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Supercritical CO_2-assisted impregnation of LDPE/sepiolite nanocomposite films with insecticidal terpene ketones: Impregnation yield, crystallinity and mechanical properties assessment

María L. Goñi[a,b], Nicolás A. Gañán[a,b,*], Silvia E. Barbosa[c], Miriam C. Strumia[a], Raquel E. Martini[a,b]

[a] IPQA, Universidad Nacional de Córdoba, CONICET, Av. Vélez Sarsfield 1611, X5016GCA, Córdoba, Argentina
[b] Instituto de Ciencia y Tecnología de los Alimentos – ICTA (FCEFYN, Universidad Nacional de Córdoba), Av. Vélez Sarsfield 1611, X5016GCA, Córdoba, Argentina
[c] Planta Piloto de Ingeniería Química, PLAPIQUI (UNS – CONICET), Departamento de Ingeniería Química, UNS, Camino La Carrindanga km. 7, 8000 Bahía Blanca, Argentina

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ABSTRACT

In this contribution, supercritical CO_2-assisted impregnation of LDPE/sepiolite nanocomposite films with two insecticidal terpene ketones (thymoquinone and *R*-(+)-pulegone) is investigated, as a strategy to enhance the loading capacity compared to pure LDPE. A factorial experimental design was applied in order to evaluate the effect of five process variables at two levels (sepiolite content: 1–10% w/w; initial ketone mole fraction: 0.0017–0.0025; pressure: 9–13 MPa; depressurization rate: 0.5–2.0 MPa/min; time: 2–4 h) on impregnation yield, at 45 °C. ANOVA test of the results indicated that pressure, time and ketone mole fraction significantly affect impregnation yield (ranging between 2.36 ± 0.18 and 8.60 ± 1.66% w/w). Thermal analysis (DSC) and X-ray diffraction (XRD) allowed to investigate the nanocomposite morphology and the modifications induced by the impregnation. The mechanical properties of the films were assessed by stress-strain tests, showing that the impregnation process had a very low impact on the material ductility and strength.

1. Introduction

Supercritical carbon dioxide ($scCO_2$) assisted impregnation of polymers with active compounds has been proposed and studied as an attractive technology for the development of active materials with potential applications in medicine, pharmacy, food packaging and pest control, among others [1–4], based on the well known properties of $scCO_2$ as "eco-friendly" solvent with tunable properties. In a typical process, the polymer (which may be in the form of films, pellets, fibers, etc.) is put in contact with a $scCO_2$ phase where the active substance to be loaded is dissolved. Under high pressure conditions, CO_2 is absorbed into the polymer, promoting its swelling and plasticization, and enhancing solute diffusion through the polymeric matrix by increasing the system free volume [1]. The sorption and swelling behavior of different polymer-$scCO_2$ systems and its dependence on pressure and temperature conditions have been studied by several authors [5–9]. After some contact time, the system is depressurized, CO_2 is desorbed, the polymer recovers (totally or partially) its original volume and morphology and the solute molecules are retained into the polymeric matrix to some extent. The final amount of solute loaded into the polymer depends on thermodynamic as well as mass transfer factors. The maximum impregnation yield is determined by the solute partition coefficient between the polymer and the fluid phase, which depends on the system temperature, pressure and composition. Besides, as the solute diffusion into the polymer is the rate controlling step, a certain time of exposure is required in order to reach thermodynamic equilibrium. Mass transfer is highly dependent on concentration gradients and the physico-chemical properties of both the polymer and the fluid (mainly density and viscosity). The occurrence of specific or strong solute-polymer interactions (such as dipole–dipole or hydrogen bonding, hydrophilic or hydrophobic interactions) will enhance solute retention and therefore polymer loading [10].

Among the most promising applications, we can mention the $scCO_2$-assisted dying of polymers and textile fibers [11,12], the impregnation of contact lenses, implants and sutures with pharmacological compounds [13–15], the incorporation of antimicrobials in food packaging materials [16–18] and biopolymers [19–21], and the direct impregnation of wood with antifungal compounds [22], as some relevant examples. Some applications have successfully reached industrial scale, such as wood impregnation [23] and textile fibers dying [24].

* Corresponding author at: IPQA, Universidad Nacional de Córdoba, CONICET, Av. Vélez Sarsfield 1611, Córdoba, X5016GCA, Argentina.
E-mail address: nganan@plapiqui.edu.ar (N.A. Gañán).

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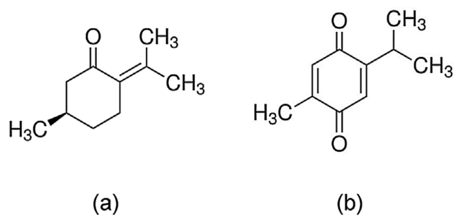

Fig. 1. Chemical structures of terpene ketones: (a) *R*-(+)-pulegone and (b) thymoquinone.

Particularly in our group, an application currently investigated is the incorporation of biopesticides into polymeric films commonly used for food packaging or crop protection, with the objective of controlling insect pests during storage or transport. In a previous work [25], we have studied the $scCO_2$-assisted impregnation of low-density polyethylene (LDPE) films with a mixture of two selected terpene ketones (pulegone and thymoquinone) with insecticidal activity against the corn weevil (*Sitophilus zeamais*) [26]. The chemical structure of these terpene ketones is shown in Fig. 1. Film samples were impregnated under different combinations of pressure, ketone mole fraction, contact time and depressurization conditions, in order to investigate the effect of these variables on the impregnation efficiency. The ketone content in the impregnated films ranged between 2 and 6% (w/w), and their fumigant toxicity against *S. zeamais* was confirmed and evaluated in laboratory bioassays [25,27].

