



Bio-based membranes for ethyl tert-butyl ether (ETBE) bio-fuel purification by pervaporation



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ABSTRACT

Ethyl *tert*-butyl ether (ETBE) is a fuel octane enhancer considered as a major bio-fuel in Europe. Blended with gasoline fuels, ETBE improves fuel combustion and reduces toxic hydrocarbon emissions. ETBE industrial synthesis leads to an azeotropic mixture EtOH/ETBE (20/80 wt%), which cannot be separated by simple distillation. According to former works, cellulose acetate (CA) membranes were extremely selective with a permeate EtOH content of 100% but their flux was too low for ETBE purification by the pervaporation (PV) membrane process. The affinity of the bio-based polylactide (PLA) for ethanol has also been reported for poly(vinyl pyrrolidone)/PLA blends for this application. In this work, new bio-based membranes were obtained by grafting CA with controlled PLA amounts by a “grafting onto” strategy. The CA-*g*-PLA copolymers were characterized by ATR-FTIR, ¹H NMR, DSC and SAXS. Their membrane properties were investigated in terms of structure-morphology-property relationships for the sorption and pervaporation of the targeted EtOH/ETBE mixture. PLA grafting onto CA strongly improved the flux ($\times 12$) while the ethanol permeate content remained in the very high range ($C' > 90$ wt%) for ETBE purification by pervaporation.

1. Introduction

Membrane separation processes have taken their place among the most important industrial and research topics and they are widely used in gas and liquid separations, waste water treatment and water desalination. Compared to conventional processes such as liquid-liquid extraction or distillation, membrane processes offer many advantages like modularity, energy saving, mild operating conditions and lower environmental impact [1–3]. In all of these processes, the membrane is a key factor and its optimization is essential.

On the other hand, the formulation of fuels with lower environmental impact and the production of new bio-fuels are two main issues for sustainable development but their production usually requires highly energy-intensive separation steps. Therefore, the search for new cost-effective separation techniques is becoming critical for the bio-fuel industry. Compared to other separation processes (*i.e.* azeotropic distillation, liquid-liquid extraction or extractive distillation), the pervaporation (PV) membrane process, alone or in hybrid processes, could offer a very good alternative and greatly contribute to the future development of bio-fuels [4–6].

Among the major bio-fuels in the European Union (EU), ethyl *tert*-

butyl ether (ETBE) is an attractive bio-ether used as oxygenated fuel additive to improve fuel combustion and reduce toxic hydrocarbon emissions. This ether has also contributed to limit the cars environmental impact by replacing the carcinogenic lead derivatives formerly used in the EU. Nevertheless, during the ETBE industrial synthesis, the separation of the azeotropic mixture EtOH/ETBE (20/80 wt%) involves a highly energy-intensive ternary distillation process [7]. This separation process could be advantageously replaced by a PV or PV/distillation hybrid process with an efficient organoselective membrane for ethanol removal [4,5].

ETBE purification by PV has been relatively rarely investigated so far and the main related works have been reviewed in recent papers [7–9]. In the following brief literature review, the membrane fluxes are normalized for a reference thickness of 5 μm for comparison. Most of the related studies were based on polymeric membranes *i.e.* cellulosic membranes, segmented copolymers, and poly(vinyl pyrrolidone) (PVP)-based copolymers and blends. In particular, a cellulose acetate (CA) membrane had nearly infinite separation factor with a permeate ethanol content of 100% but its total normalized flux of 0.08 kg/h m^2 was very low at 40 $^{\circ}\text{C}$ [10]. Several approaches have been reported for improving CA flux while maintaining its selectivity at very high level.

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Permeability and selectivity generally vary in opposite ways and the obtained results were very encouraging [10]. Blending of cellulosic esters improved the total flux in the range of 0.6–3 kg/h m² with permeate ethanol contents of 90.7–96.7 wt% at 40 °C [11]. Cellulosic blends or semi-interpenetrated networks with poly(meth)acrylic (co) polymers also offered improved membrane properties for the targeted separation [1,10,12,13]. In a former work of our team, CA was modified with short or long PEO-containing polymethacrylate grafts by a "grafting from" strategy to assess the influence of copolymer architecture on the membrane properties for ETBE purification. The best membrane properties (normalized flux of 0.87 kg/h m², C'=94 wt % at 50 °C) were obtained for the copolymer with the highest amount of short grafts [8]. We have also recently reported CA grafting by different ionic liquids for this application [14]. In the last case, the membrane flux greatly increased with the hydrogen bonding acceptor ability of the grafted ionic liquid and the best membrane properties (normalized flux of 0.182 kg/h m² and permeate ethanol content of 100% at 50 °C) were obtained with an ammonium ionic liquid.

In other respect, polylactide (PLA) is a well-known bio-based polyester derived from renewable sources such as corn starch [15]. This biodegradable and biocompatible polymer has a wide range of medical applications in drug delivery, tissue engineering and orthopedic devices investigated by some of us [16–18]. Thanks to its unique features, PLA is also widely used in packaging applications where its gas permeation properties are strongly influenced by its crystallinity [19]. O₂ permeability through PLA/polypropylene (PP) blends and clay nanocomposites was strongly dependent on film composition and PLA incorporation to PP-based films enabled to control their barrier properties with interesting prospects for packaging applications [20]. Beyond the scope of this work, PLA has also been reported for gas permeation of small molecules of great interest like He, O₂, CO₂ and CH₄.

