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Investigation of the effect of treatment with supercritical carbon dioxide on structure and properties of polypropylene microfiltration membranes

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ABSTRACT

The effects of treatment with supercritical carbon dioxide of two types of polypropylene microfiltration membranes, which may occur in novel membrane processing techniques such as membrane cleaning using supercritical carbon dioxide as solvent, were investigated. The membranes were treated with $scCO_2$ at three different pressures (8 MPa, 16 MPa, and 24 MPa) and at two various temperatures (40 °C and 70 °C) for different treatment times (5 min and 100 min). The morphology of the membranes was investigated using various analytical methods, using non-treated membranes as reference samples. No critical changes in membrane structure and properties, which would limit the usability of the membranes in microfiltration processes, were observed. Supercritical carbon dioxide can be safely applied in polypropylene membrane production, maintenance and modification.

1. Introduction

Porous polymer membranes are widely used in such fields as chemical industry, biotechnology and medicine. In numerous membrane production, maintenance and modification technologies, large amounts of organic solvents are used, which generates problems in terms of process safety, environmental hazard and the cost-effectiveness of the technologies. For example, during production of microfiltration membrane using the Temperature Induced Phase Separation (TIPS) method [1,2], the raw membrane contains oils resulting from the phase separation, which fill its porous body and which have to be removed before normal usage. In the traditional cleaning method, hot isopropyl alcohol is used for this purpose as solvent; however, this approach is characterized by high cost, potential environmental load and fire hazard due to high flammability of the organic solvent.

As in many other technologies, drawbacks related to the use of organic solvents can be reduced or even eliminated by replacing them with supercritical fluids (SCFs) [3]. Supercritical carbon dioxide ($scCO_2$) is the most commonly used SCF and exhibits numerous advantages such as moderate critical parameters, non-flammability, non-toxicity, good availability. The use of $scCO_2$ as reaction or separation medium instead of organic solvents enables to adapt established technologies to the principles of green chemistry and green engineering [4]. There are already examples of efficient membrane cleaning [5], production [6–8], and chemical modification [9]. technologies employing supercritical carbon dioxide. Supercritical carbon dioxide can be regarded as promising "green" medium for development of novel membrane processing technologies.

However, it is known that treatment with supercritical carbon dioxide ($scCO_2$) may cause significant changes in the internal structure of polymers [10]. This also applies to polypropylene [11–13], which is a common raw material for production of microfiltration membranes. Moreover, changes in structure and properties of reverse osmosis membranes after treatment with scCO2 were reported as well [14]. Such structural changes do not disqualify the use of $scCO_2$ provided that they do not affect significantly the basic mechanical properties of the membranes, which define their usability in membrane separation processes, such as mechanical strength, pore diameter distribution, etc. Preliminary tests did not identify any critical structural changes in polypropylene microfiltration membranes exposed to $scCO_2$ [15]. However, a broad range of process parameters, which may occur in novel technologies for membrane processing, should be investigated to confirm that $scCO_2$ is a safe medium for these applications.

The aim of this study was to investigate the impact of $scCO_2$ treatment in various process conditions–including typical conditions for membrane cleaning processes [5] – on structure and properties of porous polypropylene membranes used in microfiltration and to assess whether $scCO_2$ can be used as a safe

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medium for membrane cleaning, maintenance and modification technologies without destroying the membrane's key features.

2. Methods

As test material, commercially available polypropylene microfiltration membranes from two manufacturers (Membrane A–PolyMemTech Sp. z o.o., Poland, and Membrane B: Membrana GmbH, Germany) were used. The membranes have a hollow-fiber geometry with similar dimensions (Membrane A: outer diameter 2.8 mm, inner diameter 1.9, surface porosity ca. 47%; Membrane B: outer diameter 2.7 mm, inner diameter 1.8, surface porosity ca. 70%).

In the first part of experimental investigation, treatment of the membrane with supercritical carbon dioxide (99.995%, Linde Gaz sp. z o.o., Poland) in a high pressure experimental system – including a $scCO_2$ pump, a high pressure vessel and a process conditions control unit – was carried out. The following process conditions were varied: pressure (80, 160, and 240 bar), temperature (40, and 70 °C), treatment time (5, and 100 min), and depressurization rate (F–fast, i.e. instantaneous depressurization, and S–slow, with depressurization rate–2 bar/ min, only for experiments with 100 min treatment time). This range of process parameters includes typical conditions for the process of membrane cleaning using $scCO_2$. After the $scCO_2$ treatment, the structure and properties of the membranes were investigated. Membrane samples not treated with CO_2 were employed as reference samples. For assessment of changes of membrane structure and properties, four analytical methods were applied: scanning electron microscope (SEM), tensile test, contact angle measurement, and the bubble point experiment.

