Polyethersulfone membrane embedded with amine functionalized microcrystalline cellulose

Citation for published version (APA):

Rafieian Koupaei, F., Mousavi, M., Dufresne, A., & Yu, Q. L. (2020). Polyethersulfone membrane embedded with amine functionalized microcrystalline cellulose. *International Journal of Biological Macromolecules*, 164, 4444-4454. <https://doi.org/10.1016/j.ijbiomac.2020.09.017>

Document license:
TAVERNE

DOI:
[10.1016/j.ijbiomac.2020.09.017](https://doi.org/10.1016/j.ijbiomac.2020.09.017)

Document status and date:
Published: 01/12/2020

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Polyethersulfone membrane embedded with amine functionalized microcrystalline cellulose

Fatemeh Rafieian^{a,*}, Mohammad Mousavi^b, Alain Dufresne^c, Qingliang Yu^a

^a Department of the Built Environment, Eindhoven University of Technology, Eindhoven, the Netherlands

^b Department of Food Science and Technology, Agricultural College, University of Tehran, Karaj, Iran

^c University Grenoble Alpes, CNRS, Grenoble INP, LGP2, F-38000 Grenoble, France

ARTICLE INFO

Article history:

Received 4 June 2020

Received in revised form 31 August 2020

Accepted 2 September 2020

Available online 5 September 2020

Keywords:

Membrane

Microcrystalline cellulose

Metformin HCl

ABSTRACT

In this investigation, microcrystalline cellulose (MCC) was functionalized with metformin HCl using (3-chloropropyl)triethoxysilane (CPTES) as a coupling agent. Polyethersulfone (PES) membranes were incorporated with different concentrations of modified MCC (MMCC) to enhance its affinity for heavy metals during filtration of aqueous solutions. The composite membranes were characterized via fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), atomic force microscopy (AFM), Brunauer–Emmett–Teller (BET) method, porosity and contact angle measurements and mechanical analysis. The presence of MMCC in the host matrix was confirmed by FTIR. Although composites decomposed at lower temperatures, their thermal stability was sufficient to meet their performance requirements. DSC showed enhanced glass transition temperature (T_g) due to the interfacial interactions between membrane constituents which restrict the mobility of polymer chains. Microscopic imaging revealed higher surface roughness of composites compared to neat PES. Inclusion of MMCC increased the porosity and hydrophilicity of the membrane which consequently, higher permeability can be achieved.

© 2020 Published by Elsevier B.V.

1. Introduction

Pure and unpolluted water is an essential requirement for all living beings and access to drinkable water is a major global challenge for the 21st century. More than 71% of the earth surface is covered with water, but due to various pollution, only less than 1% of water is drinkable according to international standards. The main sources of water contamination include agricultural activities, environmental and global changes, municipal wastewater and also, waste water discharge from industries [1]. Various types of water pollutants are divided into the following categories: (1) inorganic pollutants including salts and metals, (2) nanopollutants, (3) nutrients and agriculture runoff, (4) organic pollutants including chlorinated and phenolic pesticides, industrial wastes, oxygen demanding wastes, pharmaceutical active compounds, polycyclic aromatic hydrocarbons, synthetic organic compounds such as endocrine disruptors, most of the synthetic dyes, petroleum and its derivatives, (5) pathogens, (6) radioactive pollutants, (7) suspended solids and sediments, and (8) thermal pollution [2].

The metal can be classified as a heavy metal, if it has a relatively high density which is at least five times more than that of water. The presence of heavy metals even in trace amounts, is very dangerous. They

are non-biodegradable, toxic, and easy to accumulate at low concentrations in living organisms in general and in the human beings specifically; they can cause serious diseases, such as cancer, kidney failures, neurological damage, and can be lethal at high concentrations. The most common heavy metals found in industrial wastewater include: arsenic, cadmium, chromium, copper, iron, lead, nickel, silver, uranium and zinc [3].

So far, a number of efficient methods have been investigated for the removal of heavy metals such as adsorption on various (bio)sorbents including modified natural material, modified biopolymers, industrial by-products and nanomaterials, cementation, chemical precipitation, coagulation, electrodialysis, flocculation, floatation, ion exchange, membrane filtration (ultrafiltration, nanofiltration and reverse osmosis), photocatalysis, etc. [4].

