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Influence of inorganic fillers on the degradation of polypropylene membranes during membrane distillation

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ABSTRACT

During water desalination by membrane distillation (MD) both process of wetting of hydrophobic polymeric membranes and their gradual degradation have been observed. The mechanical properties of polymer can be improved by the addition of fillers. The effect of introduction of inorganic fillers (mainly talc) on the properties of polypropylene membranes obtained by a thermally induced phase separation process has been investigated. Three types of capillary membranes manufactured in the industrial installation were used. A polypropylene homopolymer (Moplen HP 420 M) was applied for membranes production. Performance of the obtained polypropylene membranes was determined in the long-term studies of MD, using NaCl solutions (1–200 g/L) as a feed. The membrane resistance to thermal degradation was additionally evaluated using boiling brine enriched in HCO_3^- ions. The concentrated salt solutions slightly accelerated the membrane wetting and the electrical conductivity of distillate increased to a level of 200–500 µS/cm after 850 h of MD process. However, the retention coefficient over 99% was achieved in each case. It was confirmed that the addition of inorganic fillers significantly improved the mechanical properties of membranes and decreased the thermal degradation of polypropylene.

Keywords: Membrane distillation; TIPS process; Inorganic fillers; Polypropylene degradation; Talc

1. Introduction

In membrane distillation (MD), the porous hydrophobic membranes are used. In this process, water evaporates through the pores of non-wetted membrane, and as a result the salts and other non-volatile compounds present in the feed are retained; therefore the quality of produced distillate is close to distilled water [1,2].

Unfortunately, during a long-term exploitation of MD module, a part of the membrane pores become filled with water, which leads to the significant reduction of the permeate flux and retention coefficient [3,4]. Therefore, the membrane wetting is indicated as the main reason of limiting the industrial implementation of the MD process [3,5–7].

Experimental results from several MD studies demonstrated that the pores wettability can be prevented by the application of composite membranes or the membranes having a modified surface with enhanced resistance to wetting [2,3,6–8]. Moreover, novel polymeric and ceramic materials for MD membranes preparation are also used [9–11]. The performance and durability of new types of membranes is most often determined during the MD process carried out less than 50 h, which strongly restricted their implementation in the industrial installations. Therefore, the commercial membranes made from polytetrafluoroethylene (PTFE), polyethylene (PE), polyvinylidene fluoride and polypropylene (PP) are usually used in MD pilot plants [4,5,7,12–15]. The MD modules used in these installations

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are built, for example, with the utilization of flat-sheet PTFE membranes manufactured by Gore-Tex [7,16–18] or capillary Accurel PP membranes made from PP [13].

Several novel membranes proposed for MD process were prepared from expensive hydrophobic compounds using multistage fabrication processes [2,8–10]. However, in the works analyzing the costs of MD installation construction, the low prices of membranes are usually assumed [19,20]. This confirmed an opinion that the realization of industrial implementation requires the membranes to be manufactured by a simple method from inexpensive materials [1,2]. Such conditions are fulfilled by the capillary membranes made from polypropylene by the thermally induced phase separation (TIPS) process [1,12,21–23]. In such process, a homogeneous solution is initially prepared by dissolution of the polymer in a diluent at high temperature (453–483 K), followed by the phase separation induced by lowering temperature, which is realized in the coagulation bath. The final step is leaching of the diluents from the porous structure and membrane drying, usually in nitrogen atmosphere. The TIPS process parameters as well as diluent type and its concentration in the initial polymer/diluent system have a considerable influence on the course of the phase separation behaviour and the final microstructure of PP membranes [21,24–26].

Several investigators achieved promising results using the membranes formed via TIPS method for various applications of the MD process [22,26–28]. A disadvantage of the membranes made from PP is a rapid formation of the hydrophilic groups on their surface during MD [3,12]. It was found that the surface of PP membrane became wetted after 40–50 h of MD process operation [29]. However, the pores over the entire cross-section of wall were not wetted for more than 3 years of MD module exploitation in spite of a rapid wetting of the PP membrane surface [28,30].

The elimination of membrane wettability is of primary importance for MD process realization; moreover, the degradation of membrane matrix during a long-term module exploitation is also a very important issue. The formation of cracks, other mechanical damages in the membrane structure and the wettability exclude the application of such membranes in the MD process. Although the membrane degradation was observed during the MD pilot studies [15,18], this subject has been investigated in a slight degree.

An important point which should be noted is that the mechanical properties of polymeric materials can be significantly improved by the addition of inorganic fillers [31,32]. Similar to polymeric materials, doping of carbon nanotube, silicon dioxide, titanium dioxide, cuprum and zinc oxide into the MD polymeric membranes also improves their mechanical properties [32–35]. However, the presented works describing such blended MD membranes are usually limited to demonstrate how the application of fillers changes the pore structure and increases the values of Young's modulus and tensile strength. Undertaking a long-term research of MD process with the application of such fabricated membranes is definitely an important issue.

A concern is raised due to the susceptibility of PP membranes for mechanical damage and their poor mechanical properties have been reported in previous studies [3,26]. It has been observed that the PP membranes became rigid and fragile after several months of MD module operation [30]. A significantly larger destruction of PP membrane matrix caused by NaCl scaling was found during the studies of MD crystallizer [36]. The mechanical strength of PP depends on the arrangement of the polymer chains and the degree of crystallinity [34]. Therefore, the properties of membranes formed via TIPS method depend, to a significant degree, on the crystallization rate of molten polymer [24,31]. The applied fillers act as the nucleolus agents of heterogeneous crystallization [21,37]. These agents provide a large number of nuclei, which can significantly modify the crystallization behaviour of PP, for example, accelerate the formation of crystallites, thus improve the thermal and mechanical properties of polymer matrix [24,38].

Indeed, a significant improvement of the functional properties of polypropylene can be achieved by the addition of talc [31]. Talc exhibits a strong nucleating effect for PP due to the specific physicochemical interactions with the polymer matrix that promote epitaxial crystallization [31,39]. It is well documented that the application of talc increases the thermal resistance and the tensile strength of PP membranes [12,24,31,37,38]. This creates an opportunity to prepare the PP membranes to be more resistant to the polymer degradation during MD process.

The objective of the present studies was to determine the effect of addition of inorganic fillers, for example, talc, on the improvement of PP membrane properties, particularly during a long-term MD module exploitation. The discrepancies in the evaluation of usability of PP membranes for MD process probably result from the fact that the properties of PP membranes are strongly affected by the conditions of the their manufacture [21–26,31,37–41] and the type of PP applied for membrane formation [41]. The PP occurs in the different forms of tacticity; hence, the membranes formed from syndiotactic PP (sPP) exhibit definitely different properties than the membranes fabricated from isotactic PP (iPP) [42–44]. Moreover, the PP exhibits polymorphism and during the membrane formation by TIPS, the PP usually forms monoclinic α or trigonal β crystal phase depending on the crystallization conditions [45]. With regard to this, it is important to provide information concerning the type of PP, which was used for membrane fabrication. In the present work, the MD studies were performed with the application of polypropylene membranes manufactured from iPP under similar conditions, in the configuration of capillary membranes having the same diameter and wall thickness. Such membranes were purchased from membrane manufacturer and the present studies were carried out using three types of capillary membranes fabricated in the same industrial installation.

2. Experimental setup

2.1. Membranes

The hydrophobic polypropylene capillary membranes fabricated in the commercial installation (Polymemtech, Poland) were used in these studies. The membranes have an internal diameter of 1.8 mm and an outer diameter of 2.6 mm. A polypropylene homopolymer (Moplen HP 420M) was used for PP membranes production. Three types of the membranes were applied for research. The first one was made only from Moplen HP 420M and the others contained additionally 10 wt.% of inorganic fillers.

