The Journal of Supercritical Fluids 133 (2018) 278–290

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Carvone-loaded LDPE films for active packaging: Effect of supercritical CO_2-assisted impregnation on loading, mechanical and transport properties of the films

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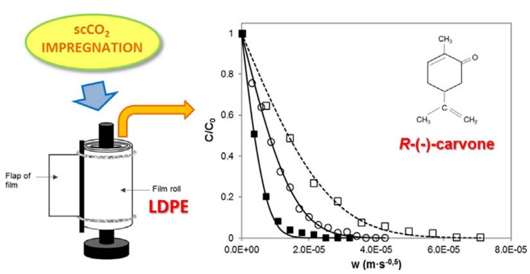
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Supercritical fluid impregnation
R-(−)-carvone
LDPE
Active packaging
Diffusion coefficient

ABSTRACT

In this work, low density polyethylene (LDPE) films were loaded by $scCO_2$-assisted impregnation with R-(−)-carvone, the main component of *M. spicata* and *A. polystachya* essential oils with antimicrobial and insecticidal activity. Impregnation runs were performed in a lab-scale high-pressure cell, and the effect of CO_2 density (240–700 kg m^{-3}) and temperature (35–60 °C) on impregnation yield was evaluated. Impregnation yields of 2.0–4.8% (w/w) were obtained, achieving higher values at low CO_2 density. Thermal and mechanical properties of the films, before and after impregnation, were also investigated. The diffusion coefficient of carvone in $scCO_2$-swollen films was estimated by impregnating film rolls and modeling the concentration profile through the roll thickness using an analytical solution of second Fick's law. Release profiles into air were determined, allowing to estimate diffusivity values in non-swollen films at ambient conditions.

1. Introduction

Supercritical CO_2 ($scCO_2$) assisted impregnation of polymeric films has been proposed and studied by several authors as a suitable technology for producing active materials for food packaging applications. In this way, a great variety of polymeric materials (petroleum-based as well as natural biopolymers) have been impregnated with antioxidant [1,2], antimicrobial [3–5] and insecticidal agents [6–8] using $scCO_2$ as solvent and swelling agent. In addition to the well-known advantages of $scCO_2$ as an eco-friendly solvent [9–12] and the high solubility of many natural active compounds even at mild conditions, $scCO_2$-assisted impregnation is based on the ability of $scCO_2$ to absorb in many polymeric matrices and swell them, increasing the system free volume and the mobility of the polymer chains, enhancing internal diffusivity in several

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http://dx.doi.org/10.1016/j.supflu.2017.10.019
Received 27 July 2017; Received in revised form 25 October 2017; Accepted 25 October 2017
Available online 28 October 2017
0896-8446/

orders of magnitude [9]. Under this state, the solute molecules dissolved in the supercritical fluid phase can penetrate more easily into the polymer network, where specific interactions may occur. After some contact time, which can lead to polymer saturation, the system is depressurized, CO_2 molecules are rapidly desorbed from the polymer and, due to the drastic decrease in solubility and diffusivity, solute molecules are retained into the matrix to a great extent. As a result, polymers are generally impregnated more deeply and faster than when liquid solvents are used.

On the other hand, in the last decades the activity of several botanic compounds has been studied and proposed for their use as active substances in replacement of synthetic additives in order to improve food safety and extend its shelf life. Simultaneously, due to the increasing consumer demands for minimally processed and preservative-free products, food industries perceive active and intelligent packaging as a promising technology for food preservation. Furthermore, this interest has been encouraged by the publication of new regulations concerning the use of these active materials in food contact applications. Consequently, the incorporation of EOs in plastic films to avoid food spoilage is nowadays considered an attractive option for packaging manufacturers and demanding consumers [13–17].

In this work, the incorporation of carvone (2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-one) into low density polyethylene (LDPE) films using $scCO_2$-assisted impregnation technology is investigated. Carvone, whose chemical structure is shown in Fig. 1, is the main component of several essential oils (EOs). This compound has been used for decades in the food industry as a flavoring agent, but nowadays it plays a new role due to its antimicrobial and insecticidal activity [16]. It is an optically active monoterpene, being a very effective bioinsectide as well as antimicrobial agent, presenting both antibacterial and antifungal activities. Moreover, many *in vitro* evaluations have demonstrated the antimicrobial properties of both optical isomers [16–18]. In particular, *R*-(−)-carvone has been proved to be very effective against storage diseases of potatoes like silver scurf and dry rot, caused by *Helminthosporium solanii* and *Fusarium sulfureum* [16]. The insecticidal activity of *R*-(−)-carvone and essential oils rich in this compound has also been reported by several authors. For instance, spearmint EO and pure *R*-(−)-carvone have proved to be highly toxic against adults moths [19] and stored product beetles [20–22].

