Influence of supercritical carbon dioxide on structure and mechanical properties of porous polypropylene membranes

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The influence of supercritical carbon dioxide ($scCO_2$) on structure and mechanical properties of porous polypropylene tubular membranes subjected to different process conditions was investigated. The membranes were treated with $scCO_2$ at pressure of 18 MPa and at three different temperatures (40°C, 70°C, and 100°C) for 2 h in a batch reactor. The obtained samples were analyzed using a scanning electron microscope (SEM) to determine the impact on the membrane structure, tensile testing for ultimate strength assessment, and bubble point test for determination of the pore size distribution and the filtration coefficient (UFC). A membrane not treated with $scCO_2$ was used as reference sample for comparison. SEM pictures of side surfaces and cross-sections of treated tubular membranes did not reveal any changes in membrane structure. Tensile testing of treated and non-treated samples showed that after $scCO_2$ treatment the ultimate strength slightly decreased (less than 10%), while the Young's modulus was reduced by almost 50%. The bubble point test showed that $scCO_2$ causes an increase in the number of pores and an increase in the UFC value. In the range 40–100°C no significant temperature dependence was observed. The results confirm that supercritical carbon dioxide can be used as a medium in porous polypropylene membrane production, maintenance and modification.

Keywords: supercritical fluid, membrane, TIPS, supercritical carbon dioxide.

Introduction

Nowadays, membranes are widely used in separation processes, in such fields as chemical industry, biotechnology, food industry, wastewater treatment, medicine, etc. Membrane processes related to porous structures comprise microfiltration, ultrafiltration, diafiltration, reverse osmosis depending on average pore size. Many different membrane production technologies are currently known (some still at development stage), and some of them require huge amounts of organic solvents. Due to high costs of processing to recycle solvents, huge amounts of organic chemicals are used up and subsequently dumped as a toxic waste. One example of such processes is membrane formation by Temperature Induced Phase Separation (TIPS), where after membrane solidification pores are filled with an organic liquid (usually oil), which needs to be efficiently removed. It is usually accomplished by extraction with an organic solvent [1]. Organic solvents are also used during membrane maintenance in order to remove contaminations accumulated during normal usage, so called membrane fouling. The usage of organic solvents is a significant problem in terms of process economy, operation hazards, environmental impact and cost--effectiveness. Supercritical fluids (especially supercritical carbon dioxide, $scCO_2$) are a promising medium, which can replace organic solvents in membrane production, maintenance and modification technologies. Properties like low kinematic viscosity (which enhances mass transfer), pressure-dependent solubility of various substances, and possible simple separation via depressurization are reasons, why supercritical fluids are gradually replacing organic solvents in various technologies. Especially, supercritical carbon dioxide — due to its non-flammability, non-toxicity and wide availability — meets the standards of green chemistry and has already been successfully applied in various fields [2]. The use of supercritical fluids for membrane production, maintenance and modification is not a common industrial practice, however, many investigations have been done in this field in the last few years [3–5]. On the other hand, unique properties of supercritical fluids may also cause unfavorable changes in material structure and properties. For instance, rubber tends to swell when exposed to supercritical carbon dioxide [6]. Penetration of supercritical carbon dioxide into polypropylene with an accompanying swelling was also observed [7]. Hence, the replacement of organic solvents by supercritical carbon dioxide must be preceded by a verification of possible $scCO_2$-related degeneration of membrane properties due to modification of membrane material. Such assessment should be done for each material and membrane type, but very few papers have dealt with this issue. Polypropylene is one of the most widely used polymers in membrane technologies, however, the influence of $scCO_2$ treatment on structure and properties of porous polypropylene membranes has not been published so far. Hence, the aim of this work was to investigate how $scCO_2$ treatment influences the structure and properties of porous polypropylene tubular membranes, which are commonly applied in microfiltration. This work should give the answer, whether $scCO_2$ can be applied for porous polypropylene membrane processing. For the assessment of possible changes of membrane structure and related mechanical properties, three different methods, well-established in membrane science, were applied. These are: scanning electron microscope (SEM), tensile test, bubble point experiment.

