J. of Supercritical Fluids 98 (2015) 25–32

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

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

Purification of post-consumer polyolefins via supercritical CO_2 extraction for the recycling in food contact applications

Ben Said Anouar[a,b], Cécile Guinot[d], Jean-Christophe Ruiz[a], Frédéric Charton[a], Patrice Dole[c], Catherine Joly[d], Chalamet Yvan[b,*]

[a] Laboratoire des Procédés Supercritiques et de Décontamination, CEA-Marcoule, DEN/DTCD/SPDE/LPSD, BP 17171, 30207 Bagnols sur Cèze, France
[b] Université de Lyon, CNRS, UMR5223, Ingénierie des Matériaux Polymères, F-42023 Saint-Etienne, France
[c] Centre Technique de Conservation des Produits Agricoles (CTCPA), Technopole Alimentec, rue Henri de Boissieu, F-01000 Bourg en Bresse, France
[d] Université de Lyon, Université Lyon 1-ISARA Lyon, Laboratoire de Bioingénierie et Dynamique Microbienne aux Interfaces Alimentaires (BioDyMIA, EA n°3733), IUT Lyon 1, Technopole Alimentec, rue Henri de Boissieu, F-01000 Bourg en Bresse, France

ARTICLE INFO

Article history:
Received 27 November 2014
Received in revised form
28 November 2014
Accepted 29 December 2014
Available online 7 January 2015

Keywords:
Supercritical CO_2 extraction
Purification
Food contact material
Polypropylene
Polyethylene
Recycling

ABSTRACT

Throughout their lifecycle or first use, polyolefins can be exposed to contaminating media which limit their recyclability, especially in food industry, such as packaging. Supercritical carbon dioxide ($SCCO_2$) extraction in dynamic mode is studied as a possible method to purify post-consumer polyolefins. As a first approach, the strategy was to remove the well-known conventional additives (i.e., antioxidant) which are already present in food grade polypropylene (PP) and linear low density polyethylene (LLDPE). The extraction yields and kinetics have been obtained by gas chromatography. A systematic study of the influence of the shape (pellets or films) and the thickness of the materials shows that it is possible to increase the speed of extraction with a thinner material: high yields (100%) are obtained with films at 300 bar, 50 °C and 5 min of extraction. Finally, the potential of $SCCO_2$ extraction was compared to that of traditional liquid extraction with methylene chloride.

1. Introduction

Due to their excellent properties, polyolefins such as polypropylene and polyethylene are widely used in food packaging applications to preserve and protect foodstuffs. Meanwhile, polymeric food packagings are not inert and migration of additives or their degradation products from packaging to food is a well-known issue, covered by European Commission (EC) regulation related to food contact materials [1–3]. Moreover, during their lifecycle or first use, substances can penetrate into polymer packagings especially with polyolefins. This possible contamination strongly limits their recyclability as recycled food contact material (closed loop recycling) due to the food contact material regulation, EC 10/2011 [3]. In fact, these previously absorbed components might be released from recycled packaging, and migrate into the foodstuff to contaminate it [4].

Nowadays, the industrial actors of the plastic packaging are facing a growing need for the use of recycled materials, due to economic, commercial or societal constraints. The recycling of post-consumer plastics into direct food contact applications requires rigorous decontamination levels and therefore effective and efficient recycling processes. Currently, the only post-consumer recycled polymeric material, after purification, in industrial applications in food contact is polyethylene terephthalate (PET). The first recycling process for post-consumer PET in direct food contact applications has been approved in USA in 1991 [6]. Today, there are several technologies commercially available to remove the potential post-consumer contaminants absorbed by PET: the processes use typically a thermal desorption step under vacuum or inert gas treatment (in the range of about 180–220 °C) followed by a solid state polymerization (SSP), all steps performed after a relevant collect, PET sorting, grinding, washing, optical assisted sorting, extrusion/pelletizing operations [5–7].

On the other hand, until today, the recycling of post-consumer polyolefins into direct food contact applications is not yet possible; the method described for PET and the other conventional methods such as devolatilization and solvent based extraction are not sufficient to reduce the concentration of unwanted contaminants

* Corresponding author at: Université de Lyon, F-42023 Saint-Etienne, France, CNRS, UMR5223, Ingénierie des Matériaux Polymères, F-42023 Saint-Etienne, France. Tel.: +33 4 77 48 15 98.
E-mail address: chalamet@univ-st-etienne.fr (C. Yvan).

http://dx.doi.org/10.1016/j.supflu.2014.12.022
0896-8446/

in the matrix to the required permissible levels or not economically acceptable by industry (solvent). In fact, unlike PET where only small molecules can penetrate (M_w < 300 g/mol), larger size molecules are able to penetrate into polyolefins (M_w could reach 800 g/mol): this is due to PET material which acts as a kinetic barrier for diffusion [8]. However, higher molecular weight contaminants cannot be efficiently or easily extracted by classical techniques, such as solvent or thermal based-extraction. These techniques present various disadvantages which limit their use in purification of polymers for the recycling in direct food contact and none of them can be considered as an optimal method for this purpose [9,10]. Consequently, the purification of post-consumer polyolefins requires an advanced technology for decontamination. One possibility can be the supercritical fluid extraction (SFE) method. This process has been widely studied as a potential alternative technique in the last decades to extract compounds, such as additives, antioxidants, UV stabilizers, residual solvents, unreacted monomers from various polymeric matrices for analytical applications and is becoming increasingly popular in polymer area [11–17].