Talc ($Mg_3(OH)_2Si_4O_{10}$) and Sirmax's mineral filled polypropylene, purchased under the brand name ISOFIL, were applied by the membranes manufacturer as a source of the inorganic fillers. According to the manufacturer's information (Sirmax S.p.A., Italy), the ISOFIL comprises 60% homopolymer and copolymer PP compounds, additionally containing 40% of minerals (talc, calcium carbonate, mica, barium sulphate, etc.), flame retardant and heat and/or UV stabilizers. According to producer information, the mineral filled ISOFIL polypropylene provides a higher mechanical stiffness and thermal stability.

The tested capillary PP membranes were prepared via TIPS method. With reference to the composition of doping solutions, the capillary PP membranes used in the present studies were marked as MD0, MD10 and MD25:

- MD0: 100 wt.% Moplen HP 420 M;
- MD10: 90 wt.% Moplen HP 420 M + 10 wt.% talc;
- MD25: 75 wt.% Moplen HP 420 M + 25 wt.% ISOFIL (accordingly 10 wt.% fillers + 15 wt.% PP).

The manufacturer (Polymemtech) of these products declared that each type of the membranes was formed under similar conditions. A formed PP capillary was cut into sections with length of 1.2 m. The capillary membranes were subsequently collected (in a random way) from obtained bundle for performed tests.

2.2. Membranes characterization

The study of membrane morphology and the composition of introduced fillers were performed using a Hitachi High Technologies Co., (Tokyo, Japan) SU8000 field emission scanning electron microscope with energy-dispersive X-ray spectrometer (EDS). The samples for cross-sectional examinations were prepared by fracture of the capillary membranes in liquid nitrogen. All the samples were sputter coated with chromium.

The thermal properties of used polypropylene membranes were determined by differential scanning calorimetry (DSC). These studies were performed using a device DSC Q100 (TA Instruments, USA), at heating and cooling rate of 10 K/min within the temperature range 183–523 K. The samples were examined in heating–cooling–heating cycles after previous drying.

The mechanical strength and elongation at break of PP capillary membranes were measured with a tensile tester (3366 Universal Material Testing Machine, Instron, USA) according to PN-EN ISO 527-1:1998 method. A sample of PP capillary membrane with an initial length of 7 cm was clamped at both ends obtaining the measurement length 3 cm, and pulled in tension at a constant elongation rate of 10 mm/min. In each case, the measurements were performed for five samples of membrane.

A crystal structure of the membranes was determined on an Empyrean PANalytical diffractometer using a monochromatized CuKα radiation (35 kV, 30 mA). The structural models were taken from ICPDS database.

In order to identify the functional groups on the polypropylene surfaces, the attenuated total reflection Fourier transform infrared (ATR-FTIR) analyses were performed using a Nicolet 380 FTIR spectrophotometer coupled with Smart Orbit diamond ATR accessory (Thermo Electron Corp., USA). At least four ATR-FTIR spectra were recorded for each PP membrane sample. These spectra were averaged 36 scans collected from 400 to 4,000 cm^{-1} wave numbers (scan resolutions 0.482 cm^{-1}).

The hydrophobicity of PP membranes was determined by dynamic contact angle measurements based on the Wilhelmy plate method. The measurements were carried out at ambient temperature using a Sigma 701 microbalance (KSV Instrument Ltd., Finland) integrated with a PC for automatic control and data acquisition. A liquid used in the contact angle measurement was ultra-pure water (Elix3 apparatus, Millipore, USA).

The membrane porosity was determined based on gravimetric measurements of the differences between dry and wetted samples [13,32,46,47]. Isopropanol was used as a solvent ensuring the complete wetting of all pores. In order to facilitate the wetting, membrane samples (length 0.33 m) were cut in half alongside the capillary. The samples were soaked for 2 h, subsequently; the excess isopropanol adhered on the surface of the membranes was wiped off with filter paper. The average value of three measurements was applied for open porosity calculations using the following equation [46,47]:

$$\%\text{Porosity} = \frac{2\left(m_W - m_D\right)}{\rho\pi\left(d_{\text{out}} + d_{\text{in}}\right)sL}100 \tag{1}$$

where: m_W and m_D are the mass of wet and dry membrane, d_{out} and d_{in} are outside and inside capillary diameter, L and s are the membrane sample length and wall thickness, respectively, and ρ is the isopropanol density (0.798 g/cm^3).

The electrical conductivity of solutions was measured with a 6P Ultrameter (Myron L Company, Carlsbad, CA, USA). The meter was calibrated for measurements as NaCl mode using TDS/conductivity standard solution (Myron L Company).

2.3. MD experiments

The studies of the direct contact MD (DCMD) process were performed using the experimental set-up shown in Fig. 1. A submerged MD module was assembled inside the feed tank (4 L). The distillate flowed inside the capillaries, and the volume of distillate loop (with tank) was 0.234 L. The peristaltic pump was used, and the distillate flow (recalculated for one capillary) was equal to 1.3 ± 0.1 mL/s (linear velocity of 0.51 m/s, Reynolds number Re = 1,140). The hydraulic pressure at the module inlet was equal to 5.4 kPa.

The submerged MD modules (SMD) were equipped with three hydrophobic capillary polypropylene membranes (MD0, MD10 or MD25). The working length of capillaries in the modules SMD0, SMD10 and SMD25 was equal to 85 ± 0.5 cm, and the active membrane area (inner capillary) was 144.2, 143.4 and 145.0 cm^2, respectively.

The MD installation was operated in a continuous mode (day and night). The temperature of the feed during

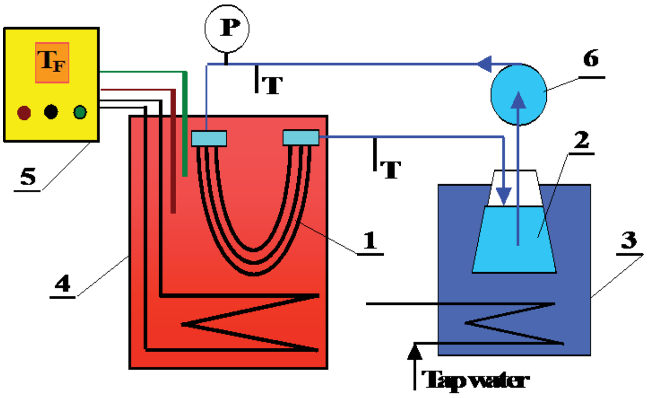

Fig. 1. MD process experimental set-up. (1) submerged MD module, (2) distillate tank, (3) cooling bath, (4) feed tank, (5) feed temperature regulator with liquid level detector, (6) peristaltic pump. T – thermometer, P – manometer.

long-term studies was 353 K. The NaCl solutions (1–200 g/L) were used as a feed. The distillate was cooled by tap water and its temperature was maintained at 290–298 K. The permeate flux was calculated on a basis of changes in the distillate volume over studied period of time.

2.4. Thermal degradation tests

The resistance of applied membranes on a high feed temperature (about 373 K) was also examined. The membrane samples 80 cm in length were immersed into brine (2 L), initially containing 35 g/L NaCl, 16 g/L $NaHCO_3$ and 8 g/L $CaCl_2$. The ends of membranes protruded above a liquid level, which protected against inflow of the brine into the capillaries. The lumen side of capillaries was filled with distilled water (2 µS/cm). Brine was heated to the boiling point and maintained at this state for 4–5 h. Subsequently, the brine heating was shutdown, and the solution was left to cool at room temperature. The above operations were repeated on the next day. In total, 20 cycles were performed obtaining about 85 h of membranes contact with boiling brine. Before the FTIR and DSC studies, a scaling layer formed on the membrane surfaces was removed by rinsing the membrane with a 5 wt.% HCl solution. The membrane samples were immersed in an aqueous solution of HCl for 15 min, followed by rinsing with distilled water (twice). The membranes were then dried in air at ambient temperature for 2 d.

3. Results

3.1. Membrane morphology

The pore size and shape are strongly affected by the addition of fillers into a dope solution [26]. The performed SEM examinations confirmed the occurrence of differences in the structure of tested membranes (Figs. 2 and 3); however, the membranes had a sponge-like structure in each case (Fig. 3). This similarity in the structure is advantageous since the membranes with finger-like pores exhibit different properties in comparison with the membranes with sponge-like structure [32]. Therefore, the application of membranes with finger-like and sponge-like structure would make difficult a comparison of the effect of the fillers presence on the studied membranes performance.

