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Characterization of polymeric membranes used in vegetable oil/organic solvents separation

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ABSTRACT

The characterization of commercial membranes used in the separation of refined soybean oil/*n*-butane and *n*-hexane mixtures was studied in this work using different commercial ultrafiltration membranes, with cut-offs ranging from 1 to 5 kDa. The membranes were used in the permeation of refined soybean oil/pressurized *n*-butane mixtures at 1:3 (w/w) and 1:1 (w/w) mass ratios in a continuous tangential flow module and in the permeation of soybean oil/*n*-hexane mixtures in a dead-end flow module. The membranes were characterized by DSC (differential scanning calorimetry), FTIR (Fourier transform spectroscopy), contact angle measurement (Goniometer), zeta potential and SEM-EDS (scanning electron microscopy with X-ray microanalysis) aiming to better understanding the phenomena involved in the permeation process. Some membranes did not show any measurable permeation flux for refined soybean oil/*n*-butane mixtures, which may be related to their low hydrophobicity. Contact angle and zeta potential measurements showed that the membrane surface hydrophilicity changes after permeation. FTIR spectra showed that the membranes were fouled with oil even after washing with solvent. Results obtained in this work showed that permeation caused few modifications on the surfaces of the tested membranes at the experimental conditions investigated. It is shown that these polymeric membranes can be used in the separation of vegetable oils/organic solvents effectively without degradations.

1. Introduction

Membrane separations have been increasingly applied in food industry. A growth in the number of studies on the application of membrane processes in vegetable oil processing has been observed in the last years [1,2]. The advantages of membrane separation processes include the possibility of operation at mild temperatures, better product quality, low energy consumption, possibility of simultaneous fractionation and concentration, easy scaling-up and operation [3–7]. One of the major limitations for implementation of this technology in the vegetable oil processing is to find membranes that are stable to oil and organic solvents [8].

Polymeric membranes seem to have disadvantages that limit their industrial applications, since the performance of polymeric membranes would deteriorate with time when they are used in harsh environment [9]. Some classes of polymers used in the manufacture of membranes exhibit excellent resistance to organic solvents. Polysulfone, polyethersulfone, polyamides, and others classes of membranes polymers have promising uses in separations of vegetable oils of organic solvents. Polysulfone (PSU) is one of the most popular thermoplastic materials used in the manufacturing of various types of MF and UF membranes. This polymer provides structural and chemical stability, which increases the robustness of such membranes. PSU, however, is hydrophobic, which makes these membranes more susceptible to adsorptive fouling of hydrophobic solutes [10]. Polyethersulfone (PES) is an engineering plastic, which presents many interesting characteristics such as high mechanical resistance and heat distortion temperature, good heat-aging resistance and easy processing, hence becoming an important membrane material [11]. Aromatic polyamides (APA) are considered to be high-performance materials due to their superior thermal and mechanical properties, which make them useful for advanced technologies [12–15].

The application of polymeric membranes in vegetable oil processing has been considered in several studies in the literature [2–7,16]. However, systematic studies on the characterization of the polymeric membranes after permeation of organic solutes and solvents are still scarce in the literature.

In a previous work of our group, a method for separation of soybean oil and pressurized *n*-butane using polymeric membranes was developed [16]. The purpose of the present study was to characterize the membranes used in the separation of oil/*n*-butane and oil/*n*-hexane using different methods (DSC, FTIR, contact angle, zeta

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Table 1
Supplier membranes specifications used in this work.

Class[a]	Supplier	Membrane material	Trade name	MWCO[c] or rejection	pH range (25 °C)	Typical water flux[d] (L/m^2 h)
UF	GE-osmonics	Composite polyamide	Sepa GE	1 kDa	2–11	30.6 (at 27.6 bar)
UF	GE-osmonics	Polyamide/polysulfone[e]	Sepa GH	1 kDa	2–11	34 (at 10.3 bar)
UF	GE-osmonics	Polyamide/polysulfone[e]	Sepa GK	2 kDa	2–11	28.9 (at 5.2 bar)
UF	GE-osmonics	Polyamide/polysulfone[e]	Sepa GM	4 kDa	2–11	34 (at 2.8 bar)
UF	GE-osmonics	PES[b]	Sepa PT	5 kDa	–	153 (at 3.4 bar)

[a] UF: ultrafiltration.
[b] PES: polyethersulfone.
[c] Molecular weight cut-off.
[d] According to supplier data sheet.
[e] Exact composition not informed.

potential and SEM-EDS) to check for membrane modification and fouling during the oil/solvent permeation process.

2. Materials and methods

2.1. Permeation experiments

The permeation experiments using refined soybean oil and pressurized *n*-butane as solvent were carried out according to Tres et al. [16]. Permeation using mixtures of refined soybean oil/*n*-hexane (Vetec, 99% purity) were carried out in a stainless-steel dead-end flow module (capacity 500 mL) with membrane area of 35.3 cm^2. In the latter module, mixtures of refined soybean oil/*n*-hexane at 1:3 (w/w) and 1:1 (w/w) mass ratios were used in the feed. The feed pressure varied from 2 to 25 bar, achieved by pressurization of the dead-end cell with nitrogen (results not presented). Table 1 presents the characteristics of the membranes used in this work.

