C [61]. On the other hand, an increase in pressure tends to increase the solubility of CE [62,63], along with the solubility of its individual compounds, in scCO₂ [64,65]. The values are reported in Supporting Information—Table S1. A high solubility means high affinity of the solutes for CO₂. This can lead to the partitioning of the solutes for the CO₂ phase, to the detriment of the polymer phase, which is deleterious to its impregnation [11,36,37]. Thus, CE–CO₂ interactions were probably favored over the CE–PC interactions at higher pressures, negatively affecting the CL% in PC.

Varona et al. [66] reported similar results for the supercritical impregnation of lavandin essential oil in starch modified with n-octenyl succinate (OSA). They investigated the effect of pressure in the range of 10–12 MPa and observed that the amount of essential oil impregnated per unit mass of OSA-starch decreased with increasing pressure. In another study, Belizón et al. [36] investigated the effect of pressure in the range of 10–20 MPa and observed that the most favorable conditions for impregnating mango polyphenols into a multilayer polyethylene terephthalate (PET)/polypropylene (PP) food-grade film were obtained at 10 MPa.

3.1.2. Effects of Temperature

ScCO₂ temperature globally positively affected CL% in PC (Figure 4). Temperature impacts the extract solubility in scCO₂ and the CO₂ sorption of PC. The influence of temperature on the solubility of a solute in scCO₂ depends on the pressure. Below the so-called crossover pressure, the solubility of the solute decreases with increasing temperature due to the decrease in CO₂ density. However, above the crossover pressure, the solubility increases due to the increase in the vapor pressure of the solute that overcoming the effect of the CO₂ density diminution. The crossover pressure of CE can be estimated from the results of Wei et al. [63] at the intersection of the three isotherms, which is between 9 and 12 MPa [63] (Figure 5).



Figure 5. Solubility of clove extract in scCO₂ [63].

The general influence of the temperature on the CO_2 sorption in PC is related to the CO_2 density [60,61] and to the plasticizing effect of CO_2 on PC [61,67]. CO_2 can increase PC chain mobility, which is favorable for CO_2 sorption, but it has also been reported to enhance PC crystallization and thus be detrimental to CO_2 sorption [67]. Crystallization of PC after scCO₂ treatment was observed in the literature [67–69]. However, in the range of temperatures investigated, no crystallization was expected [45,67] which was further confirmed by DSC curves (Section 3.5). Concerning CO_2 density, it tends to decrease

with increasing temperature in isobaric conditions. Tang et al. [59] reported that at a CO₂ density lower than 700 kg/m³, a decrease in CO₂ sorption with an increase in temperature occurred. The contrary was observed at densities greater than 700 kg/m³ due to increased chain mobility, which permitted accommodating more CO₂ molecules [61]. Zhao et al. [60] reported a similar trend with a change in the effect of temperature observed at 11.2 MPa. Below 11.2 MPa, the CO₂ sorption in PC ranged from 3.85 to 5.87 m/m% at 80 and 40 °C, respectively. Between 11.2 and 18 MPa, the CO₂ sorption increased to a small extent up to 6.56 m/m% at 40 °C, whereas it rose to 7.83 wt% at 60 °C [60]. The authors suggested that the PC glass transition temperature (Tg) must have been reached at 11.2 MPa. Above this point the decrease in CO₂ density was adverse to CO₂ diffusivity in PC, and consequently, CO₂ sorption. Note that the absorbed CO₂ has a strong plasticizing effect on PC, since the Tg drops from ~ 140 °C to a temperature between 40 and 60 °C in situ [61,70].

Thus, the positive effect of temperature on CL% is dominated by different phenomena depending on the temperature. At 10 MPa, the pressure is close to the crossover pressure of CE (Figure 5), and the CO₂ density varies between 712.8 and 289.9 kg/m³ at 35 and 60 °C. Thus, the increase in temperature leads to a decrease in both the extract solubility in CO₂ and, to a small extent, the CO₂ sorption in PC. The decrease in extract solubility in CO₂ must increase the affinity of the extract for the polymer phase and favor the impregnation, dominating the negative effect of CO₂ sorption.

At 20 and 30 MPa, the temperature tends to increase the extract solubility (above the crossover pressure) and the CO_2 sorption in PC due to high chain mobility. Furthermore, an increase in temperature may have caused an increase in the free volume of the matrix (i.e., swelling), thereby enhancing the extract loading while reducing the resistance to solute diffusion in PC. Thus, as a result of all these combined factors, the temperature positively affected CL% [35–38,71,72].