Several authors have studied and reported the incorporation of active EOs (and their purified components) as well as other extracts from plants into a wide spectrum of both bio- and petroleum-based polymeric matrices commonly used for food packaging by different methodologies [23]. Nevertheless, active packaging systems are mostly based on polyolefin-based films −due to their good technological properties (mechanical, barrier, optical and thermal)– combined with antimicrobial or antioxidant additives [24,25].

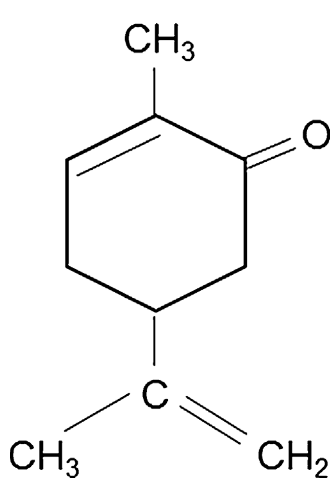

Fig. 1. Chemical structure of *R*-(–)-carvone.

Several techniques are conventionally used at industrial scale for incorporating active substances or additives into polymers. Some of them imply the risk of thermal decomposition of sensitive organic compounds due to they operate above the polymer melting temperature, such as hot melt extrusion or casting techniques. In other processes organic liquid solvents are used which must be removed afterwards in order to meet the rigorous regulations concerning materials for food, biomedical and pharmaceutical applications [26]. $ScCO_2$-assisted impregnation overcomes both limitations, allowing to operate at mild temperature conditions and without liquid solvents, and it has been proven to be very effective for developing active packaging materials exhibiting the same kind of activity as the pure active compounds [1,3,4,27–29]. Nevertheless, to the best of our knowledge, the incorporation of carvone in LDPE films using $scCO_2$-assisted impregnation has not been yet reported in the literature.

Although in most studies single films are impregnated (generally until saturation), industrially it is more convenient to deal with film rolls. In this sense, the few studies that have undertaken pilot or industrial scale research −which are related to $scCO_2$-assisted dying of textile polymers [30,31] have included the impregnation of entire rolls of film. The design and optimization of such processes require some knowledge of the diffusion coefficient of the loaded substance into the swollen polymer at supercritical conditions, as well as the saturation (thermodynamic) loading limit.

Moreover, it is also important to assess the possible effects of the supercritical impregnation treatment on the thermal and mechanical properties of the material. Morphological changes −such as the modification in crystallinity degree, or the rearrangement of crystalline domains–may be induced by $scCO_2$ sorption and the incorporation of additives, which can in turn affect the mechanical behavior, in terms of strength, ductility and elasticity. These properties represent relevant parameters for evaluating an application, as they indicate the ability of the material to maintain integrity under the stress conditions related to processing, handling and storage [3,32,33].

Based on these facts, the objectives of this work are: (a) to determine the impregnation yield of *R*-(–)-carvone in LDPE films at different temperature and pressure conditions; (b) to determine the diffusion coefficient of *R*-(–)-carvone in $scCO_2$-swollen LDPE at different operation conditions, using a film-roll method [34]; (c) to evaluate the thermal and mechanical properties of the obtained films and detect possible modifications due to the impregnation treatment; (d) to study the release kinetics of *R*-(–)-carvone from the impregnated films, determining its diffusion coefficient under ambient conditions.

2. Materials and methods

2.1. Materials

Commercial films of low density polyethylene (LDPE, density: 896 kg m^{-3}, thickness: 30 ± 1 μm) used as polymeric matrix in the impregnation tests, were kindly provided by Converflex (ARCOR Group, Córdoba, Argentina).

R-(–)-carvone (purity: 98%; bp: 227–230 °C; MW: 150.22 g/mol) was purchased from Sigma-Aldrich (Steinheim, Germany) and industrial extra-dry carbon dioxide (water content ≤ 10 ppm v/v), used as impregnation solvent, from Linde (Argentina).

Ethanol (96% v/v, food grade, Porta, Argentina) was used as solvent in the characterization tests.

2.2. Supercritical impregnation experiments

$ScCO_2$–assisted impregnation runs were carried out in a lab-scale batch system described in a previous work [26] and schematically shown in Fig. 2. In brief, each impregnation run was performed in a high-pressure cell (a stainless-steel vessel of 50 cm^3 of internal volume), under constant pressure, temperature and agitation conditions for a