Materials and methods

In experiments, porous polypropylene tubular membranes (outer diameter 2.2 mm, inner diameter 1.8 mm, length ca. 1300 mm, volumetric porosity ca. 70%, manufactured by Membrana GmbH, Germany) were used. This type of membranes is usually produced using the "traditional" TIPS method, in which an organic solvent is applied in order to remove to liquid present in the membrane pores after phase separation. Hence, $scCO_2$ can potentially replace the organic solvent used in the production, maintenance or modification of such membranes, provided the processing with $scCO_2$ turns out to be non-destructive. The experimental system is depicted in Fig. 1. A 1200 ml high pressure titanium reactor (PARR Inc., USA) equipped with a stirrer and temperature regulation was used for $scCO_2$ treatment of the tubular membranes. Supercritical carbon dioxide was fed to the reactor from a CO_2 cylinder with dip tube by a SFT-10 CO_2 pump manufactured by Supercritical Fluids Technologies, Inc, USA. An additional helium cylinder was used to provide a helium head pressure in the carbon dioxide cylinder. Carbon dioxide of purity grade 5.2 and helium of purity grade 4.5 were supplied by Linde Gaz Sp. z o.o., Poland.

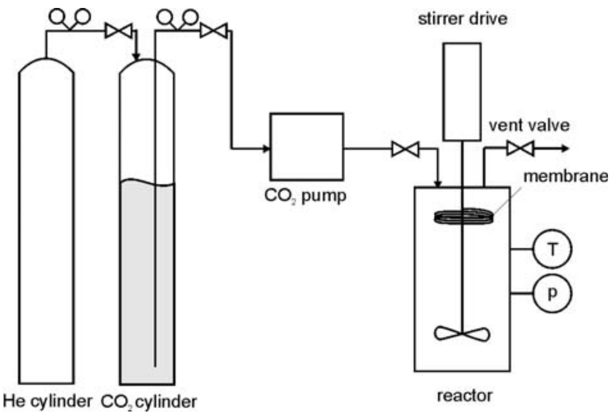

Fig. 1. Sketch of experimental system.

A series of three variants of $scCO_2$ treatment for one pressure (18 MPa) and three temperatures (40°C, 70°C, and 100°C) was carried out. The procedure was as follows: a tubular membrane was placed in the high pressure reactor. Afterwards, the reactor was purged with CO_2 for five minutes in order to remove air from the vessel. Then, the reactor was closed and the system was set to the desired conditions using the temperature adjustment system and the CO_2 pump. Once the target conditions were achieved, the treatment lasted for 2 h with agitation speed equal to 300 rpm. After the process, the vessel was depressurized and the membrane was taken out from the reactor for investigations. Membranes not treated with $scCO_2$ were considered as reference samples.

The structure of membranes was investigated using a Phenom scanning electron microscope (SEM). Side surface and cross-section fracture of the membranes were analyzed at different magnifications in order to check the preservation of membrane structure. The membranes were also subjected to tensile tests using a universal testing machine Instron 5566, which enabled to evaluate the mechanical parameters of the membranes. Treated and reference membranes were cut to 50 mm long samples, spanned in the machine and underwent the tensile tests. Elongation rate was set to 15 mm/min and five samples for each variant were tested. For each sample, a stress-strain curve was plotted, and following parameters were calculated as average values from five samples: Young's modulus, ultimate tensile strength and maximum elongation at break. Finally, bubble point measurements were carried out in order to determine the number of pores, pore size distributions, surface porosities and filtration coefficient values (UFC). For this purpose, special test modules were constructed. Each module comprised three tubular membrane parts (135 mm in length), sealed on one end. The module was placed in a bubble point test rig, completely immersed