The SEM examinations revealed that a structure of the external surfaces differs from the structure of the internal wall regions for tested membranes. The same observation has been reported for the other capillary membranes [3,27,48,49]. A magnitude of noted differences in the membrane structure depends on the rate of solvent leaching and the cooling conditions of fabricated capillaries [48]. In the present study, the similar conditions of TIPS process were used; hence, it can be assumed that a structure of tested membranes was mainly affected by a composition of dope solution.

The membranes fabricated only from a pure Moplen HP 420 M polymer (MD0) possess a linear structure of the capillary external surfaces. In this case, the internal surface was more porous than the external surface of capillary (Figs. 2a and b). The addition of inorganic fillers into the polymer disordered the linear structure and increased the surface porosity (Figs. 2c–f). The largest pores (5–10 µm) were observed on the external surface of membranes formed from dope solution containing only talc (MD10 – Figs. 2c and d). A similar distribution of pores size, namely larger pores located on the external surface and the smaller pores on the lumen side, also possess the capillary Accurel PP membranes, manufactured from PP by Membrana (Germany) [27].

Importantly, the SEM observations of the membranes cross-section revealed that the membranes with fillers addition (Figs. 3c–f) had a larger pore size than those of the membrane MD0 formed only from PP (Figs. 3a and b). However, in the case of MD25 membrane, the individual pores were more compact and possessed less “windows” connecting the cells of the adjacent pores.

It has to be pointed out that the examinations of porosity (Eq. (1)) demonstrated that the addition of inorganic fillers enhanced the membrane porosity. The MD0 membranes were characterized by porosity at a level of 74.0% ± 1.5%, whereas the membranes MD10 and MD25 had the porosity of 81.0% ± 2.8% and 79.0% ± 2.4%, respectively.

The MD studies (Section 3.4) demonstrated that the vapour permeability of MD25 membrane was over sixfold lower than those obtained for membranes MD0 and MD10. Since the wall thickness and capillary diameter of the tested membranes were similar, and the total porosity differed only by a few percentage, these parameters should not cause such a significant difference in the yield of tested modules [32]. The performed SEM examinations of membrane cross-sections revealed that a low efficiency of MD25 membranes could result from the presence of a smaller number of “windows” between the particular pore cells in the wall of MD25 membrane. Moreover, the layers adjacent to the membrane surface (Fig. 3e) were more compact in the case of MD25 membrane, which also increased a resistance for the mass transfer. Such results indicate that the membrane, MD25, produced for microfiltration, is not useful for MD process. However, this membrane was applied for presented studies (for comparison purposes), because its matrix contained beside talc also several other fillers, which enables to determine their influence on the membrane stability during the MD process.

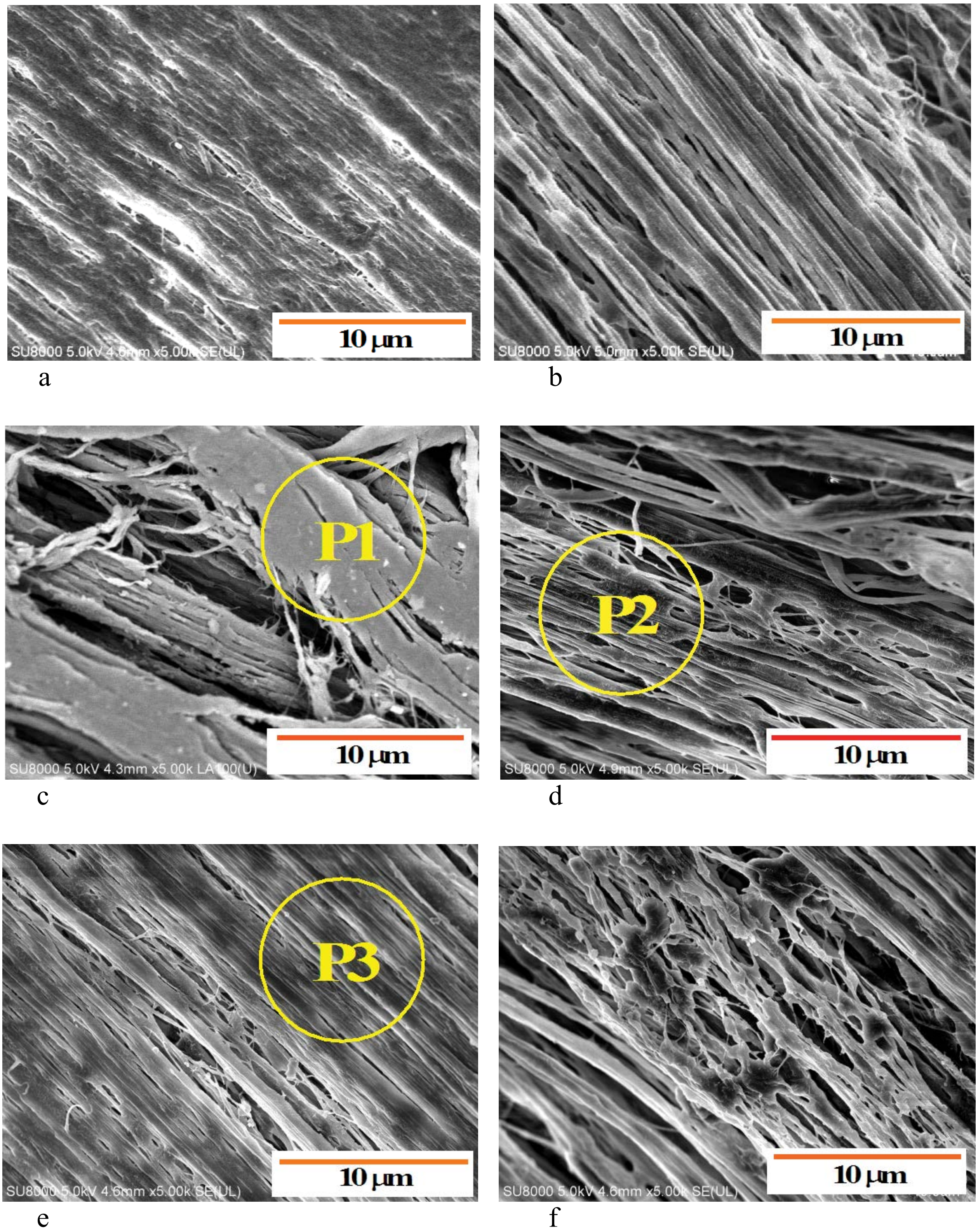

Fig. 2. SEM images of membrane surfaces. MD0: (a) external and (b) internal; MD10: (c) external and (d) internal; MD25: (e) external and (f) internal. P – area of SEM-EDS analysis (Table 2).