A scanning electron microscope Phenom G2 Pro (Phenom-World, The Netherlands) was used for assessment of the morphology of the membranes. Side surface and cross-sections (obtained by fracture after immersion in liquid nitrogen) of membranes were investigated at different magnifications in order to detect possible changes of the structure. In order to estimate the mechanical strength of the membrane samples, tensile tests were conducted using a universal testing machine Instron 5566 (Instron, USA). In each series, six samples (50 mm in length) were stretched until break (elongation rate: 15 mm/min), stress–strain curves were plotted and mean values of selected parameters (Young's modulus, ultimate tensile strength and maximum elongation at break) were determined. The wetting properties of the membranes were investigated by measurement of the contact angle (dynamic Wilhelmy method) using the Krüss Processor Tensiometer K12 (Krüss, Germany). Advancing and receding contact angle values were calculated as average values from ten measurements in each series. The bubble point method was employed in order to evaluate other parameters of the porous membranes, such as the number of pores, pore size distribution, filtration coefficient UFC and surface porosity. Membrane modules were prepared and immersed in an isopropyl alcohol bath. The volume flow rate of air was measured as function of increasing transmembrane pressure. From this relationship, the pore size distribution was reconstructed and the abovementioned parameters were calculated.

3. Results and discussion

In Table 1, a summary of experimental results is presented. For both membrane types, the reference values are shown together

Table. 1
Summary of experimental results.

Parameter	Membrane A			Membrane B		
	Reference	Max. value (conditions)	Min. value (conditions)	Reference	Max. value (conditions)	Min. value (conditions)
Tensile tests						
Young's modulus [MPa]	92,01	103.74 (+13%) (160/70/100/S)	85.39 (−7%) (80/70/5/F)	87.61	95.08 (+9%) (160/40/100/S)	81.78 (−7%) (80/40/5/F)
Ultimate tensile strength [MPa]	3.54	3.84 (+8%) (160/70/100/S)	3.20 (−10%) (240/40/5/F)	3.73	3.79 (+2%) (80/40/100/F)	3.67 (−2%) (240/70/5/F)
Max elong. at break [%]	168.25	177.97 (+6%) (240/70/5/F)	66.88 (−60%) (240/70/100/F)	172.82	183.34 (+6%) (240/70/5/F)	170.29 (−1%) (80/70/5/F)
Contact angle						
Advancing [°]	100.9	114.3 (+13%) (80/40/100/S)	96.1 (−5%) (80/40/100/F)	115.2	117.4 (+2%) (80/70/100/S)	101.1 (−12%) (160/70/5/F)
Receding [°]	51.4	61.7 (+ 20%) (80/40/5/F)	44.7 (−13%) (240/70/100/F)	48.7	49.8 (+2%) (160/70/5/F)	38.5 (−21%) (80/70/100/S)
Bubble point						
Mean pore size [μm]	0.284	0.352 (+24%) (160/70/100/F)	0.249 (−12%) (240/70/100/S)	0.447	0.456 (+2%) (160/40/100/F)	0.425 (−5%) (160/40/5/F)
Pore size SD [μm]	0.068	0.069 (+24%) (160/70/100/F)	0.039 (−43%) (240/70/100/S)	0.071	0.078 (+10%) (80/70/5/F)	0.040 (−44%) (160/40/100/F)
No of pores [10^9/ m^2]	19943.76	65907.12 (+230%) (240/70/100/S)	12705.69 (−36%) (160/70/100/F)	7065.42	22586.79 (+220%) (160/40/100/F)	7001.57 (−1%) (160/70/100/F)
UFC [ml/bar cm^2 min]	0.89	1.10 (+24%) (160/40/100/F)	0.66 (−26%) (240/70/100/F)	1.36	1.98 (+46%) (160/70/5/F)	1.17(−14%) (80/70/5/F)

(Process conditions: (pressure [MPa]/temperature [°C]/time [min]/decompression mode: Slow/Fast)