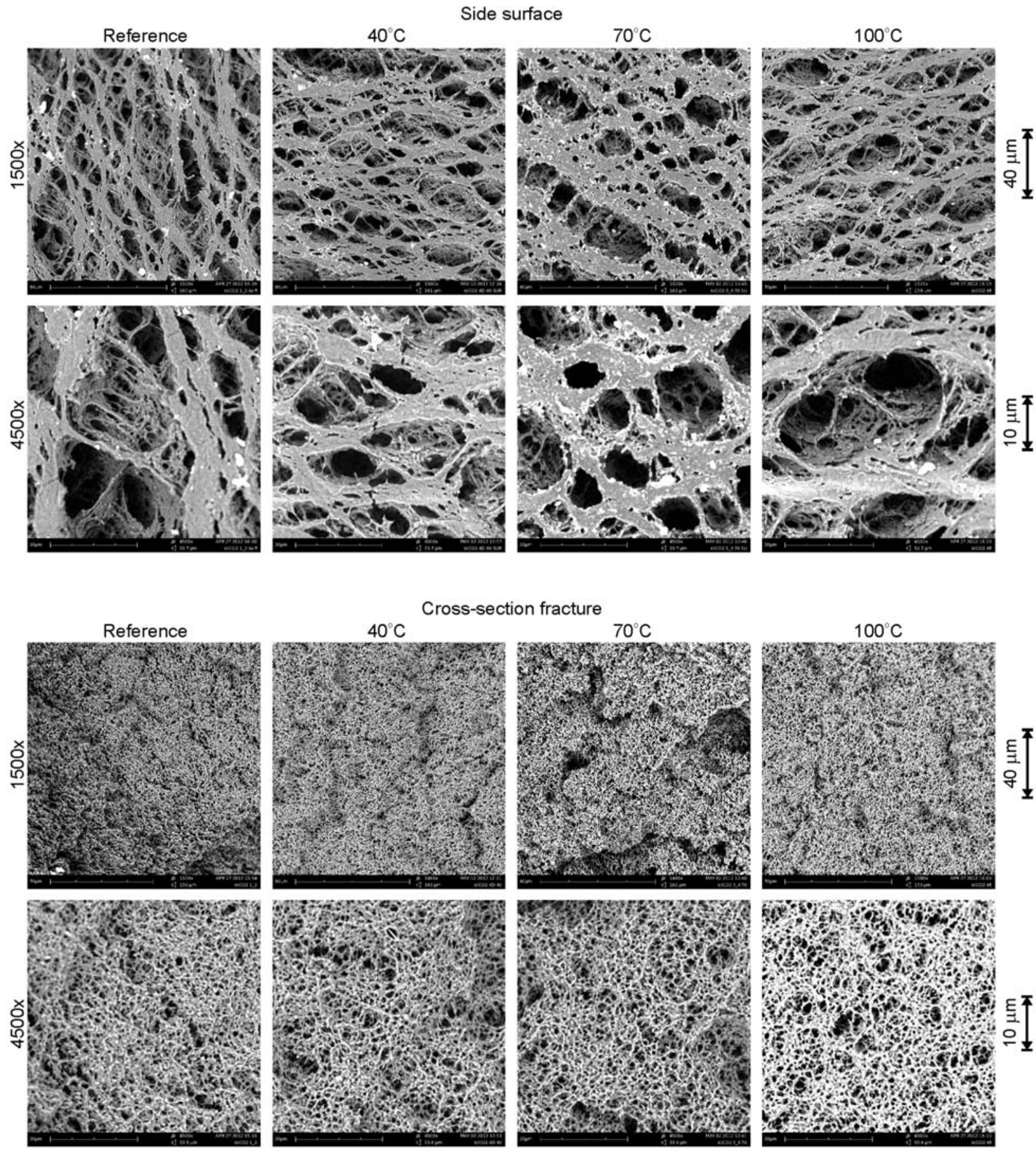

Fig. 2. SEM microphotographs of porous polypropylene tubular membranes.

in a vessel containing isopropanol. At first, a constant transmembrane pressure was applied and isopropanol volume flow rate was determined, which enabled to calculate the UFC. Afterwards, the transmembrane pressure was increased by means of compressed air supply and the air volume flow rate was measured. Finally, the pore size distribution was reconstructed from the obtained pressure/volume flow rate dependence. A description of the bubble point method and apparatus is presented in detail in [8].