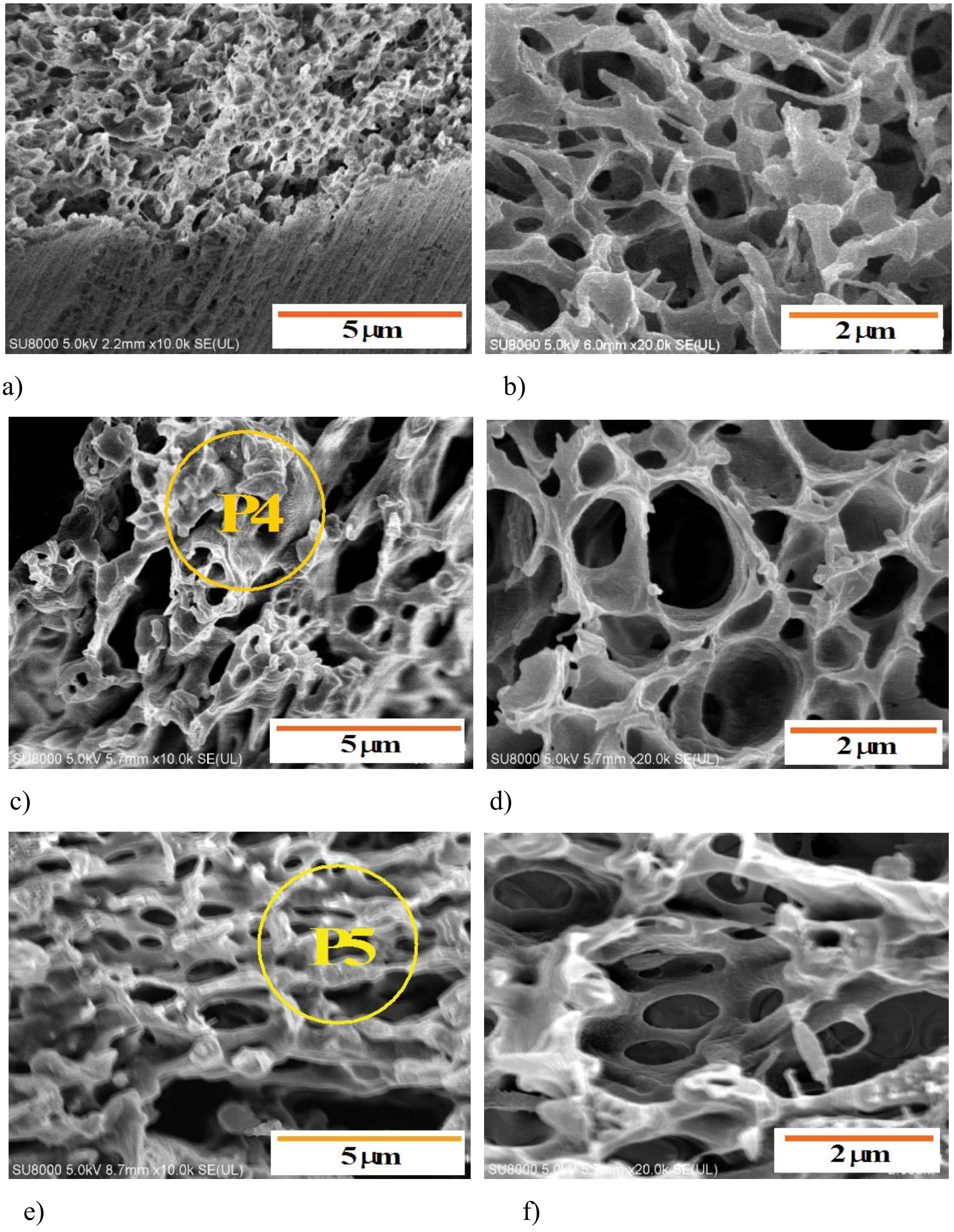

Fig. 3. SEM images of a membrane cross section. MD0: (a) boundary between membrane cross-section and membrane surface (lumen side). (b) inside membrane wall; MD10: (c) edge of the lumen side; (d) inside membrane wall; MD25: (e) edge of the lumen side; (f) inside membrane wall. P – area of SEM–EDS analysis (Table 2).

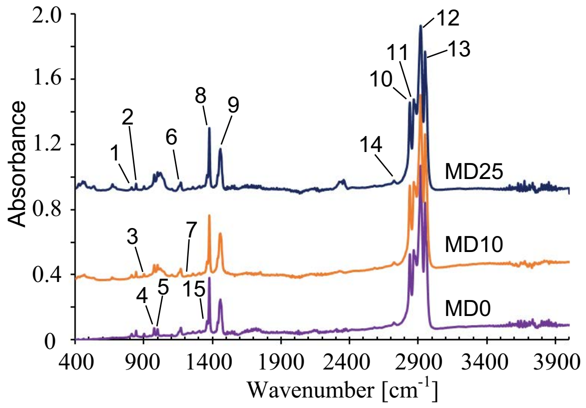

Fig. 4. Results of FTIR analysis of tested virgin membranes. Peak No. – Table 1.

3.2. Chemical composition

A composition of the membrane matrix was analysed using FTIR and XRD methods (Figs. 4 and 5). The results of FTIR analysis including peaks position, functional groups and references are presented in Table 1. The obtained FTIR spectra have a methyl absorption band at 1,375 and 1,450 cm^{-1} characteristic for PP [40] and few peaks (Table 1, No. 1–7) attributed to the presence of iPP [1,28,50]. The X-ray diffraction patterns characteristics for iPP [42,50,51] were also recorded (Fig. 5). Thus, the performed investigations confirmed that isotactic PP was the main component of membranes matrix in each studied case.

A condition advantageous for the formation of α phase in polypropylene is a fast crystallization at high temperatures. The TIPS process is carried out at a high temperature (453–463 K), which enables the iPP crystallization in the form of αPP [52]. The performed XRD analysis confirmed (card 00-061-1416) that the iPP occurred as α crystal phase in the tested membranes. The additional peaks visible in Fig. 5 at angle 2θ equal to 9.5, 19.5 and 28 were identified as silicon oxides, which most probably resulted from the presence of talc ($Mg_3(OH)_2Si_4O_{10}$). The presence of talc in the membrane matrix was also confirmed by FTIR analysis. When the surface of membrane MD0 was covered by talc in the form of powder (Finntalc M03, Elementis, UK) a particularly large intensity of the absorption bands was observed around 450, 660 and 1,010–1,050 cm^{-1} (Fig. 6). These additional peaks were only observed in the case of MD10 and MD25 membranes blended with talc. The appearance of the absorbance peak at 1,018 cm^{-1} is attributed to the stretching vibrations of Si–O–Si [53].

3.3. Membrane hydrophobicity

The addition of fillers into a membrane matrix, depending on their properties, can either increase or decrease the membrane hydrophobicity [8,32,46]. In the case of MD membranes, it is essential that the fillers did not accelerate the pores wetting. This phenomenon was analysed by measurements of the value of the contact angle, which is commonly utilized for evaluation of wettability of fabricated MD membranes [46]. Usually, a tensile drop method is applied for determination of the contact angle values [21,25]. In this case not only the performance of polymer matrix but also the surface morphology (pores shape, surface roughness) has a significant influence on the obtained results [3,9].

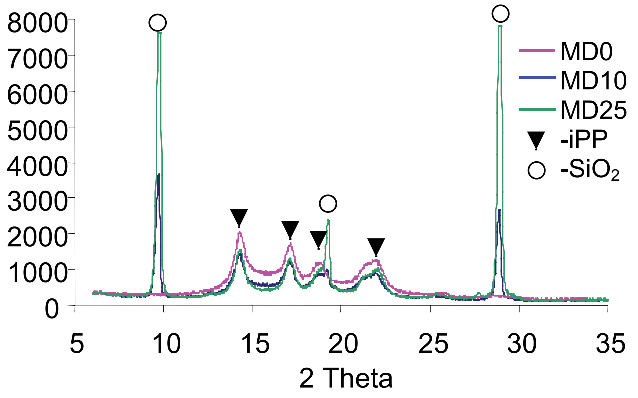

Fig. 5. Results of XRD analysis of tested virgin membranes.

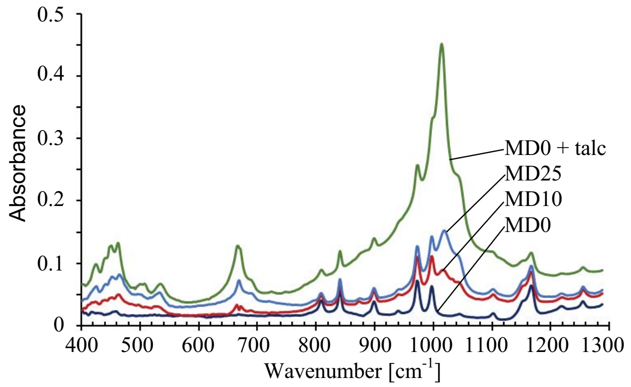

Fig. 6. Results of FTIR analysis with peaks characteristic for talc.