Recently, adsorptive membranes, which have the simultaneous advantages of membrane technology and adsorptive process, have been introduced as an effective way for this purpose. These membranes' surfaces contain reactive functional groups (NH_2 , SO_3H and COOH) with ion exchange or surface complexation mechanism for attraction of metal ions and their removal from aqueous solutions.

The aim of this investigation was the fabrication and characterization of a polyethersulfone (PES) membrane loaded with modified microcrystalline cellulose (MMCC) in terms of morphological, thermal and mechanical properties. PES is widely applied as membrane material

* Corresponding author.

E-mail address: farafieian61@gmail.com (F. Rafieian).

Table 1
Compositions of the casting solutions.

Membrane	PES (wt%)	PVP (wt%)	DMSO (wt%)	MMCC (wt%)
PES-0	18	9	73	0
PES-0.5	18	9	72.5	0.5
PES-1	18	9	72	1
PES-3	18	9	70	3

because of its extra features such as high strength, outstanding chemical resistance against aggressive materials, wide temperature tolerances, and high dimensional stability to be fabricated into membranes under various conditions [5]. Also, cellulose has shown impressive properties including renewability, biodegradability, low density, transparency, high aspect ratio, crystallinity, mechanical properties and large surface area, which make it an ideal candidate as a filler in composite membranes [6]. Furthermore, the presence of numerous hydroxyl groups on the surface of MCC, results in the ability to react with various functional groups such as amide, amine, carbonyl, carboxyl, hydroxyl, imidazole, phenol, phosphate, sulfate, sulfhydryl, and thioether moieties that are responsible for heavy metal adsorption and removal from aqueous solution [7]. In the present work, MCC was modified with metformin HCl as an amine containing material by using (3-chloropropyl) triethoxysilane (CPTES) as a coupling agent and the resulting MMCC was applied as an absorbent constituent in the synthesized membrane.

2. Materials and methods

2.1. Materials

PES, polyvinylpyrrolidone (PVP), dimethyl sulfoxide (DMSO), PH-101 microcrystalline cellulose (98%) and chemicals needed for amine functionalization of MCC including acetonitrile ($\geq 99.5\%$), (3-chloropropyl)triethoxysilane (95%), ethyl alcohol (96%), glacial acetic acid ($\geq 99.85\%$), metformin HCl ($\geq 99.0\%$), potassium carbonate (K_2CO_3 , $\geq 99.0\%$), and potassium iodide (KI, $\geq 99.0\%$) were provided by Sigma-Aldrich Inc. (St Louis, MO, USA).

2.2. Methods

2.2.1. Membrane preparation

The fabrication method employed for preparing membranes in this study was the phase inversion technique. A pre-determined amount of PES and PVP were added to DMSO solvent. PVP plays the role of pore former during the membrane synthesis via phase inversion and also increases the membrane hydrophilicity without formation of any covalent bonds with PES. Then, different concentrations of modified microcrystalline cellulose were added to the PES solution. By changing the content of MMCC over a range of 0, 0.5, 1 and 3 wt%, a series of

membrane films were obtained and coded as PES-0, PES-0.5, PES-1 and PES-3, respectively. Table 1 shows the composition for all membranes. The solution was stirred for 24 h by magnetic stirrer followed by sonication at ambient temperature for 30 min to eliminate air bubbles. Then, the solutions were cast on a glass plate using a film applicator with a casting knife of 300 μm gap size. The casted films were subsequently immersed in a coagulation bath containing distilled water for 1 h and exchange between the solvent (DMSO) and the non-solvent (distilled water) was induced. The membranes were peeled off from the glass plate by phase inversion process and repeatedly washed with distilled water to complete phase separation and remove the remaining solvent before further characterization. Fig. 1 shows a schematic diagram of membrane preparation procedure.

2.2.2. Membrane characterization

2.2.2.1. Fourier transform infrared spectroscopy (FTIR). FTIR spectra of membranes were obtained for spectroscopic investigation. All FTIR spectra were recorded by using Perkin Elmer 1000 FT-IR spectrometer (Perkin-Elmer, Ltd., Buckinghamshire, UK). 32 scans were taken with 4 cm^{-1} resolution in the range of $4000\text{--}400\text{ cm}^{-1}$.