Results and discussion

SEM enables to investigate morphological properties of membranes and is widely used, e.g. in [4]. In Fig. 2, SEM microphotographs of side surfaces and cross--sections of treated tubular membranes and reference tubular membranes are presented in two different magnifications. After $scCO_2$ treatment, the membrane should keep its initial structure, otherwise it can become unsuitable for a given application. In the case of

Table 1. Tensile test results

	Reference sample	Sample treated at 40°C	70°C	100°C
Young's modulus [MPa]	214.3 (±1.3)	136.1 (±5.1)	131.4 (±3.8)	112.2 (±2.7)
Ultimate tensile strength [MPa]	9.41 (±0.06)	8.76 (±0.06)	8.72 (±0.05)	8.70 (±0.13)
Maximum elongation at break [%]	161.9 (±1.3)	170.0 (±4.5)	158.6 (±5.7)	173.5 (±5.0)

membranes treated with $scCO_2$, no significant changes in membrane structure were observed when compared to the reference sample, neither for side surfaces nor for cross-sections. No swelling effects were noticed. Hence, the SEM microphotographs did not reveal any visible structure changes or destruction.

A membrane should also preserve its mechanical properties, especially mechanical strength, as it is exposed to tensile stresses due to transmembrane pressures present during separation processes. Typically, microfiltration membranes operate at relatively low transmembrane pressures, which usually do not exceed 1 bar. Tensile tests were conducted in order to estimate mechanical strength changes induced by $scCO_2$ treatment. In Table 1, selected parameters obtained from tensile test experiments are summarized, namely the Young's modulus, the ultimate tensile strength and the maximum elongation at break. Standard errors are shown in brackets. In Fig. 3, two exemplary stress-strain curves (one for a reference sample and one for a sample treated at 100°C) are plotted. One can observe that the stress--strain curves for the reference sample and the sample treated with $scCO_2$ are different. In Fig. 4, Young's modulus values of the samples listed in Table 1 are presented. Young's modulus, a parameter describing the stiffness of an elastic material, was significantly influenced by $scCO_2$, as its value is significantly lower after treatment. The influence of the treatment on this parameter was even more distinct for higher temperatures. However, this effect is rather negligible bearing in mind the values of relatively low transmembrane pressures acting upon membranes in microfiltration. The observed drop of the Young's modulus value does not restrict the normal use of the membranes. Another parameter, which is crucial for the application of membranes, is the ultimate tensile strength, as it affects the rupture pressure — the maximum value of transmembrane pressure, at which the membrane will be destroyed. The values of ultimate tensile strength for all samples listed in Table 1 are plotted in Fig. 5. The ultimate tensile strength was also influenced by the treatment, but in this case the change is much smaller (less than 10%), and no temperature dependence was noticed. Moreover, during bubble point tests all membranes were exposed to high transmembrane pressures (about six times higher than normally used transmembrane pressures) and none of them burst during the experiment. One can conclude that the tubular membrane operates

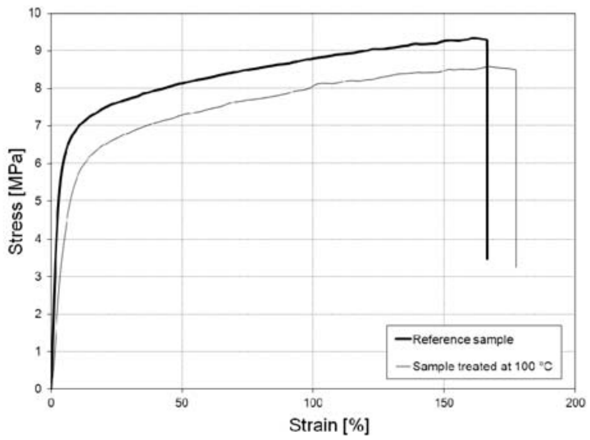

Fig. 3. Stress-strain curve.