Similar to the tensile drop method, a morphology of the membrane surface is important for the first immersion of membrane samples during the dynamic measurements of the contact angle using the Wilhelmy plate method. The advancing and receding angles were obtained by this method. During the first immersion, all the studied membranes had the contact angle (advancing) close to 100°. However, the repetition of immersion–emersion cycles caused that the values of contact angle decreased and finally stabilized at a level of 88° (MD10), 85° (MD25) and 80° (MD0).

A number of fillers were observed on the membrane surface when the polymers were blended with PTFE or TiO_2 particles [46]. In such case, the introduced fillers significantly affected the membrane wettability. However, the presence of filler particles was not found on the surface of MD10 and MD25 membranes, although the SEM examinations were performed with large magnifications of the order of 100 k. The SEM-EDS analysis (Table 2) also revealed that the concentration of applied fillers on the membrane surface (Fig. 2; P1–P3) was significantly lower than that determined inside the membrane walls (Fig. 3; P4 and P5). The presence of filler components in the area P1–P3 resulted probably

Table 1
Characteristic peaks/bands observed during FTIR examination of polypropylene

Peak No.	Frequency (cm^{-1})	Functional groups/performance	References
Bands characteristic for iPP			
1	809	CH_2 rocking, C–C chain stretching	[15,50,57]
2	841	CH_2 rocking, C–CH_3 stretching	
3	899	CH_3 rocking, CH_2 rocking, CH bending	
4	972	CH_3 rocking, C–C chain stretching	
5	997	CH_3 rocking, CH_2 wagging, CH bending	
6	1,167	CH_3 rocking, C–C chain stretching, CH bending	
7	1,219	CH_2 twisting, C–C chain stretching, CH bending	
PP spectra			
5	997	(–CH_3) methyl group, changes due to polymer degradation	[55,59]
8	1,370–1,378	Angular deformation of (–CH_2–)	[28,39]
9	1,453–1,460	(–CH_3) angular deformation of methyl group	[50]
10	2,840	(–CH_2–) methylene group	[40,46]
11	2,870	(–CH_2–) methylene group	[55]
12	2,910	CH_2 – changes due to polymer degradation	[55]
13	2,970	(C–H) stretching of –CH_3 group	[55]
14	2,722	(C–H) characteristic vibration stretching band of PP, not affected by thermal oxidation	[45]
15	1,354	(–CH_2–) angular deformation	[50]
2,5,6	841, 997 and 1,167	Bands indicated the crystallinity level	[24,27]
10–14	2,840–2,980	C–H stretching of CH/CH_2/CH_3 groups	[50,55,57]
Degradation products			
Range	1,600–1,800	Carbonyl groups formed as a result of thermal oxidation	[45]
16	1,630	C–H bond is split up and oxidized to a C–O–H bond	[54]
17	1,641/1,650	C=C stretching vibration. This bond can accrue by abstraction of hydrogen atoms of two abreast carbon atoms by oxygen to H_2O	[41,58]
18	1,713–15	Carboxylic acids	[45,55]
19	1,720	Aldehydes	[58]
20	1,730	C=O carbonyl peak a result of oxidation of carbon atoms	[56]
21	1,735/1,743	Esters	[2,45]
22	1,769–75	Ketone (C=O): this bond can accrues by abstraction of two hydrogen atoms of a single carbon atom by oxygen to H_2O	[54,55]
23	1,780	γ–Lactones	[54,55]
24	3,100–3,500	Hydroxyl groups	[58]

Table 2
Results of SEM-EDS analysis (atom %). Analysed area (*P*) indicated in Figs 2 and 3

Elements	P1	P2	P3	P4	P5
C	98.3	97.4	97.3	91.2	86.5
O	1.1	1.6	1.7	5.4	7.6
Mg	0.2	0.4	0.3	1.5	3.1
Si	0.4	0.6	0.5	1.9	2.4
Ca	–	–	0.2	–	0.3
Ti	–	–	–	–	0.1

from the fact, that during SEM–EDS analysis, the obtained data are taken not only from the surface but also from a layer with depth of 1–2 μm. The presence of tested fillers inside this layer should not directly change the wettability of used polypropylene membranes. Hence, the differences in the wettability may rather result from the changes in the surface roughness, porosity and the pores shape caused by the addition of fillers into a dope solution [46].

3.4. MD studies

To demonstrate whether the presence of inorganic fillers in the membrane matrix resulted in enhancement of the membrane resistance to degradation, the long-term MD studies were carried out. The stability of obtained permeate flux and the changes of the distillate conductivity (salt rejection) were determined during the continuous MD studies. The MD process was realized with the submerged modules assembled in the feed tank, whereas the distillate flows on the lumen side (Fig. 1).

The PP in the bulk phase is resistant to the degradation by brines, although a contact with salt solutions for several months can cause slight changes on its surface [59]. This fact is important in the case of MD membranes, because their wettability is affected by the changes in polymer chemistry proceeding in a very thin surface layer. The formation of hydrophilic compounds on the membrane surface due to the transformations proceeding in the polymer results in PP membrane wetting [29]. Such changes are mainly initiated by the peroxides, which are responsible for the degradation process of polymer chains [58]. Moreover, higher temperatures will lead to faster degradation rates; hence, the studies were carried out at temperature of 353 K, typically used during MD process. The NaCl solutions were used as a feed and its concentration was gradually increased up to 200 g/L.

The obtained results of long-term studies were presented in Fig. 7. During the first 15 h of studies, the maximum permeate flux for feed concentration equal to 1 g/L (point A) and 200 g/L (point B) was determined. For such a high concentrated brine, the obtained permeate flux was equal to 8.1, 10.2 and 2.3 L/m^{2}h for MD0, MD10 and MD25 membranes, respectively. In the next step, the continuous MD studies were started using the feed containing 35 g NaCl/L, which was supplied to the modules for nearly 300 h. In all cases, the obtained permeate fluxes were almost constant for the initial 100 h of MD process, and after this period the yield of the MD modules has started to decline. Importantly, these results demonstrated that MD studies carried out for a period shorter than 50 h are not sufficient to evaluate the performance (e.g., wettability) of tested MD membranes.

The permeate flux obtained for the membranes MD10 and MD25 was decreased by 11% and 9%, respectively, and by over 20% for membrane MD0, after 300 h of MD studies. The obtained distillate conductivity was low (2–4 μS/cm) for the membranes MD10 and MD25 and remained constant during the first 300 h. Such a low value of conductivity indicates that a decline of MD efficiency observed over the initial 300 h period was due to the pore wetting on the membrane surfaces [29]. A slighter worse result was obtained in the case of MD0 membranes, for which the value of distillate conductivity increased up to 10 μS/cm, although that the salt rejection close to 100% (feed 35 NaCl g/L) was still achieved.

A significantly larger increase in the distillate conductivity (up to 100 μS/cm) was noted for membranes MD0 during the period of 350–500 h of MD process, and it was correlated with a similar decline of the permeate flux observed for SMD0 module (Fig. 7a). Such a result suggests that a greater number of pores were wetted in the membranes MD0 than those in the membranes MD10 and MD25 during the same period. Although the tested membranes MD10 and MD25 exhibited enhanced resistance to wetting, it does not necessarily mean, that it was associated with the presence of applied fillers in the membrane matrix. A slower wetting most probably resulted from different shape and size of the pores in the membranes, due to the addition of fillers into the dope solution [46].

In each case, it was found that an increase in the feed concentration caused a significant decrease of the permeate flux. Systematic, but a relatively slow decrease of module yield was also observed during the MD process carried out at constant feed concentration (Fig. 7). Finally, the obtained permeate flux was stabilized at a level of 6.00, 2.65 and 1.83 L/m^{2}h for MD10, MD0 and MD25 membranes; respectively, at the feed concentration equal to 200 g/L. Thus, after 850 h of modules exploitation, the obtained permeate fluxes were about 40% and 20% (MD10 and MD25) and 67% (MD0) lower than the maximum permeate flux determined for such concentrated feed (Fig. 7, point B). These results suggested that not only a high salt concentration but also the duration time of modules exploitation was the major reason of pores wetting. As a result of feed leakage, the final conductivity of obtained distillate was 186, 288 and 456 μS/cm for MD10, MD25 and MD0 membranes, respectively. Although the feed concentration was 200 g/L, the salt rejection over 99% was still maintained.