2.2.2.2. Thermogravimetric analysis (TGA). Thermal stability of the composites was evaluated using a Netzsch STA 449 F1 Jupiter thermal analyzer (Selb, Germany). The analysis conditions were: sample mass between 130 and 150 mg, ceramic pans, temperature range of 45 to $800\text{ }^\circ\text{C}$, heating rate of $5\text{ }^\circ\text{C}$, isotherm for 1.2 min and a nitrogen atmosphere with flow rate of $20\text{ mL}\cdot\text{min}^{-1}$.

2.2.2.3. Differential scanning calorimetry (DSC). DSC studies of the composites were carried out by V2 6D TA instrument model DSC 2010. A 3–5 mg film sample was cut as small pieces and placed into a hermetically sealed sample pan. The reference was an empty pan. Previous heat treatments can significantly have an influence on the shape of the DSC curve of semicrystalline polymers. To compare the thermal data of PES/MMCC composites with values reported in the literature, a standardized thermal history is needed that can be obtained via a heating/cooling/reheating DSC method. The standard procedure performed in non-isothermal scans was as follows: samples were heated from 0 to $180\text{ }^\circ\text{C}$ at a scan rate of $10\text{ }^\circ\text{C}/\text{min}$ and held for 1 min. The samples were non-isothermally crystallized from 180 to $0\text{ }^\circ\text{C}$ at a cooling rate of $10\text{ }^\circ\text{C}/\text{min}$. Subsequently, the glass transition temperature (T_g) were measured by raising the temperature to $250\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C}/\text{min}$. The 1st heating process erases any previous thermal history (based on the assumption that the maximum temperature has been enough for removal of any remained nuclei without causing sample degradation), the cooling process imparts a known thermal profile to the samples, and the 2nd heating process allows them to be evaluated with a known thermal history. In order to ensure accuracy, each analysis was repeated three times.

Fig. 1. Schematic diagram of membrane preparation procedure.

2.2.2.4. Scanning electron microscopy (SEM). The microstructure of the films was analyzed using a scanning electron microscope (JSM-IT100, JEOL Ltd., Japan). Membranes were mounted onto sample studs via double-sided adhesive tapes and coated with a thin layer of gold using an Emitech K575X sputter coater (Quorum Technologies Ltd., UK) to make them electrically conductive. The images were taken at an accelerating voltage of 10 kV.

2.2.2.5. Atomic force microscopy (AFM). Surface roughness of the membranes was characterized using TS-150 NT-MDT AFM (Moscow, Russia). The samples were cut into square pieces with area of approximately 0.25 cm² and attached to the sample holder in the scanner tube and the membrane surfaces were imaged using a tapping mode scanning over 10 × 10 μm areas with 256 × 256 pixel width resolutions, and an adaptive scan rate of 1.01 Hz. The surface roughness parameters of the membranes including S_a , S_q and S_z were calculated from AFM images using Nova v.1.26.0.1443 for Solver software. S_a is defined as the arithmetic mean or average of the absolute distances of the surface points from the mean plane and represented as follows:

$$S_a = \frac{1}{MN} \sum_{j=1}^N \sum_{i=1}^M |z|(\mathbf{x}_i \mathbf{y}_i) \quad (1)$$

where M and N are the number of columns and rows in the surface, respectively.

S_q is defined as the root mean square of the surface departures from the mean plane within the sampling area and is indicated by the following equation:

$$S_q = \sqrt{\frac{1}{MN} \sum_{j=1}^N \sum_{i=1}^M z^2(\mathbf{x}_i \mathbf{y}_i)} \quad (2)$$

S_z is defined as the height difference between the average of five highest peaks and five lowest valleys in a sample region of 1 μm × 1 μm and is calculated by the equation displayed below:

$$S_z = \frac{\sum_{i=1}^5 |z_{pi}| + \sum_{i=1}^5 |z_{vi}|}{5} \quad (3)$$

where z_{pi} ($i = 1, 2, 3, 4, 5$) are the five highest peaks and z_{vi} are the five lowest valleys [8].