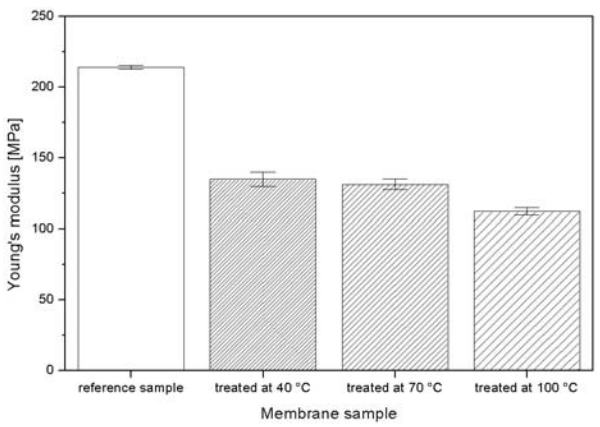

Fig. 4. Young's modulus.

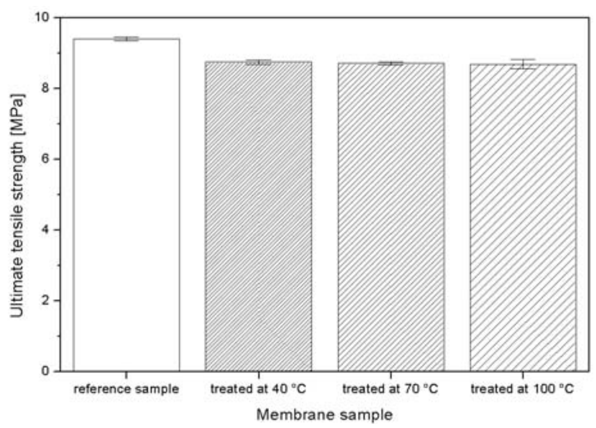

Fig. 5. Ultimate tensile strength.

Table 2. Bubble point test results

	Reference sample	Sample treated at		
		40°C	70°C	100°C
Number of pores [#·10^9/m^2]	2478 (±5%)	3740 (±5%)	4098 (±5%)	3339 (±5%)
Mean pore size [mm]	0.481 (±0.079)	0.466 (±0.079)	0.445 (±0.079)	0.476 (±0.079)
Surface porosity [%]	39 (±5)	55 (±5)	54 (±5)	51 (±5)
Filtration coefficient UFC [ml/(bar·cm^2·min]	2.76 (±0.4)	3.18 (±0.4)	3.11 (±0.4)	3.41 (±0.4)

with a considerable safety margin. Hence, the change of the ultimate strength value has no impact on normal application of the membranes. In general, tensile tests revealed an unfavorable effect of $scCO_2$ on mechanical properties of the membranes. It can be explained by penetration of $scCO_2$ into the polymer matrix of the membrane. CO_2 molecules can alter the interactions between polymer chains and affect the crystallinity of the membranes [4]. Moreover, it was observed, that CO_2 plasticizes the polymer matrix of polypropylene, which in turn leads to a decrease of crystallization temperature [9, 10]. Furthermore, swelling might have occurred, even if it is not visible in the SEM microphotographs. All mentioned phenomena could cause the observed changes of mechanical properties of the membranes.