4. Membrane degradation

A high temperature of TIPS process (e.g., 453 K) makes that the degradation processes of polymer proceeds already at the stage of membrane fabrication [12,50,59]. Although this phenomenon can be limited by performing the process of membrane formation in the inert gas atmosphere, a slight degradation of molten PP was also observed in the nitrogen atmosphere [34,48]. Moreover, the complete

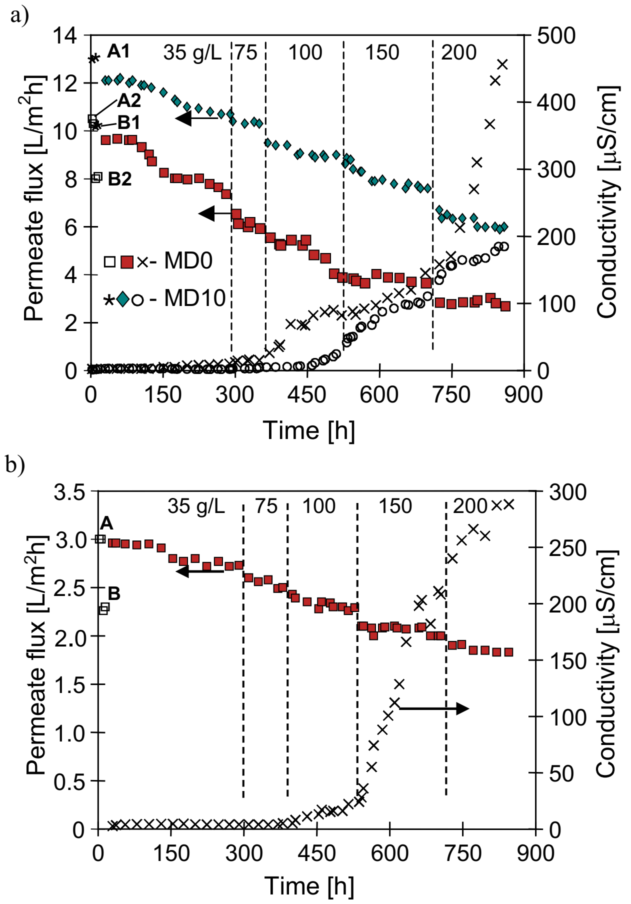

Fig. 7. Changes of the permeate flux and distillate electrical conductivity as a function of process time and feed concentration (NaCl solutions). Module: Module: (a) SMD0 and SMD10, (b) SMD25. Initial permeate flux for feed concentration: 1 g/L (points A, A1 and A2) and 200 g/L (points B, B1 and B2).

elimination of the presence of oxygen is difficult in the industrial installation. Hence, the products of thermal degradation process were also detected on the surface of virgin membranes as revealed by the FTIR examinations (Fig. 8). The studies of membranes obtained from manufacturer, demonstrated the presence on their surface the C=C bonds (1,641–50 cm^{-1}), carboxylic acids (1,713–15 cm^{-1}), aldehydes (1,720 cm^{-1}), the C=O groups (1,730 cm^{-1}), esters (1,735–45 cm^{-1}), ketones (1,769–75 cm^{-1}) and γ-lactones (1,780 cm^{-1}). The peaks with several times lower intensity were noticed for the membranes MD10 and MD25, which confirms a well-known fact that the addition of fillers limits the PP degradation during its thermal processing [12,34].

In the performed MD studies, the feed temperature amounted to 353 K. It is worth noting that the application of such temperature or higher allows to significantly increase the efficiency of MD process [14,27]. On the other hand, it can also accelerate the polymer degradation, especially during a long-term module exploitation [30,36]. However, the results of FTIR analysis of the membranes MD10 and MD25 after 850 h of MD process operation were similar to those obtained for the new membranes (Fig. 9).

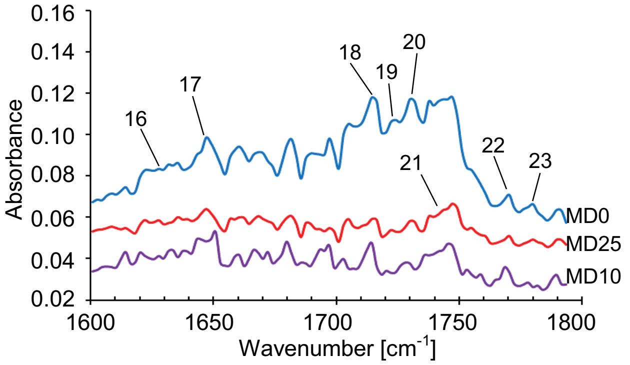

Fig. 8. Results of FTIR analysis of the virgin membranes MD0, MD10 and MD25. Numbers – products of thermal degradation described in Table 1.

A slight increase in the intensity of the peaks associated with the presence of C=C bonds (1,641–50 cm^{-1}), carboxylic acids (1,713–15 cm^{-1}) and esters (1,735–45 cm^{-1}) was only found. A definitely larger increase in the intensity of peaks associated with the products of PP thermal degradation was found in the case of the membranes MD0 (Fig. 9, line MD0-B). Such a result demonstrates that the addition of inorganic fillers to the membranes allows to limit their degradation during the MD process.

4.1. Results of membranes annealing

To the best of author's knowledge, the performed studies of MD are one of the longest that were presented in the literature for PP membranes blended with talc. However, the effective periods of the industrial exploitation of MD modules can be estimated to be at least 30 times longer, hence, the degree of membrane degradation will be enhanced. The degree of degradation significantly increased along with a temperature elevation and a rapid PP degradation was observed during annealing the PP at 373 K in air [45].

A similarly high temperature was applied for the tested membranes, which were subjected to annealing in the boiled brine (4–5 h/d) for a period of month. The FTIR spectra recorded for these membranes were presented in Fig. 10. The obtained results showed that a long-term annealing of the membranes at 373 K caused a slight increase of the intensity of peaks in the range of 1,600–1,800 cm^{-1} (compared with the results presented in Fig. 6). However, a significant increase of bonds intensity in the range 1,100–1,200 cm^{-1} (changes in PP crystallinity) and 3,400–3,600 cm^{-1} attributed to the formation of the hydroxylic groups has been found. Moreover, the intensity of peaks in the range 1,360–1,480 cm^{-1} and at 2,910 cm^{-1} were decreased for MD0, which indicated the thermal degradation of this membrane [28,39,54]. The membrane destruction is accelerated by scaling [1,3,4]. Therefore, in order to enhance the intensity of membrane degradation, this part of studies was carried out with the precipitation of $CaCO_3$ deposit. However, the presence of this deposit makes difficult the observation of changes in above-mentioned ranges of wave numbers (Fig. 10, MD0 + $CaCO_3$). With regard to

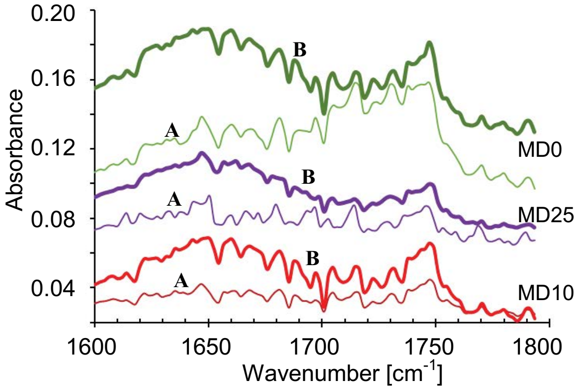

Fig. 9. Results of FTIR analysis of the membranes MD0, MD10 and MD25 collected from MD modules after 850 h process duration (lines B). Lines A – results for virgin membranes (Fig. 8).