However, the separation of liquid mixtures by PLA-based membranes has been very rarely reported so far [9,15,21]. Ethanol permeation through PLA films has been investigated for bottle packaging applications [15]. In the latter work, the PV of aqueous solutions containing 0–50 wt% of ethanol showed that water permeability was much higher than that of ethanol. The preferential water permeation was mainly ascribed to the much higher diffusion coefficient of water ($\times 1000$) compared to ethanol. Even more closely related to this work, organoselective membranes made of PLA/PVP blends have also been reported for the PV separation of two azeotropic mixtures (ethanol/cyclohexane and ethanol/ETBE) [9,21]. The latter works clearly showed the interesting features of PLA for removing ethanol from liquid organic mixtures. For ETBE purification, the best membrane properties corresponded to a very high flux of ca. 2.7 kg/h m² and to an ethanol permeate content of 80 wt% at 30 °C for a PLA(97 wt %)/PVP(3 wt%) blend [9].

In this work, we are considering new bio-based membrane materials combining the unique features of CA and PLA in grafted copolymers. Apart from PLA grafting of cellulose by polycondensation of lactic acid affording very small grafts [22], PLA grafting of cellulose and cellulose derivatives was achieved by ring-opening polymerization (ROP) of lactide from the polysaccharide hydroxide side groups in homogeneous conditions in aprotic dipolar solvents (DMAc/LiCl or DMSO) or in ionic liquids (1-allyl-3-methylimidazolium chloride AmimCl and 1-butyl-3-methylimidazolium chloride) [22–30]. A related strategy was also described for obtaining CA-*g*-PLA copolymers by "one pot" cellulose acetylation followed by lactide ROP in AmimCl with 4-dimethylaminopyridine (DMAP) catalyst [28]. Cellulose nanocrystals (CNC) and nanowhiskers (CNW) were also grafted by PLA surface-initiated ROP or melt polycondensation of lactic acid for producing PLA-based nanocomposite films with improved mechanical properties [31–34]. Biodegradable cellulose-based fibers with improved surface properties were obtained by *in situ* graft polymerization of L-lactide onto cellulose by reactive extrusion [30]. Another reactive

processing method was successfully developed for preparing CA-*g*-PLA for drug delivery [29]. To the best of our knowledge, the most efficient methods reported so far for PLA grafting of cellulose, cellulose derivatives and nanocelluloses were all based on "grafting from" strategies using ring opening polymerization (ROP).

For the first time, this paper reports CA modification by a simple "grafting onto" strategy of low molecular weight PLA oligomers by "click" chemistry based on the copper(I) catalyzed 1,3-dipolar cycloaddition of azides and alkynes (CuAAC). The low molecular weight for the PLA grafts was chosen to ensure the best membrane properties according to the results obtained in our former work on CA grafted with PEO-based polymethacrylates [8]. The new grafting strategy enabled to precisely control the number and the length of the PLA grafts in the membrane materials. The chemical structure and morphology of the grafted cellulosic copolymers were investigated by ATR-FTIR, ¹H NMR, DSC and SAXS. The sorption and permeability properties of the new bio-based membranes were then assessed for the separation of azeotropic mixture EtOH/ETBE (20/80 wt%) by the PV sustainable process. The influence of the PLA content on the membrane properties was analyzed on the basis of structure-properties relationships revealing the key features of the new bio-based membranes for ETBE purification by PV.

2. Material and methods

2.1. Materials

CA (CA, acetyl 39.7 wt%, M_w=50,000 g/mol), 6-bromohexanoic acid (97%), stannous octoate (SnOct₂, 92.5–100.0%), copper bromide (CuBr, 99.99%), propargyl alcohol (99%), 4-dimethylaminopyridine (DMAP, $\geq 99\%$), sodium azide (NaN₃ $\geq 99.99\%$) and *N,N,N',N''*-pentamethyldiethylenetetramine (PMDETA, 99%) were purchased from Sigma-Aldrich. ¹H NMR analysis confirmed the acetyl content of CA, corresponding to 2.46 of acetyl groups and 0.54 of hydroxyl groups per glycosidic ring. The degrees of substitution (DS) of the side groups were commonly defined as the number of side groups per glycosidic ring. 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC.HCl, $> 98\%$) and dimethyl sulfoxide (DMSO, 99.7%) were purchased from TCI Company and Fisher Scientific, respectively. These reagents were used as received without further purification. D,L-Lactide was purchased from Lancaster, recrystallized in dry toluene twice and dried under vacuum before using. Toluene was refluxed, distilled over calcium hydride (CaH₂) and then added in the reaction media via cannula under nitrogen atmosphere. The solvents dichloromethane (DCM, $\geq 99.9\%$) and tetrahydrofuran (THF, 99.7%) were dried over activated molecular sieves before using. To avoid contamination by atmospheric moisture, all reagents and solvents were stored under nitrogen atmosphere.

2.2. CA functionalization and grafting

2.2.1. Modification of CA with azide side groups

In three necks round bottom reactor, 15 g of virgin CA (corresponding to 56.54 mmol of glycosidic rings and 30.53 of hydroxyl groups) were dissolved in 300 mL of dry THF under argon flow and vigorous stirring at room temperature. A solution of 4 g (25.48 mmol) of 6-azidohexanoic acid (see Supporting information) and 0.373 g (2.29 mmol) of DMAP in 150 mL of dry DCM were added to the CA solution. After cooling the mixture at 5 °C, 4.84 g (25.24 mmol) of EDC.HCl were added to the reaction medium and stirred for 48 h at room temperature. The crude polymer was precipitated from 2 L of ethanol (96%), washed twice in ethanol, filtered and dried under vacuum at 60 °C overnight. The polymer was obtained as white solid fibers with a yield of 88%. The degree of substitution of CA by azide groups DS_{azido}=0.39 was estimated by ¹H NMR in CDCl₃ using equation (1):

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