2.2.2.6. Brunauer–Emmett–Teller (BET) analysis. The surface area and pore volume of the synthesized membranes were evaluated with a Specific Surface Area and Porosity Analyzer PHS-1020 (PHS, China). The samples with an approximate weight of 0.04 g were degassed at 70 °C for 4 h, and then subjected to BET analysis at −196 °C. The specific surface area was calculated using the Langmuir (LAN) and BET methods (from the linear region of the isotherms' adsorption branch in the P/P_0 range of 0.05–0.3). Pore size distribution was obtained using the Barrett–Joyner–Halenda (BJH) method and the total pore volume was estimated from the amount of adsorbed N₂ at $P/P_0 = 0.98$.

2.2.2.7. Porosity measurement. The surface porosity was determined by the dry–wet weight method. The membranes were immersed in water for 24 h at room temperature, carefully wiped off with a clean tissue, and weighted. Then the membranes were dried in an oven at 50–60 °C for 24 h and weighed again in dry state. The membrane surface porosity was calculated using the following equation:

$$\text{Porosity} = \frac{W_w - W_d}{S \times l \times d} \quad (4)$$

where W_w is the weight of the wet membrane (g), W_d is the weight of the dry membrane (g), S is the surface area of the membrane (cm²), l is

the thickness of the membrane (cm) and d is the density of pure water at room temperature (g/cm³).

2.2.2.8. Contact angle measurements. Static and dynamic water contact angle (CA) measurements were performed at 25 °C using an OCA-30 Optical Contact Angle Meter (Dataphysics Instruments GmbH, Filderstadt, Germany). The membrane sample was firstly fixed onto a flat glass plate with double side tape. A 5 μL droplet of deionized water was detached from the stainless steel needle tip of syringe and stroked onto the membrane surface. Image of the droplet was recorded by a digital camera and static contact angle between the water and the membranes was determined according to the captured image and by using the evaluation software (SCA 20) provided by the instrument manufacturer. To minimize the experimental error, 4 samples for each membrane and 4 random locations for each sample were measured and the mean value of these 16 measurements was reported as the CA. Also, a video was recorded during spreading of the droplet on the surface of the glass slide from initial contact to equilibrium position.

The surface energy (W_A) was calculated using the following equation:

$$W_A = \gamma_w \cdot (1 + \cos\theta) \quad (5)$$

where γ_w is the surface tension of water equal to 7.28×10^{-2} N/m at room temperature.

2.2.2.9. Mechanical properties. The tensile tests of the specimens were carried out at room temperature by using a MTS Universal Testing Machine (Criterion. Model 42, Eden Prairie, MN, USA), equipped with a 100 N static load cell. PES composites were cut into 15 mm wide strips with a cutter. The film thickness of the tensile test specimen was determined by a hand-held micrometer (B.C. Ames, Waltham, MA) and reported as a mean of five measurements taken over the length of the strip. It was then used to estimate the cross-sectional area. The gauge length (i.e., the gap between the two jaws) at the start of each test was adjusted to 100 mm. Ends of film strips were mounted and clamped by using steel grip jaws. The measurements were performed with a crosshead speed of 10 mm/min.

The force (F) was recorded as a function of the sample elongation ($\Delta L = L - L_0$, where L_0 was the original gauge length) at room temperature and two properties were determined from the curves: (1) tensile strength (TS) or maximum nominal stress (σ), calculated by $\sigma = F/S_0$, where S_0 was the initial cross-sectional area of the sample, (2) elongation at break (EB), obtained as %elongation through dividing the extension at break by the initial sample length.

3. Results and discussion

3.1. Infrared spectroscopy analysis

Fig. 2 shows the FTIR spectra for synthesized membranes. The most representative bands of PES can be summarized as follows:

The band at 697 cm^{−1} is characteristic of C₆H₅ (phenyl groups) [9], the band at 717 cm^{−1} is ascribed to C—S groups [10], signals around 800 cm^{−1} are out-of-plane vibrations of the C—H bond [11], the band at 1010 cm^{−1} is assigned to stretching vibration of diphenyl C—O—C bond [12], the band at 1105 cm^{−1} is attributed to aromatic ring vibration [13], the sharp peak at 1144 cm^{−1} in the spectrum of PES belongs to the symmetric stretching of —SO₂— group [14], the bands at 1151 and 1244 cm^{−1} can depict the stretching vibrations of sulfur groups (S=O) [15], 1296 cm^{−1} is due to asymmetrical vibrations of the sulfone group [16], 1484 cm^{−1} is originated from benzene ring skeletal stretching mode [12], 1657 cm^{−1} is owned to aromatic in-plane ring bend stretching vibration.