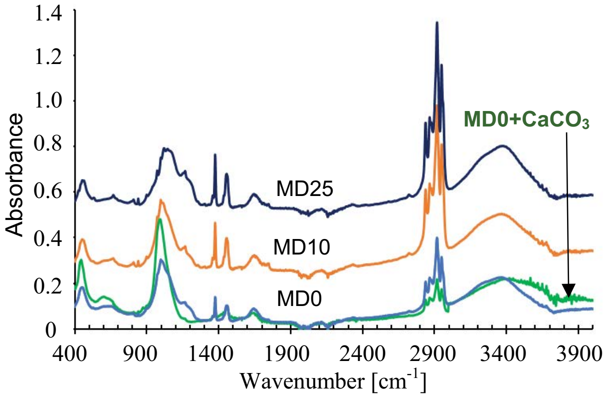

Fig. 10. Results of FTIR analysis of the membranes MD0, MD10 and MD25 after 1 month annealing in boiled brine. Line (MD0 + $CaCO_3$) – membrane with $CaCO_3$ deposit.

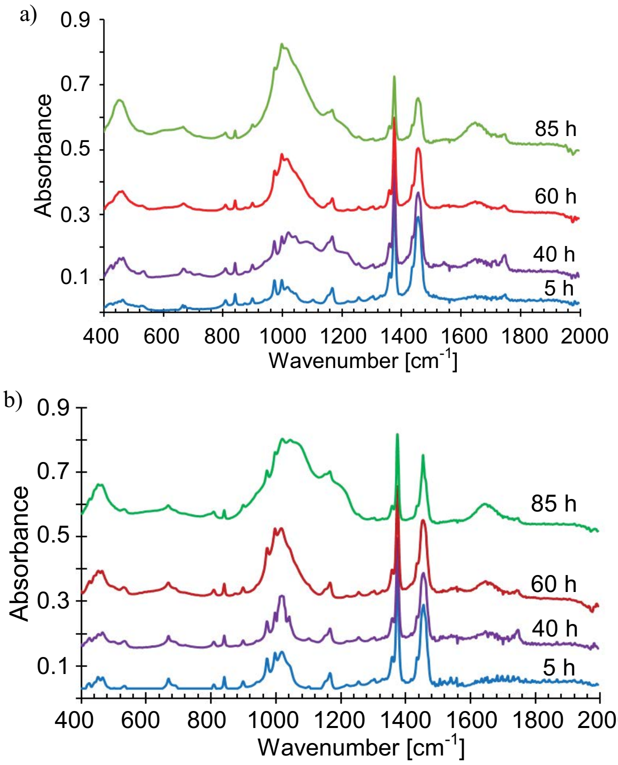

Fig. 11. Results of FTIR analysis of the membrane MD0 (a) and MD25 (b) periodically performed during membrane annealing in the boiled brine.

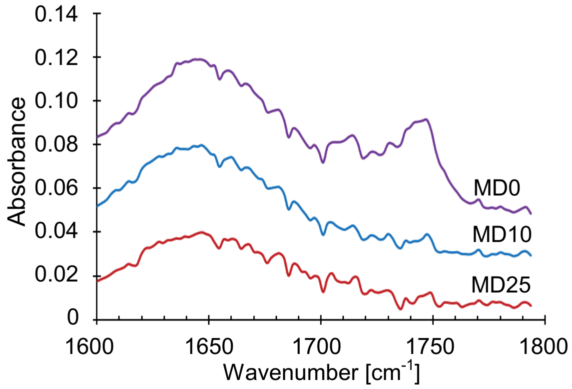

Fig. 12. Results of FTIR analysis of the membrane MD0, MD10 and MD25 after 85 h annealing in the boiled brine.

this, the deposit was removed by rinsing the membranes in dilute HCl solution before FTIR examinations.

The course of PP degradation intensity during membranes annealing was additionally studied by periodical FTIR examination of membrane samples. The obtained results demonstrated that the changes in the surface chemistry were limited during the initial period, equal to 40 h in the case of MD0 membrane (Fig. 11a). A similar character of changes was recorded; however, the significant changes were observed after 60 h (Fig. 11b). The largest intensity of peaks associated with PP degradation, after 85 h of annealing the membranes in the boiling brine, was observed for MD0 membrane and smaller for MD10 and MD25 membranes (Fig. 12). This indicated that the applied fillers led to an increase in the thermal resistance. These results are in a good agreement with previous studies [45,55], where the similar changes of PP degradation as a function of time have been reported.

It should be pointed out that the new groups, such as carboxylic and hydroxylic, formed due to the PP degradation are hydrophilic, which enhanced the wettability of the membrane surface. This fact was confirmed by the contact angle measurements. In each case, its values were lower than those for the new membranes (Fig. 13). In this figure were presented the results obtained after the 20 repetitions of immersion–emersion cycles (Wilhelmy method), when the values of contact angle were stabilized.

4.2. Degradation of polymeric membrane matrix

It must be stressed that a decrease of the membrane hydrophobicity is a serious limitation for MD process; moreover, the polymer degradation can also cause unfavourable changes in the membrane matrix. After completing the studies with the membranes boiled in brine, it was found that the tested membranes become more rigid and they were not as flexible as new membranes. The similar changes, but in a lower degree, were observed for the membranes collected from MD modules after 850 h exploitation. A loss of flexibility was particularly noticeable for the MD0 membrane, which was without the addition of fillers. The degree of degradation and changes of polypropylene crystallinity was determined by DSC examination (Table 3).

The new MD0 membranes were characterized by a value of the crystallinity at a level of 38.7%, and an increase to a value of 41.9% and 40.8% was found for the MD10 and MD25 membranes, respectively. The obtained results confirmed the advantageous effect of fillers addition on the formation of the crystal phase inside PP matrix during membrane manufacture by TIPS method. A long-term annealing improves the lamellae orientation and uniformity; thus, it can change the distribution of the crystal and amorphous phase [41]. The results of DSC examinations indicated that the crystallinity of MD0 membrane increased from 38.7% to 44.4% after about 850 h of MD process operation, while the crystallinity of membranes MD10 and MD25 increased to 42.3% and 42.0%, respectively. A slightly larger increase in crystallinity was found after heating membranes with fillers (MD10-boiled and MD25-boiled) but definitely higher in the case of MD0 membrane – from 38.7% to 51.6%.

Moreover, in each case, it was observed that the membranes after MD and annealing process exhibited a slight decrease of T_m values. An exemplary course of melting curves obtained in the determination of T_m is shown in Fig. 14. It was reported that the thermodynamic melting temperature of semi-crystalline polymers decreases as the molecular weight decreases and/or as the number of defects increases, that is with an increase in branching and/or crosslinking [41].

The observed increase in the crystallinity for the tested membranes (Table 3) does not mean that the properties of

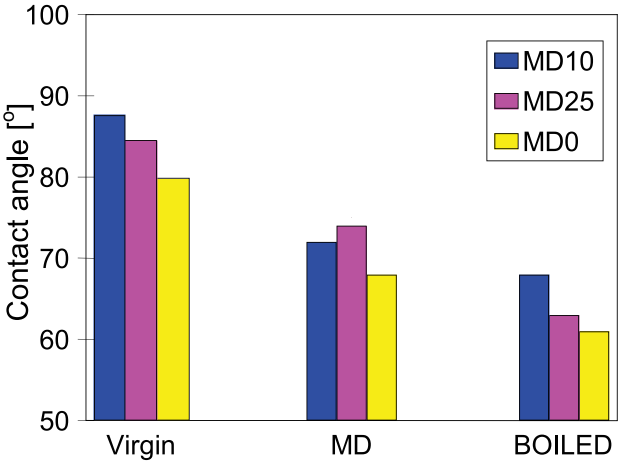

Fig. 13. Comparison of changes of contact angles (advancing) for tested membranes.