Medeiros et al. [19] investigated the impregnation of CE in linear low-density polyethylene, an apolar polymer, in the temperature range of 25–45 °C and at 15 and 25 MPa. The higher impregnation yield was obtained at 45 °C (the effect of pressure was insignificant), leading to a CL% of 4.02% [19].

3.1.3. Optimum Conditions for the Clove Extract Loading

Based on the experimental data (Table 1) and with the aid of the Protimiza Experimental Design software, a mathematical model (Equation (5)) was obtained that relates the extract loading (CL%) to the coded values of pressure (x_1) and temperature (x_2).

$$CL\% = 10.47 - 4.43x_1 + 1.82x_1^2 + 1.18x_2 + 1.07x_2^2 - 0.70x_1x_2$$
(5)

To assess the quality of the model's fit (Equation (5)), Table 2 presents the ANOVA data. The model can be considered valid, wherein the coefficient of determination (\mathbb{R}^2) is 0.9433 (the model represents 94.33% of the experimental data), that is, close to unity. Moreover, $F_{regression/residuals} \geq F_{tab}$ and $F_{lack of fit/pure \, error} \leq F_{tab}$. Thus, when adjusting to the experimental data, the model can be used for predictive purposes, thereby satisfying the requirements for the construction of the response surface and contour plot (Figure 6).

As observed in Figure 6, the model confirmed that increasing the pressure from the lowest (10 MPa) to the highest (30 MPa) level induced a decrease in CL%. The negative effect of pressure outweighed the effect of temperature. As shown in Figure 6b, the maximal CL% (>18%) can be achieved within the following optimal ranges: pressures of 10–12 MPa and temperatures of 55–60 °C. Furthermore, the optimal values (> 18%) in Table 1 are a pressure of 10 MPa and a temperature of 60 °C.

Variation Source	Sum of Squares	Degrees of Freedom	Mean Square	F ¹	F _{tab} ²	<i>p</i> -Value
Regression	143.2	5	28.6	16.6	5.05	0.00392
Residuals	8.6	5	1.7			
Lack of fit	7.6	3	2.5	4.9	19.16	0.17552
Pure error	1.0	2	0.5			
Total	151.8	10				
R ^{2,3}	94.33%					

Table 2. Analysis of variance (ANOVA) of the predictive model for the clove extract loading in PC.

¹ F distribution (calculated); ² F distribution (tabulated); ³ coefficient of determination.



Figure 6. (a) Response surface and (b) contour plot for extract loading (CL%) of clove extract in PC as functions of pressure and temperature.

3.2. Influences of the Impregnation Conditions on the Composition of the Loaded Extract

GC analysis confirmed that the crude CE from *Eugenia caryophyllus* is composed of four main compounds: eugenol, eugenyl acetate, β -caryophyllene, and α -humulene (Table 3). Eugenol is the majoritarian compound (70.1%), followed by eugenyl acetate (17.06%). Both compounds are phenylpropanoids and have a tri-substituted phenyl group. Eugenyl acetate is derived from eugenol, having an acetate ester instead of the hydroxyl group in eugenol. β -caryophyllene (10.67%) and α -humulene (2.20%) are two sesquiterpenes; they are bicyclic and monocyclic, respectively. α -Humulene is a ring-opened isomer of β -caryophyllene. Both are commonly found as a mixture in various extracts.

The extraction of the compounds from impregnated PC was performed in ethyl acetate for one week; we submitted the solution to ultrasound for 1 h per day. Preliminary tests proved that this procedure was efficient in guaranteeing the complete extraction and that no compounds were detected in a second extraction in a fresh solvent. This confirms the efficiency of the protocol tested with other systems [54,73].