The aim of this work is to explore the application of $scCO_2$-assisted impregnation for the incorporation of this mixture of terpene ketones into LDPE/sepiolite nanocomposite films. Polymer/clay composites have been studied as suitable carrier and packaging materials for the controlled release of active substances [28], as a result of the adsorption of solute molecules onto the dispersed clay nanoparticles. Besides release control, the adsorption onto the porous structure of nanoclays also preserves active compounds from degradation due to sunlight irradiation, temperature, oxygen and reduces losses by leaching or excessive evaporation, for example in the case of pesticides [29]. Therefore, the use of a LDPE/sepiolite nanocomposite as impregnation matrix is presented as a potential strategy for enhancing the loading capacity as well as the final properties with respect to pure LDPE films.

Sepiolite is a hydrated magnesium silicate clay whose half-unit formula is $Si_{12}O_{30}Mg_8(OH,F)_4(OH_2)_4.8H_2O$. Its structure consists of talc type sheets, i.e., planes formed by an octahedral layer (Mg) between two external tetrahedral layers (Si), and these sheets are separated by so-called zeolitic channels, characterized by the presence of water molecules, as can be seen in Fig. 2 [30]. The particular arrangement of atoms produces a needle-like (acicular) structure, instead of typical plate-like one. For this reason sepiolite has one of the highest surface area of all clay minerals: about 300 m^2/g [31]. Their particles are arranged forming loosely packed and porous aggregates with an extensive capillary network which explains the high porosity and light weight because of the high void space fraction. The high surface area and porosity account for the remarkable adsorptive and absorptive properties of this clay: it adsorbs vapor and odors and can absorb approximately its own weight of water and other liquids [31]. The presence of a high number of silanol groups (Si–OH) exposed at the pores surface can interact with water and polar substances (such as ketones). Besides its excellent sorption properties, sepiolite also enhances the mechanical resistance and thermal stability of polymeric materials. Sepiolite and other related clays have been applied as nanofillers in the development of active films and coatings loaded with essential oils and related volatile compounds. For example, Tornuk et al. have reported the incorporation of nanoclays grafted with thymol, eugenol and carvacrol to LDPE films for meat products preservation [32], while Gimenez et al. have investigated the dispersion of sepiolite in gelatin-egg white films for the controlled release of clove oil as antioxidant and antimicrobial agent [33]. Chevillard et al. have studied the role of different montmorillonites in modulating the diffusion rate of a model pesticide in wheat gluten-based polymers [34]. In these applications, the active substance is generally adsorbed onto the nanofiller before its dispersion into the polymeric matrix, or added directly to the molten polymer (or polymer solution) before film casting. However, to the best of our knowledge, the direct impregnation of LDPE/clay type nanocomposite films by $scCO_2$-assisted impregnation has not been previously reported in the literature.

In this study, the effect of the main process variables (impregnation pressure, ketone mole fraction, contact time and depressurization rate), as well as the sepiolite content in the polymer, on the impregnation performance is investigated, using a factorial design of experiments (DOE). This approach allows a rapid screening and determination of the variables that affect significantly the process output [35] and provides useful information for further optimization purposes. The morphology of the nanocomposite matrix, as well as the modifications induced by the impregnation process, are investigated by thermal analysis and X-ray diffraction (XRD). Finally, the mechanical performance of the impregnated material is assessed.

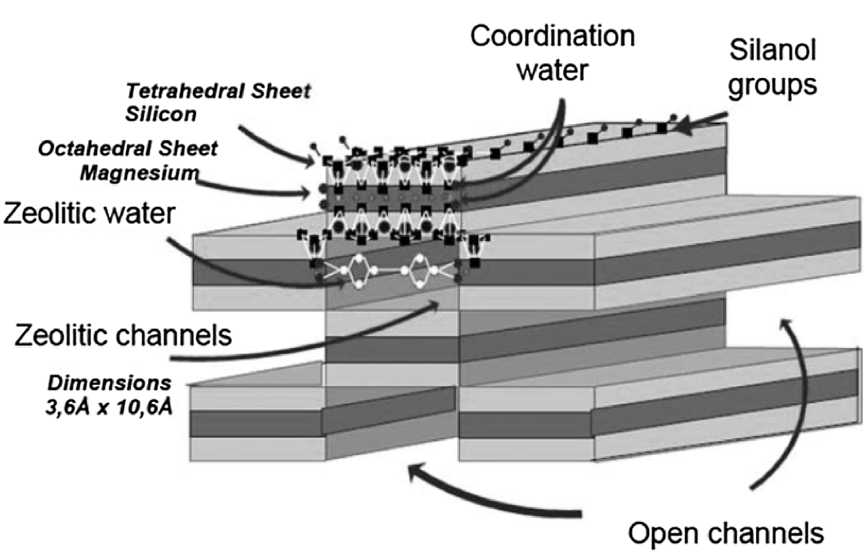

Fig. 2. Scheme of sepiolite structure [30].