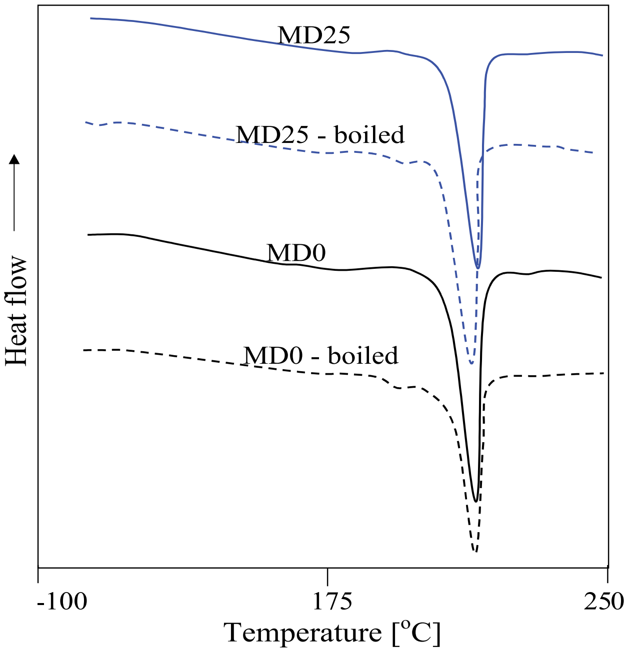

Fig. 14. Differential scanning calorimeter melting curves obtained for virgin membrane samples (MD0 and MD25) and for membranes after 85 h annealing in boiled brine.

Table 3
Results of DSC analysis of new membranes, and membrane samples after MD and annealing studies

Membrane	T_m (°C)	ΔH_m (J/g)	T_C (°C)	ΔH_C (J/g)	X (%)
MD0	167.1	81.0	110.1	83.8	38.7
MD0-MD	166.8	92.9	112.8	96.8	44.4
MD0-boiled	165.8	107.9	113.7	107.9	51.6
MD10	166.9	87.6	119.2	95.8	41.9
MD10-MD	166.7	88.4	121.9	94.4	42.3
MD10-boiled	166.8	96.1	121.2	95.6	46.0
MD25	167.7	85.4	124.9	95.4	40.8
MD25-MD	167.5	87.7	125.1	95.2	42.0
MD25-boiled	164.5	92.6	125.2	94.6	44.3

$X = \Delta H_m/\Delta H$, where $\Delta H = 209$ J/g [53].

Table 4
Mechanical properties of tested PP membranes

Membrane	Young's modulus (MPa)	Elongation at break (%)	Tensile strength (MPa)
MD0	102.0 ± 10.3	98.0 ± 24.3	2.28 ± 0.18
MD0-MD	106.0 ± 12.3	86.0 ± 24.1	2.49 ± 0.17
MD0-boiled	109.0 ± 11.8	70.0 ± 15.8	2.76 ± 0.19
MD10	117.0 ± 8.9	153.0 ± 34.3	2.65 ± 0.22
MD10-MD	108.0 ± 8.6	121.0 ± 37.5	2.54 ± 0.13
MD10-boiled	121.0 ± 16.1	108.0 ± 16.3	2.16 ± 0.45
MD25	140.0 ± 12.8	113.0 ± 29.2	2.62 ± 0.15
MD25-MD	158.0 ± 7.3	111.0 ± 32.4	2.82 ± 0.21
MD25-boiled	147.0 ± 13.0	110.0 ± 11.9	3.18 ± 0.11

these membranes were improved during MD process. This also provides evidence of PP degradation [44]. As a result of this phenomenon, the polymer chain length is shortened, and they become more mobile. Hence, the polymer chains undergo the arrangement into the crystalline phase more readily during polymer annealing [41,42], and some phenomenon occurs in the MD process (T_F = 353 K). It was found that a faster propagation of oxidation takes place for PP chains with a longer isotactic sequence [44]. The addition of fillers decreased the intensity of this phenomenon.

4.3. Changes of membrane strength

The mechanical and chemical stability of MD membranes, similarly as high hydrophobicity, constitute very important properties for MD process performance. The new PP capillary membranes had a white colour and they were characterized by a good flexibility. However, the examinations of tensile strength revealed significant differences in the properties of tested capillary membranes. These tests confirmed that the addition of inorganic fillers improved the mechanical properties of PP membranes (Table 4). The Young's modulus and elongation at break were significantly higher compared with the values of these parameters measured for membrane without the fillers (MD0). The obtained results are almost two times better than those obtained for PP blended with nanosilica [34]. Talc exhibits a strong nucleating effect for PP; therefore, its application results in the improvement of PP mechanical properties [31].

The experimental results confirmed that the mechanical properties of PP membranes are closely related to the polymer crystallization conditions [26]. The addition of nucleating agent (e.g., talc) increases the number of nuclei; therefore, the crystallization rate is also accelerated [24,31]. A fine crystal grain improves the impact strength of polymer and impedes the degree of orientation of the polymer. Moreover, the addition of fillers enables the formation of "more sponge-like" structure (Fig. 3), which caused that MD10 and MD25 membranes exhibit better mechanical properties than the MD0 membrane (Table 4). It was found that the tensile strength was increased when the pore structure changed from spherulitic to interconnected [21].

The changes of the crystallinity also affected the mechanical properties of PP [26,31,41]. The PP degradation results in the enhancement of stiffness and brittleness of the membranes. A significant increase of stiffness of MD0 membranes caused that the fractures were formed most likely on their surface (Fig. 15), taking place probably during the preparation of samples for SEM examinations. Such fact was not observed in the case of membranes with inorganic fillers, although the MD10 membranes were a slightly more rigid in comparison with MD25 membranes. These results confirmed that the properties of PP membranes were significantly improved by blending PP with talc [31].

5. Conclusions

The results obtained in the present studies confirmed that the thermal degradation of polypropylene membranes significantly affected the performance of MD modules during their long-term exploitation.

Inorganic fillers, such as talc, are commonly used in the polymeric materials both for long-term stabilization and to prevent a deterioration of polymers performance.

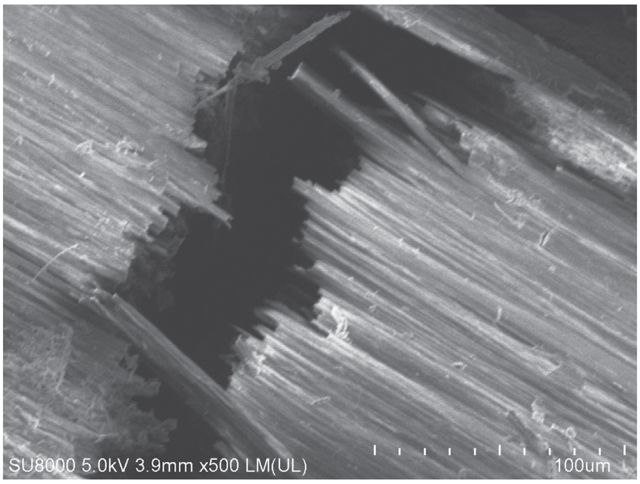

Fig. 15. SEM image of external surface of MD0 membrane samples collected from module after 850 h of MD study.

The performed studies confirmed a positive effect of the addition of inorganic fillers into the dope solutions used for the formation of membranes via TIPS process. The polypropylene membranes with fillers exhibited better mechanical properties and they were more resistant to the thermal degradation of polymer.

The addition of inorganic fillers (talc) caused that a linear system of the chains forming the polymers was disordered. Moreover, the fillers increased the membrane porosity, and improved the formation of sponge-like structure; and the formed pores achieved a more spherical shape. The mass transfer through the membranes with a similar porosity depends in a significant degree on the amount of connection ("windows") between the particular pore cells.

It has been demonstrated that all tested membranes exhibited a good resistance to wetting during the MD process. The addition of inorganic fillers changed the morphology of the membrane surface, but the membrane wettability was not significantly affected by the fillers. Therefore, the applied fillers restricted but not eliminated the partial wettability of surface of tested PP membranes.

The annealing of membranes in the boiling brine confirmed that the application of higher feed temperature during the MD process accelerates the formation of hydrophilic functional groups, such as carboxylic and hydroxylic, on the surface of polypropylene membranes.

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