Table 3 shows the compositions of the extracts impregnated into PC in the different conditions and the crude CE. These results indicate that the composition of the extract impregnated in PC depends on the impregnation conditions. First, eugenol content significantly increased from 70.06 to values ranging between 81.31 and 86.28%, whereas the eugenyl acetate decreased from 17.06 to 11.22–13.86%, depending on the conditions. The proportions of the two sesquiterpenes were lower in the loaded extract than in the crude one. The content of β -caryophyllene dropped from 10.67 to 2.07–4.83%, whereas the content of α -humulene decreased from 2.20 to values below 0.51. These results suggest the selectivity of the impregnation process. Cejudo Bastante et al. [54] also reported the selective character of the process, as only four of the eleven compounds of the red grape pomace

extract were impregnated in jute fibers [74]. Catechin and *p*-coumaric acid, which are two low-molecular weight phenolic compounds, were the compounds impregnated in higher proportions, even though they were not the main compounds of the extract. On the other hand, anthocyanins present in high quantity in the extract were not impregnated. In a previous study, Cejudo Bastante et al. [54] observed that the proportions of compounds in the impregnation of olive leaf extract polyphenols in PET/PP films varied with the pressure (10–40 MPa) and time (5 min to 22 h). Oleuropein was the majoritarian compound in the impregnated films, representing 58 to 71% of the total polyphenols, depending on the impregnation pressure. The authors also highlighted that the proportions of the compounds varied with time. They explained that each compound had a different affinity for CO_2 and for the polymer, and different molecular weights (the higher the molecular weight, the lower the diffusion coefficient in the matrix).

Table 3. Compositions of the extracts impregnated into PC and the crude clove extract, shown aspercentage weight for each compound.

Assay	Pressure (MPa)	Temperature (°C) ¹	Eugenol (%)	Eugenyl Acetate (%)	β-Caryophyllene (%)	α-Humulene (%)
1	10 (-1)	35 (-1)	84.62 ± 0.29	12.57 ± 0.13	2.33 ± 0.14	0.48 ± 0.03
2	30 (+1)	35 (-1)	85.25 ± 0.65	11.95 ± 0.69	2.32 ± 0.05	0.48 ± 0.01
3	10(-1)	60 (+1)	81.31 ± 0.73	13.86 ± 0.79	4.83 ± 0.05	0.00 ± 0.00
4	30 (+1)	60 (+1)	85.43 ± 1.28	12.02 ± 1.39	2.13 ± 0.13	0.43 ± 0.02
5	10(-1)	47.5 (0)	84.16 ± 0.68	12.53 ± 0.35	3.31 ± 0.33	0.00 ± 0.00
6	30 (+1)	47.5 (0)	85.52 ± 0.44	11.55 ± 0.32	2.43 ± 0.09	0.50 ± 0.04
7	20 (0)	35 (-1)	85.52 ± 0.03	11.67 ± 0.00	2.33 ± 0.02	0.49 ± 0.01
8	20 (0)	60 (+1)	85.39 ± 0.05	11.64 ± 0.06	2.16 ± 0.01	0.51 ± 0.01
9	20 (0)	47.5 (0)	86.28	11.22	2.07	0.43
10	20 (0)	47.5 (0)	85.80	11.59	2.19	0.43
11	20 (0)	47.5 (0)	85.96	11.23	2.34	0.47
Clove extract			70.06	17.06	10.67	2.20

¹ Coded values in parentheses.

The coded models and the results of the analysis of variance (ANOVA) are presented in Table 4. In this study, coded statistical models (the quadratic polynomial equation) were used to predict the compositions of the extracts impregnated into PC (eugenol, eugenyl acetate, β -caryophyllene, α -humulene) as a function of the pressure and temperature. The adjustment quality of these models was evaluated using the ANOVA results, and the experimental data were analyzed in the Protimiza Experimental Design software at a fixed significance level of 0.05.

Table 4. Coded models and results of analysis of variance (ANOVA).

Model ^a	Regression/ Residual		Lack of Fit/ Pure Error		R ²
	F _{cal,1} b	F _{tab,1} ^c	F _{cal,2} ^b	F _{tab,2} ^c	
Eugenol = $86.04 + 1.02 x_1 - 1.24 x_1^2 - 0.54 x_2$ - $0.63 x_2^2 + 0.87 x_1 x_2$	15	5.05	5.8	19.16	93.76%
Eugenyl acetate = $11.29 - 0.57 x_1 + 0.83 x_1^2 + 0.22 x_2 + 0.45 x_2^2 - 0.30 x_1 x_2$	17.4	5.05	1.6	19.16	94.56%
β-caryophyllene = $2.20 - 0.60 x_1 + 0.66 x_1^2 + 0.36 x_2 + 0.04 x_2^2 - 0.67 x_1 x_2$	8.6	5.05	12	19.16	89.53%
$\alpha\text{-humulene} = 0.43 + 0.15 x_1 - 0.17 x_1^2 - 0.08 x_2 + 0.08 x_2^2 + 0.11 x_1 x_2$	5.5	5.05	34.5	19.16	84.69%

^a x_1 : coded pressure; x_2 : coded temperature; ^b F_{cal} : F distribution (calculated); ^c F_{tab} : F distribution (tabulated).

