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Supercritical CO_2 extraction of contaminants from polypropylene intended for food contact: Effects of contaminant molecular structure and processing parameters

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ABSTRACT

Supercritical CO_2 ($SCCO_2$) extraction has been employed to remove model molecules (surrogates) which simulate the real and potential contaminants which can be present into recycled post-consumer polypropylene, limiting the recyclability for food contact applications. Different substances covering a wide range of molecular weights were extracted and evaluated. The effects of contaminant molecular structure and several processing parameters (pressure, temperature, extraction time, solvent flow rate, and matrix shape and size) upon extraction rate were investigated. The operating conditions studied were: pressure ranges of 100–300 bar, temperature ranges of 50–90 °C, indicating CO_2 densities varying from 0.20 to 0.87 g/mL, and solvent flow rate ranges of 60–160 mL/min. Two shapes of contaminated material were studied: pellets and films (thickness ranges of 100–300 μm). Quantitative results for extraction kinetics have been obtained by gas chromatography. High extraction yields (100%) were achieved with films at restricted extraction times and, likewise, with pellets at reasonable extraction times. Operating conditions of 200 bar, 90 °C and 7.5 h of extraction were sufficient to achieve a complete extraction from pellet matrix (2.5 mm of diameter), even for the heaviest contaminant (807 g/mol).

1. Introduction

Polymeric plastic packagings are widely present on the market in a lot of applications, mainly in the food packaging area. Their versatility, excellent properties and availability in large quantities with relatively low costs allowed the exceptional rise of these materials. Today, packaging applications represent the largest application sector for the plastics industry and in Europe represent about 40% of the total plastics demand, of which more than 65% are polyolefins (POs) (polypropylene and polyethylene) [1]. Meanwhile, plastic packagings are often used on a very limited period of time and quickly generate an important volume of waste to be managed through incineration, land filling or recycling, which can cause environmental and economic problems. Nowadays, only 26% of post-consumer plastics (including POs and polyethylene terephthalate (PET)) are recycled [1]. For POs, after washing (surface decontamination), the material is crushed into flakes, sorted out, before being regenerated by plastic processing under vacuum or nitrogen flux and high temperature, for the re-use in non-food applications. This last step is proposed in order to decontaminate plastic pellets by volatile chemical compounds thermo-desorption [2].

Nowadays, the requirements of food packaging industries are focused in the development of new technologies able to recycle plastics into direct food contact applications in order to better "absorb" the huge actual plastic waste issued from food packaging. The method briefly described previously is most often not sufficient to recycle post-consumer POs for food contact applications because this kind of application requires materials very well selected on the base of their original first use to comply with the food contact material regulation, European Commission EC 10/2011 [3]. Indeed, this method removes only volatile compounds and surface contaminants, whereas recycled POs packaging waste may contain residues from previous use, misuses and contaminants from non-authorised

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substances such as the so-called neoformed products [4] and relatively high-molecular-weight contaminants adsorbed from their surroundings during their lifecycle or first use due to their permeability [5]. This bulk contamination strongly limits the recyclability of post-consumer POs as recycled food contact material. In fact, these contaminants might be released from recycled packaging and migrate into the foodstuffs to contaminate it [6,7]. Consequently, the decontamination of POs intended for food contact applications requires a necessary removal of these potential contaminants. Green and advanced technologies like $SCCO_2$ extraction could be a highly recommendable technique for this purpose.

Supercritical fluids have become potential solvents for various polymers processing [8,9] and during the last decades, they have been widely employed for the extraction of polymeric matrices, especially $SCCO_2$, due to their suitable properties for this application [10–13]. Supercritical fluid extraction (SFE), as environmentally friendly technology and promising alternative, exhibits several benefits over classical solvent extraction methods, such as the improvement of mass transfer, better extraction time and efficiency, minimal residues in the final product, and no organic waste. Moreover, SFE is less expensive than other conventional methods, rendering this technique a promising prospect in extraction realm [14].