In Table 2, results from bubble point experiments are summarized. Experimental errors of the obtained values are shown in brackets. In Fig. 6, pore size distributions obtained from bubble point experiments are shown. A proper pore size distribution is an important feature of a porous membrane, as it controls, which particles are able to pass through the membrane and which are retained. As can be seen in Fig. 6 and in Table 2, $scCO_2$ treatment caused an increase in the overall number of pores and the number of the smallest pores, while the mean pore size slightly decreased. Surface porosity also increased. This can be explained by the fact, that $scCO_2$ treatment induced opening of the smallest pores, which remained closed after organic solvent treatment during the manufacturing process. Another effect of the $scCO_2$ treatment was that values of the filtration coefficient (UFC) were also higher for treated membranes when compared with non-treated ones. These changes of membrane properties can be potentially beneficial, as a higher UFC value means higher flow rate for a given transmembrane pressure, while no negative change in pore size distribution was observed. Hence, supercritical carbon dioxide can be applied for modification of porous polypropylene membranes in order to improve their filtration properties. On the other hand, the increase of the number of pores can also explain the decrease of the Young's modulus value after $scCO_2$ treatment. A higher porosity leads to a lower stiffness and mechanical stability of the porous structure.

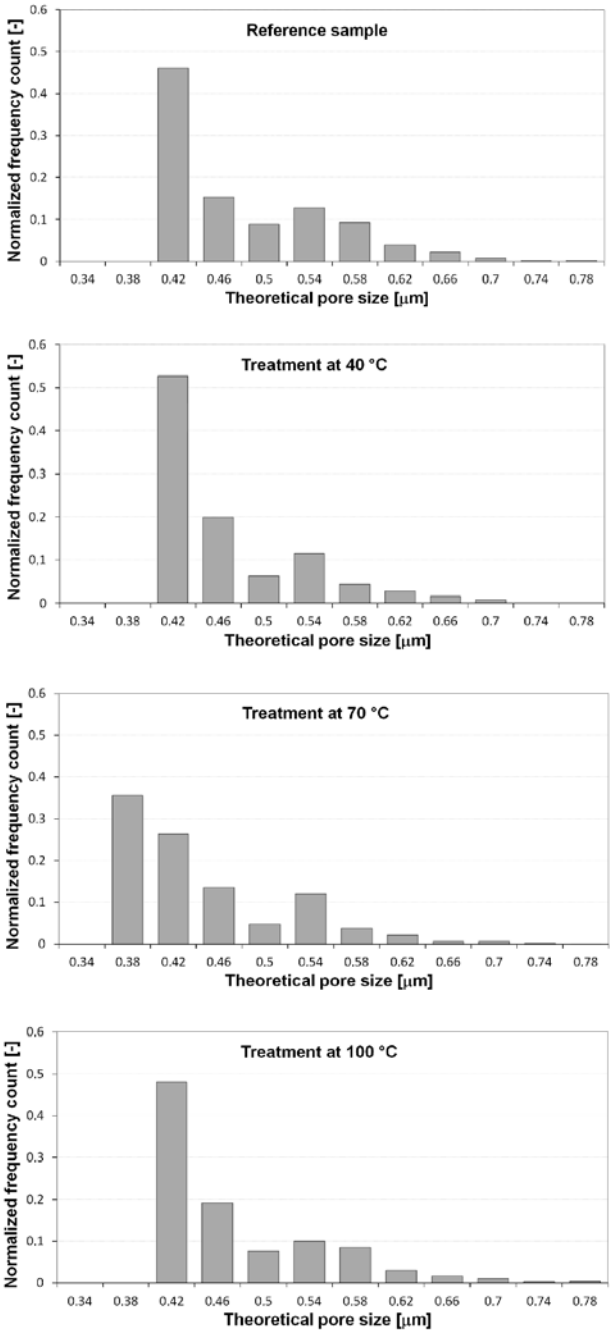

Fig. 6. Pore size distribution — bubble point results.

The influence of $scCO_2$ treatment on structure and mechanical properties of porous polypropylene membranes has not been published so far, therefore it is impossible to compare the obtained results with similar studies. However, in another paper, porous polypropylene membranes were treated with various inorganic solvents (aqueous solutions of NaOH, HCl and NaOCl) and were investigated using the tensile test and the bubble point method [11]. Like in the present work, the membranes showed a slightly decrease of the ultimate tensile strength value after treatment. However, membranes treated with inorganic solvents became fragile and could not be used in membrane separation processes.