The models to describe β -caryophyllene and α -humulene proportions in the loaded extract were not valid because the values of the determination coefficient (R²) were lower than 90% (R² = 89.53 and 84.69%, respectively). In contrast, the models used to describe eugenol and eugenyl acetate were valid, as the R² values were greater than 90% (93.76 and 94.56%, respectively). Moreover, the data presented in Table 4 shows that F_{cal,1} was greater than F_{tab,1}, and that F_{cal,2} was less than F_{tab,2}. When adjusting the experimental data, the model could be used for predictive purposes, which meets the requirements for constructing the response surfaces (Figure 7).



Figure 7. The response surface for (a) eugenol; (b) eugenyl acetate.

As seen in Figure 7, the pressure and temperature exhibited statistically significant effects (with 95% confidence) on the eugenol and eugenyl acetate content in the extract impregnated into PC. As shown in Figure 7a, there was a positive correlation (*p*-value < 0.05) between the pressure and the overall eugenol content. Thus, the higher the pressure used in the impregnation, the higher the proportion of eugenol in the loaded extract. However, there was a negative correlation (*p*-value < 0.05) between the temperature and the proportion of eugenol in the extract. The higher the impregnation temperature, the lower the content of eugenol. As shown in Figure 7b, there was a negative correlation (*p*-value < 0.05) between the pressure and the eugenyl acetate content. The higher the impregnation pressure, the lower the eugenyl acetate content in the loaded extract.

As mentioned in Section 3.1.1, the high solubility of a compound in $scCO_2$ does not ensure its plentiful impregnation in the polymer, but on the contrary, it can favor its partitioning in the CO_2 phase. However, a high affinity of a compound for the matrix is the driving force for its partitioning in the polymer. The differences between the compositions of the crude and impregnated extracts can be accounted for by the affinities between PC and the diverse compounds, which are evaluated by their solubility parameters and by the establishment of strong interactions such as H-bonds between a compound and PC [75–77]. The Hansen-type solubility parameters at 25 °C were estimated by the group contribution method, using Van Krevelen and Hoftyzer's method, and are reported in Table 5 for PC and the four compounds of CE. β -caryophyllene and α -humulene have low affinity for PC, as shown by their very different solubility parameters. Moreover, they do not possess chemical groups that can establish strong secondary bonds with the matrix, and they have high molecular volumes. Thus, the two sesquiterpenes had lower proportions in the impregnated PC than in the crude CE. Conversely, eugenol was impregnated in a higher proportion than according to its proportion in the crude extract. The solubility parameter of eugenol is not the most similar to that of PC, but its loading is promoted by H-bonding between OH groups of eugenol and the C=O group of the carbonate of PC. The lower

proportion of eugenyl acetate in the impregnated extract compared to the crude extract (11.22–13.86 vs. 17.06%) is more difficult to explain. Eugenol and eugenyl acetate exhibit similar solubility in scCO₂ (see Supplementary Materials—Table S1), and their molecular volumes are similar, so their diffusion in PC should be comparable. Eugenyl acetate has a similar solubility parameter to PC's, suggesting a good affinity, but it may compete with eugenol during the impregnation process [11,54].

It has been reported that CE and eugenol have antimicrobial activity against foodborne pathogens. Cui et al. [15] reported that 0.5 mg/mL of CE irreversibly affects the cell membrane of *Listeria monocytogenes*, causing its extermination by 99.99% after 8 h. Pérez-Conesa et al. [78] observed cellular destruction of *Escherichia coli* O157:H7 (strains 4388 and 43895) after 10–20 min exposure to 0.9% eugenol. In a study conducted by Móran et al. [79], eugenol showed high antimicrobial activity (bacterial growth inhibition >90% at 100 µg/mL) towards *Staphylococcus epidermidis* and *Staphylococcus aureus*. Data from the literature indicates that PC impregnated with CE would also have antibacterial properties.

Table 5. Estimation of Hansen-type solubility parameters at 25 °C by the group contribution method, using the Van Krevelen and Hoftyzer method [80].