2.2. Characterization of flat sheet membranes

Five characterization methods were used for the membranes. Differential scanning calorimetry (DSC) analysis was performed using a Perkin Elmer (DSC 7) calorimeter. Analyses were performed from 0 to 300 °C at a heating rate of 10 °C/min to measure T_g, in order to provide an estimation of the flexibility of polymer chains. Fourier transform infrared spectroscopy (FTIR) study was carried out using a Perkin Elmer (Spectrum 100) FTIR spectrometer over the range of 4000–650 cm^{-1}. Contact angle measurements were accomplished using a Dataphysics (OCA15EC) goniometer with 15 μL of drop volume. Evaluation of modification of electrical charges on the surface of membranes was performed using an Anton Paar (SurPASS) zeta potential meter from pH 3.0 to 10.0. Zeta potentials were calculated from the measured streaming potentials using the Helmholtz–Smoluchowski equation. A SEM-EDS, scanning electron microscopy with X-ray microanalysis (Quanta 200, FEI Company and INCA Penta FETx3, Oxford Instruments, respectively) was used to monitor the structure morphology and to observe modifications on the surface of the membranes. Prior to the SEM analysis, membrane samples were fractured in liquid nitrogen. The membranes were mounted on a stainless-steel disk with a double sided tape and sputter-coated with a thin gold film (300 Å). All membranes were cleaned with *n*-pentane, *n*-butane and dried before the analysis.

3. Results and discussion

3.1. FTIR

In infrared spectroscopy the presence of certain vibrational bands related to characteristic functional groups assist in the qualitative identification of the likely constituents of polymer blends formed by more than one polymer, while their intensities give an estimate of their proportionality [17]. Fig. 1 presents the FTIR spectra of Sepa GE and Sepa PT membranes before permeation of the soybean oil/organic solvents. For quantitative purposes they were obtained using the same mass of sample.

According to information provided by the manufacturers Sepa GE and Sepa PT, membranes are based on polyamide and polyethersulfone, respectively (Table 1). The spectra of both membranes show a band at 3300 cm^{-1}, which refers to the stretching (ν) of the NH group of the peptide bond typical of polyamides, and bands between 1000 and 1400 cm^{-1}, referring to sulfonic groups (S=O, O=S=O) characteristic of polysulfone and polyethersulfone [17,18]. This same spectrum was observed for the other membranes of mixed composition (polyamide/polysulfone) used in this study, only with small variations in the intensities of the signals. The results suggest that all membranes, including those identified by the manufacturer as polyamide (Sepa GE) and polyethersulfone (Sepa PT) have a mixed composition of polyamide/polysulfone or polyethersulfone. Comparatively, this proportionality can be estimated from the variation of intensities observed in the bands at the stretches mentioned above (Figs. 2 and 3).

The Sepa GE membrane presents the spectrum with the highest band intensity around 3300 cm^{-1}, among all the membranes examined. In the absence of quantitative information from the manufacturer, this result was used to identify this membrane as the one with the highest level of polyamide in its composition. Considering the values of intensities observed for this stretching, the content of polyamide follows the trend: Sepa GE > GK > GH ≈ GM > PT. The opposite trend (PT > GM > GH > GK > GE) was observed for the intensity of the bands in the region between 1075 and 1350 cm^{-1}, referring to the sulfonic groups, characteristic of polysulfones and polyethersulfones. These observations are correlated with membrane hydrophobicity and will be discussed later with the results of contact angle.

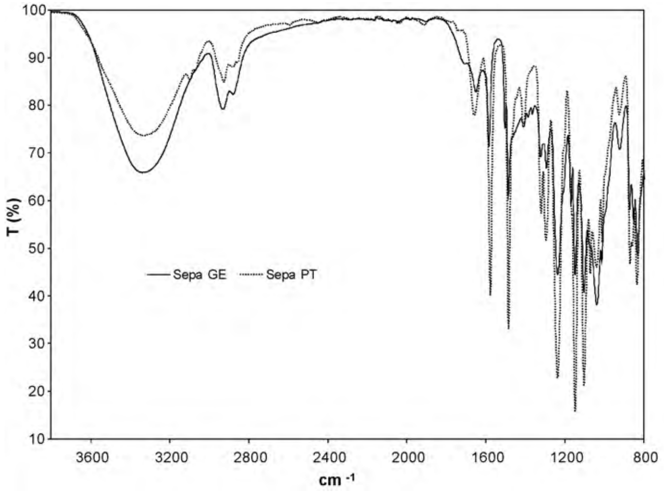

Fig. 1. FTIR spectra for the new Sepa GE and PT membranes.