Within the last years, several research activities on SFE of different polymeric matrices have been published. In their works, Scialdone et al. [15] investigated the extraction of ammonium carboxylate perfluoropolyether surfactants from poly(vinylidenefluoride) and poly(tetrafluoroethylene) via $SCCO_2$, resulting in rapid and effective extraction. They found that quantitative recoveries higher than 90% were obtained at 200 bar, 40 °C after 240 min. A strong influence of pressure, temperature and extraction time on the extraction recovery was, furthermore, observed. This research suggests that $SCCO_2$ extraction can be a process of applicative interest for the removal of this class of stabilizers from fluoropolymers. Guerra et al. [16] proved that SFE is a useful tool in the analysis of additives in polymeric materials. They extracted citrate and benzoate plasticizers from poly(vinyl chloride) and they found that a maximum extraction is obtained at pressures and temperatures higher than 400 bar and 80 °C, respectively. In another type of application, Barry et al. [17] demonstrated that conventional post-lithography treatments of pure polyacrylate and polyacrylate/hydroxyapatite composites followed by $SCCO_2$ processing dramatically increased biocompatibility. Indeed, the $SCCO_2$ processing of these materials extracts toxic residuals (unreacted monomers and initiators) from all structures, leading to cleaner microporous structures. In recent publication, Arias et al. [18] extracted successfully antioxidant additives from low density polyethylene and high density polyethylene using $SCCO_2$ extraction. They obtained an effective and fast extraction, mainly at higher pressures and temperatures. More recent study has been devoted to the potential of $SCCO_2$ extraction to extract lithium-ion battery electrolytes from polyethylene fleece as separator material used in battery, resulting in a successful extraction [19].

In previous work [20], we studied the remove of low-molecular-weight additives (i.e., antioxidants) already present in food grade polyolefins and which act as contaminants in food packaging materials. We adapted the $SCCO_2$ extraction in dynamic mode to the post-consumer POs depollution. We extracted unidentified low-molecular-weight compounds from two POs and we compared the results obtained for $SCCO_2$ extraction to that of classical organic extraction with methylene chloride. The results demonstrate that a successful and potential extraction was obtained and that the $SCCO_2$ extraction was found to be the most advantageous technique in terms of simplicity, efficiency and speed in comparison to that with methylene chloride.

In this study, $SCCO_2$ extraction in dynamic mode is investigated to decontaminate polypropylene intended for food contact applications. The first step was devoted to the manufacturing of pellets and films intentionally contaminated with known concentrations, selecting model contaminants set to be removed playing with their molecular weights and structures. In the whole, this work aims, at first hand, to investigate the effects of contaminant molecular weight and structure on the extraction in terms of efficiency and speed. On the other hand, to study the effects of processing parameters, such as pressure, temperature, extraction time, CO_2 flow rate, and matrix shape and size upon the extraction rate, as well as to identify the process parameters that better affect and enhance the $SCCO_2$ extraction kinetic. The final goal of this study was to investigate and understand the mechanisms involved in the $SCCO_2$ extraction.

2. Materials and methods

2.1. Chemicals

Polypropylene (PP) Moplen HP456J was selected for this study as a food contact polyolefin used in food packaging. It is a homopolymer suitable for extrusion and thermoforming applications. It had a density of 0.9 g/mL, a melt flow rate of 3.4 g/10 min (230 °C, 2.16 kg) and a melt volume flow rate of 4.6 mL/10 min (230 °C, 2.16 kg) (by ISO 1133 method). PP samples were commercially obtained as pellets.

The model contaminants studied in this work were: Stearin [1-monooctadecanoyl-rac-glycerol], Dilaurin [1,3-didodecanoylglycerol], Trilaurin [1,2,3-tridodecanoylglycerol], and Tripalmitin [1,2,3-Propanetriol tris(hexadecanoate)] (see Table 1). The structures of these molecules may be consulted in Fig. 1.

Research grade carbon dioxide was used as the supercritical fluid in the experiments. It had an ultra-high purity of 99.999% and supplied by AIR LIQUIDE.

2.2. Choice of the model contaminants

The bulk contamination of POs by food constituents or accidental pollutants during packaging shelf life depends on:

- The diffusion properties of the substances: the higher the diffusion rates (described by a diffusion coefficient D), the higher is the contamination.
- The affinity: the higher the affinity toward POs, the higher is the contamination of the material at equilibrium of diffusion; this affinity is controlled by a partition coefficient (K).

Globally, a high contamination level before equilibrium of diffusion requires a combination of both high D and K (high value of DK product). Indeed, POs are non-polar resin and therefore they have more affinity to non-polar molecules, which makes it difficult for the polar molecules to penetrate through them. In the same time, obviously, the larger molecules penetrate more laboriously in these polymeric matrices than smaller ones (kinetic barrier). Consequently, only low molecular weight polar compounds

Table 1
Model contaminants data.

Molecule	Chemical formula	M_w (g/mol)	Purity (%)
Stearin	$C_{21}H_{42}O_4$	358.56	99
Dilaurin	$C_{27}H_{52}O_5$	456.70	99
Trilaurin	$C_{39}H_{74}O_6$	639.00	99
Tripalmitin	$C_{51}H_{98}O_6$	807.32	95