Polymer/Compound	δ _d (Mpa ^{0.5})	δ _p (MPa ^{0.5})	δ _h (MPa ^{0.5})	Solubility Parameter (δ _t) (MPa ^{0.5})	$ \delta_{\mathrm{t}\mathrm{PC}} - \delta_{\mathrm{t}\mathrm{compound}} $ (MPa ^{0.5})
PC	17.9	3.1	6.9	19.4	-
Eugenol	18.5	4.1	12.2	22.5	3.1
Eugenyl Acetate	17.5	3.3	7.2	19.3	0.1
β -caryophyllene	15.2	0.0	0.0	15.2	4.2
α-humulene	15.7	0.0	0.0	15.7	3.7

3.3. ATR-FTIR

The FTIR spectra of clove extract, neat PC, and impregnated PC are shown in Figure 8. Peak assignments are presented in Supporting Material D. The characteristic peaks of clove extract are centered at 1765 cm⁻¹ due to C=O stretching in eugenyl acetate; 1638 cm⁻¹ due to vibrations of allyl groups in eugenol and eugenyl acetate; 1606 and 1512 cm⁻¹ due to C=C vibrations in the aromatic rings in eugenol and eugenyl acetate [81]; 1266, 1232, and 1199 cm⁻¹ due to =C-O-C asymmetric stretching and =C-O-H vibrations in eugenol and eugenyl acetate [82]; and 912 cm⁻¹ due to =C-H bending of aliphatic groups [81]. The characteristic peaks of PC are 1769 cm⁻¹ due to C=O stretching; 1502, 1014, and 828 cm⁻¹ due to C=C vibrations in aromatic rings [82]; and 1220, 1188, and 1159 cm⁻¹ due to O-C-O stretching [83]. The spectrum of impregnated PC exhibits characteristic peaks of clove extract, evidencing its impregnation in high concentration; the peaks centered at 1638, 1122, 1034, and 912 cm⁻¹ present in the clove extract spectrum could be clearly observed on the impregnated PC spectrum at 1639, 1123, 1035 and 915 cm⁻¹; other peaks were superposed on the neat PC peaks, causing their broadening [81–85].



Figure 8. ATR—FTIR spectra of crude clove extract, neat PC, and PC impregnated with clove extract at 60 $^{\circ}$ C and 10 MPa with CL = 18.5%.

3.4. Film Morphology

SEM images enable the analysis of the impact of impregnation on the film's surface and cross-sectional morphologies. Figure 9 shows the cross-section and surface of neat PC, scCO₂-treated, and of PC impregnated at 60 °C and 10 MPa. The cross-sections of neat PC (Figure 9b) and scCO₂-treated PC (Figure 9d) were dense and homogeneous, and their surfaces were smooth and free of cracks (Figure 9a,c). The SEM images show that submitting PC to CO₂ in such impregnation and depressurization conditions did not impact the morphology and did not create pores. Ma et al. studied PC foaming using scCO₂ as a blowing agent and showed that microcellular structures were formed after saturating PC with CO₂ at 60 °C and depressurizing at 60 °C for 30 s [86]. On the other hand, in the present study, the high-pressure cell was quenched down to -78 °C, which resulted in the CO₂ freezing and a pressure reduction to about 2 MPa. Then, the pressure cell was opened, and the frozen sample was left at room temperature. This way, the remaining gaseous CO₂ in PC, which justifies the smooth surface and dense cross-sections observed in the SEM images (Figure 9c,d) [77].

Regarding the morphology of impregnated PC, surface cracking was observed (Figure 9e), and the cross-section obtained by cryo-fracture was also dense, and no micropores were observed after high clove loading (18.5%). The surface cracking might result from the high CL% accommodated into the matrix and from the plasticizing effect of CE. Jiang et al. observed that the infusion of the plasticizer tributyl citrate in poly(bisphenol A carbonate) at ambient pressure and 60 °C for 12 h resulted in the formation of pores and of a network of cracks on the surface and of pores that were present in a greater extent compared to our results [87]. Another possibility is that the samples suffered mechanical stress during the process. These cracks must influence the release kinetics of CE, which will be an issue for future investigation.