According to the literature, the following peaks are observed in the FTIR spectrum of PVP: 572 cm^{−1} is ascribed to δ(N—C=O) [17],

Fig. 2. FTIR spectra for PES membranes with various MMCC contents (a), spectra zoomed in the 3800–3000 cm^{-1} range (b).

735–657 cm^{-1} is assigned to amide or CH_2 rocking band [18], 839 cm^{-1} is attributed to the vibrations occurred due to C–C ring bending [19], the vibrational peak observed at 894 cm^{-1} belongs to CH_2 rocking [20], 933 cm^{-1} corresponds to the C–C bonding [21] or out-of-plane rings C–H bending [22], 1017 cm^{-1} depicts the CH_2 rocking of PVP [23], 1072 cm^{-1} may be due to the C–N bond stretching mode [24], 1229 cm^{-1} is originated from the CH_2 twisting [25], 1288 cm^{-1} is owned to C–N stretching or CH_2 twisting or wagging [26], 1321 cm^{-1} is proportioned to CH_2 wagging [27], the absorption peak at ~1371 cm^{-1} is related to the C–H bond in PVP [28], ~1421 cm^{-1} and ~1458 cm^{-1} are ascribed to the $-\text{CH}_2$ absorption [28] or $\text{C}_4\text{N}-$ of PVP bond absorption [29], a small absorption band at about 1496 cm^{-1} is assigned to the characteristic vibration of $\text{C}=\text{N}$ (pyridine ring) [30], the band at 1663 cm^{-1} is attributed to the amide group of PVP [31], the vibrational peak observed at 2135 cm^{-1} belongs to CN stretching vibration [20], 2919 cm^{-1} corresponds to symmetric CH_2 stretching [32], 2955 cm^{-1} depict C–H bond vibrations [29] or asymmetric of $\nu(\text{CH}_2)$ pyrrole ring [17], and 3454 cm^{-1} is due to O–H bond vibrations [29].

As reported in the literature, the main observed FTIR bands and their assignments for cellulose are as follows: 665.5 cm^{-1} is ascribed to C–OH out-of-plane bending [33], the peak at 896 cm^{-1} is assigned to ring CH_2 rocking [34], ~1031 cm^{-1} is attributed to C–O–C stretching absorptions, 1106 cm^{-1} and 1160 cm^{-1} belong to C–O–C pyranose ring skeletal vibration, 1315 cm^{-1} depicts CH_2 wagging vibration in cellulose, 1364 cm^{-1} is due to CH bending, 1426 cm^{-1} is originated from CH_2 bending vibration, 1568 cm^{-1} is owned to N–H bending vibration, 1645 cm^{-1} is proportioned to O–H bending vibration of adsorbed

water, 2890 cm^{-1} is related to the asymmetrically stretching vibration of C–H in a pyranoid ring, and the band at 3332 cm^{-1} is ascribed to stretching vibration of –OH [33].

As can be seen, the position of the last FTIR peak with the highest wavenumber for neat PES membrane shifted toward lower wavenumber values for composite membranes. By this observation, polymer–filler interactions can be evidenced.

3.2. Thermal stability

Figs. 3 and 4 illustrate the TGA and differential thermogravimetry (DTG) curves of the samples, respectively. DTG curve of PES-0 membrane shows the presence of two main degradation peaks. The first peak, around 400 $^{\circ}\text{C}$, represents the decomposition of PVP and the second one occurs at around 500 $^{\circ}\text{C}$ and is due to the structural degradation of PES as the main phase in the membranes. PES and PVP have different chemical structures which in turn, result in differences in their decomposition temperature.

Three major degradation peaks can be characterized from the DTG curves for composite membranes. This additional peak that takes place at about 358.5, 349 and 337 $^{\circ}\text{C}$ in DTG curves for PES-0.5, PES-1 and PES-3, respectively, results from the decomposition of MMCC. The authors have previously reported that MMCC undergoes a single-step weight loss and starts to decompose at 270 $^{\circ}\text{C}$ [33]. The elevated decomposition temperature of MMCC when it is incorporated in the composite membrane can be an indication of strong interfacial matrix–filler

Fig. 3. TGA curves for membranes filled with different MMCC contents.