The results presented in this study show that supercritical carbon dioxide does not increase the fragility of the membranes. Moreover, the process of modification of porous polypropylene membranes by $scCO_2$ treatment does not produce harmful waste materials and $scCO_2$ is easy to recycle after treatment.

Conclusions

The influence of supercritical carbon dioxide on mechanical properties of porous polypropylene tubular membranes treated at different conditions was experimentally investigated. For membrane structure analysis, a scanning electron microscope (SEM) was used. Tensile tests were performed for the determination of stress--strain curves and mechanical strength, and bubble point tests were carried for assessment of the pore size distribution, the number of pores, surface porosity and the filtration coefficient (UFC). SEM pictures of side surfaces and cross-sections of treated membranes did not reveal any visible changes in membrane structure. Tensile tests of treated and non-treated samples showed, that after $scCO_2$ treatment the ultimate tensile strength value of the membranes slightly decreased (7–8%), while the Young's modulus was reduced by 36–48%. Both effects can be regarded as a negative change in terms of membrane strength characteristics, although neither of them affects significantly any potential application. The bubble point method showed, that $scCO_2$ causes an increase in the number of pores (35–65%) and an increase of the UFC value (13–24%), which in turn has a positive effect on the course of microfiltration using treated membranes. The obtained results show that supercritical carbon dioxide can be potentially applied as a medium in polymer membrane production, maintenance and modification technologies, replacing organic solvents. However, one has to bear in mind of both beneficial and unfavorable changes in the structure and mechanical properties of the membranes.

Acknowledgements

This work was supported by NCBiR Grant (NR05 0051 06/2009). The authors gratefully acknowledge the help of Wojciech Fabianowski and Maciej Dębowski during tensile tests.

References

[1] Berghmans, S., H. Berghmans, and H.E.H. Meijer. "Spinning of hollow porous fibres via the TIPS mechanism". *Journal of Membrane Science* 116 (1996): 171–189.

[2] Brunner, G. *Supercritical Fluids as Solvents and Reaction Media.* Elsevier, 2004.

[3] Xinli, Z. et al. "Preparation and pore structure of porous membrane by supercritical fluid". *The Journal of Supercritical Fluids* 49 (2009): 111–116.

[4] Akin, O., and F. Temelli. "Effect of supercritical CO_2 flux, temperature and processing time on physicochemical and morphological properties of commercial reverse osmosis membranes". *The Journal of Supercritical Fluids* 60 (2011): 81–88.

[5] Li, Z. et al. "Preparation and characterization of microporous poly(vinyl butyral) membranes by supercritical CO_2-induced phase separation". *Journal of Membrane Science* 312 (2008): 115–124.

[6] Kojima, M. et al. „Phase behavior of crosslinked polyisoprene rubber and supercritical carbon dioxide". *The Journal of Supercritical Fluids* 35 (2005): 175–181.

[7] Lei, Z. et al. „Solubility, swelling degree and crystallinity of carbon dioxide–polypropylene system". *The Journal of Supercritical Fluids* 40 (2007): 452–461.

[8] Szwast, M., J. Salwocki, and W. Piątkiewicz. „Badania kapilarnych membran polipropylenowych stosowanych w procesach ochrony środowiska". *Inżynieria i Aparatura Chemiczna* 5 (2006): 130–132 [in Polish].

[9] Kishimoto, Y., and R. Ishii. "Differential scanning calorimetry of isotactic polypropene at high CO_2 pressures." *Polymer* 41 (2000): 3483–3485.

[10] Varma-Nair, M. et al. "Effect of compressed CO_2 on crystallization and melting behavior of isotactic polypropylene". *Thermochimica Acta* 396 (2003): 57–65.

[11] Szwast, M. et al. "Modyfikacja własności filtracyjnych i mechanicznych kapilarnych membran polimerowych". II Konferencja Naukowo-Techniczna Doktorantów i Młodych Naukowców *Młodzi naukowcy wobec wyzwań współczesnej techniki*. Warsaw, 2007: 57–63 [in Polish].