Figure 9. SEM images of the surfaces (left column) and cross-sections (right column) of (**a**,**b**) neat PC film, (**c**,**d**) PC only submitted to scCO₂ at 60 °C and 10 MPa, and (**e**–**g**) PC impregnated with clove extract at 60 °C and 10 MPa with CL% = 18.5%.

3.5. DSC Analysis

The DSC thermograms of neat PC, $scCO_2$ -treated PC, and PC impregnated at 60 °C and 10 MPa, which is the condition that resulted in the highest CL%, are compared in Figure 10. As shown in the first heating curve, the Tg of neat PC slightly decreased from 144.3 to 139.8 °C after $scCO_2$ treatment and dropped to 109.9 °C after impregnation. Other authors have reported that PC can crystallize when submitted to $scCO_2$ above its glass transition [61,67], which was estimated to be lower than 60 °C at 40 MPa [61] due to the interaction of the carbonyl group of PC interacting with CO_2 [61,88]. The impregnated PC film was semi-crystalline with a crystallinity of 18.6% and a melting temperature (Tm) of 207.8 °C. The crystallinity can be explained by the plasticizing effect of the $scCO_2$ -cloveextract solution on PC chains, which led to crystallization. The plasticizing effect of the clove extract was also demonstrated in DSC second-heating thermograms (Figure 10b), which accounts for the PC in the presence of 18.5% of CE getting rid of the thermal history produced by the impregnation process. Tg was decreased to 47.7 °C, which is below the working impregnation temperature, and a large melting peak from 174.9 to 220 °C was observed in the impregnated PC. Furthermore, an exothermic peak appeared at 124.5 °C, indicating that the presence of CE facilitates the cold crystallization of PC. Both CO_2 and CE plasticize PC during the impregnation process, enhancing CO_2 sorption and impregnation. However, the increased mobility of the chains leads to their reorganization and crystallization in situ, which is detrimental for the impregnation (since it reduces the amorphous regions that are the ones impregnated [75]), though high CL% were obtained after an impregnation time of 3 h.



Figure 10. DSC thermograms of (**a**) the first heating and (**b**) second heating of neat PC, PC after scCO₂ treatment, and PC impregnated with clove extract (CL = 18.5%) at 60 °C and 10 MPa.

4. Conclusions

This study investigated the impregnation of clove extract (CE) into PC by $scCO_2$ to develop rigid food packaging with antibacterial properties. The influences of the impregnation conditions on the composition of the loaded extract were also explored by determining the proportions of the four compounds of CE. Face-centered design models were applied to evaluate the influences of temperature (35–60 $^{\circ}$ C) and pressure (10–30 MPa) on the total clove loading and the composition of the loaded extract. The clove loading (CL%) ranged from 6.8 to 18.5%, and the maximal CL% was reached at 60 °C and 10 MPa. The temperature favored the impregnation, whereas the pressure was deleterious. The composition of the extract impregnated in PC was different from the crude extract, suggesting the selectivity of the impregnation process. The eugenol content increased from 70.06 to 81.31-86.28%. The eugenvl acetate, β -caryophyllene, and α -humulene contents decreased from 17.06 to 11.22–13.86%, 10.67 to 2.07–4.83%, and 2.20 to below 0.51%, respectively. The pressure enhanced the eugenol content, whereas it decreased the eugenyl acetate content in the loaded extract. Moreover, the temperature decreased the eugenol content. The results were rationalized using the Hansen-type solubility parameters and the intermolecular interactions between PC and each compound. Differential scanning calorimetry showed a high plasticizing effect of CE on PC, which is responsible for increased chain mobility that is favorable to the impregnation, and a concomitant in situ crystallization of the polymer, which is deleterious to the impregnation. Besides that, the high loading of the polymer was responsible for the cracking of the PC surface, but no pores were observed on the

cross-section. The impregnated polymer is promising for antibacterial food containers due to the high loading of clove extract that is enabled and the high eugenol content.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/pr10122661/s1. Figure S1: ¹H NMR of polycarbonate. Figure S2: Evolution of the clove extract loading in PC with impregnation time in the conditions of highest CO₂ density (35 °C; 30 MPa), and of lowest CO₂ density (60 °C; 10 MPa) among the investigated conditions. Table S1: Solubility of oil extract and of its four individual compounds in scCO₂ in conditions close to the one studied. Data reported from the literature. Table S2: FTIR peak assignments of clove extract, neat PC and impregnated PC. References [65,81–85,89] are cited in the supplementary materials

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