The utility of supercritical fluids in extraction processes relies on the properties of the supercritical fluid state: adjustable solvent strength, high diffusivity, low viscosity and low surface tension. These properties are very convenient for the extraction. In SFE, carbon dioxide is the most commonly used supercritical fluid, because its critical conditions are relatively mild (P_c = 73.8 bar and T_c = 31 °C), it is easily removed, and it is recyclable. In addition, CO_2 is non-toxic, non-flammable and available with high purity. SFE presents several advantages in relation with conventional techniques like the improvement in mass transfer, better extraction time and efficiency, minimal residues in the final product and the possibility to adjust the solvation power with simply changing the pressure and temperature conditions [18].

Several researches have studied the extraction of antioxidants, additives and oligomers from polymeric matrices by $SCCO_2$. Kuppers [19] extracted selectively low molecular weight compounds from PET fibers using SFE. A selective two steps extraction was used, firstly from the fiber cover and, then, from the core of the fiber. He also studied the effect of pressure and temperature as factors affecting SFE. Bartle et al. [20] also investigated the SFE of oligomers from PET films. They showed that extraction of cyclic ethylene terephthalate trimer from PET was possible. Porter and Taylor [21] performed a systematic study for the removal of nylon 6,6 oligomers with SFE. In this study, the effect of CO_2 pressure, temperature, and extraction time were examined and results of SFE were compared to results of conventional solvent extraction. They found a reduction in sample handling compared to solvent extraction. SFE has been used successfully to extract citrate and benzoate plasticizers from poly(vinyl chloride) [22] and volatile organic components (VOCs) from polyethylene pellets [23]; quantitative extractions are obtained. Recent studies with polyethylene additives [9] and ungrafted monomers from polypropylene-graft-maleic anhydride [11] have shown that SFE is as efficient as conventional extraction but less time-consuming. More recent article describes the optimization of SFE parameters for the removal of residual glycidyl methacrylate monomers and benzoyl peroxide initiator from medium density polyethylene after grafting. In this study, authors showed that the optimum conditions in which, temperature, pressure and extraction time were 53 °C, 209 bar and 74 min, respectively, and they also found that SFE method is more effective than Soxhlet method [24].

The aim of this study is to adapt the $SCCO_2$ extraction in dynamic mode to the post-consumer polyolefins depollution with high cleaning efficiencies so that the decontaminated post-consumer recyclates could be re-used in direct food contact. The first investigations have been made to remove or reduce greatly the additive content already present in polyolefins as stabilizers: in this approach, these additives are playing the role of contaminants, especially the heaviest molecular weight ones, which could be present in post-consumer recycled polyolefins. The investigated parameters are the temperature and the material shape and thickness upon the extraction efficiency. The final goal of the research was to evaluate $SCCO_2$ extraction in terms of efficiency and speed via systematic comparison with methylene chloride ($MeCl_2$) extraction.

2. Materials and methods

2.1. Polyolefins and chemicals

Food grade polypropylene Isplen PB 199 A3M (an extra high fluidity heterophasic copolymer, density of 0.905 g/mL and melt flow index MFI (230 °C, 2.16 kg) = 55 g/10 min) and linear low density polyethylene LL 1001XV (density of 0.918 g/mL and MFI (190 °C, 2.16 kg) = 1.0 g/10 min) were selected. These matrices were originally and variously formulated with additives. PP and LLDPE have been chosen as model polyolefins for their very different behavior: indeed, amongst polyolefins, PP acts as the higher diffusion barrier polymer as contaminants can be sorbed in the highest amounts by LLDPE.

PP and LLDPE samples were commercially obtained as pellets (approximately from 2 to 3 mm of diameter). Three series of extruded blown film were made from LLDPE. The thicknesses of the films were 25, 50 and 100 μm.

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. Irganox 1010 [pentaerythritol tetrakis 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] (an antioxidant frequently used to retard the degradation of polymers due to air oxidation, the chemical structure is shown in Fig. 1) and methylene chloride (purity ≥ 99.9%, grade for GC analysis) were purchased from Sigma–Aldrich

A set of linear alkanes used in combination with the Irganox 1010, as references, for the calibration is listed in Table 1.

2.2. Supercritical CO_2 extraction

2.2.1. Apparatus and procedure

The supercritical apparatus used for the extraction in this study is shown in Fig. 2. $SCCO_2$ extraction is used in dynamic mode with recycling of CO_2. This system operates at a temperature range of 25–90 °C with a maximum pressure of 300 bar and a maximum mass flow of 160 mL/min. It includes an extractor and three separators which consist of pressure gauges and temperature control systems. The extractor is equipped with a specific high-pressure basket with two stainless filters located at its either end. The whole of this extractor is out of stainless steel (P_{max} = 300 bar, T_{max} = 90 °C, volume = 1 L). The lines under

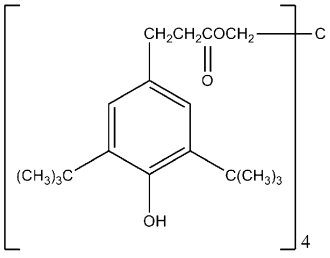

Fig. 1. Chemical structure of Irganox 1010.