Fig. 4. dTG curves for membranes filled with various MMCC contents.

Table 2

Parameters extracted from TGA, DTG and D²TG for membranes filled with various MMCC contents.

Membrane	T ₀ (°C)	dT ₁₀ (°C)	dT ₅₀ (°C)	T _{max} (°C)	MT _{max} (°C)	MT ₈₀₀ (°C)
PES-0	381	400.01	517.96	409.01	0.236	18.68
PES-0.5	376	393.96	515.96	409.5	0.242	20.03
PES-1	371	378.48	503.23	407	0.257	26.23
PES-3	309	333.89	471.15	399	0.266	26.81

interactions through hydrogen bonds formation between functional groups of PES and hydroxyl groups of cellulose. As can be inferred from Fig. 4, in the first step, corresponding to MMCC decomposition, the maximum weight loss belongs to the membrane incorporated with the highest MMCC content, 3%, while in the region of about 500 °C, attributed to the PES decomposition, this membrane reveals the lowest peak height. This observation is explained by the fact that samples containing more MMCC have a lower PES content, and consequently, a lower weight loss at PES decomposition temperature is expected.

Table 2 presents some data extracted from the DTG curves: onset decomposition temperature (T₀), the temperature at 10 and 50% weight loss (T₁₀ and T₅₀, respectively), the temperature with the maximum decomposition rate and the percentage of weight loss corresponding to this temperature (T_{max} and MT_{max}, respectively). These results revealed a reduction in heat resistance with increasing the filler content and the composites exhibited thermal stability intermediate between the blend constituents, MMCC, PVP and neat PES. However, the thermogravimetric curve for the composite membrane did not show obvious weight loss at temperatures below 300 °C which indicates that they could fully satisfy the requirements for various membrane applications. Another parameter was the percentage of solid mass fraction remained at the final temperature, 800 °C, marked as MT₈₀₀ [35]. The differences in residual weight could be due to the chemicals used for MCC modification and introduction of MMCC into the composite membrane, which could induce higher char formation.

3.3. DSC analysis

Fig. 5 represents the DSC thermograms for membranes filled with different MMCC concentrations. Cellulosic fibers have marked hydrophilic character due to the preponderance of hydroxyl groups, located at equatorial positions on the glucopyranose ring. This hydrophilicity and consequently, their tendency to interact with water molecules cause that endothermic peaks corresponding to water vaporization occurs at elevated temperature for composite membranes compared to PES-0. Furthermore, T_g increased slightly by MMCC inclusion and all composites had higher values compared to neat PES (Table 3). This

Table 3

Glass transition temperature (T_g) of membranes loaded with different concentrations of MMCC.

Membrane	T _g (°C)
PES-0	211.6
PES-0.5	214.6
PES-1	213.3
PES-3	213.3

corresponds to polymer chains with constrained segmental motions as a result of increased interactions with the cellulose microcrystals surfaces.

3.4. SEM characterization

SEM images of the membrane surfaces are displayed in Fig. 6. The images demonstrated that all the composite membranes have rougher surface than the neat one.

Fig. 7 shows the SEM cross sectional images for neat and composite membranes. The micrographs revealed an anisotropic structure, comprising of a thin dense top-layer supported by a thicker and finger-like porous substructure. Also, large macro-voids are formed beneath the pores. SEM images show that the size of macro-voids in the sublayer for composites with 0.5 and 1 wt% is slightly larger compared to the neat PES membrane. The findings from microstructural imaging are corroborated by the total porosity measurements and also, by the surface area calculated via BET analysis (Table 5).

Upon immersion of the cast polymer solution in coagulation bath, the diffusional flow of DMSO (solvent) and water (non-solvent) is initiated which causes solvent/nonsolvent exchange that takes place across the interface of cast film and water. The diffusion of water into the cast film and incompatibility of PES chains with water molecules cause large repulsive forces between them and occurrence of polymer nucleation. Because of the continuation of the diffusional flow of solvent from the film solution to the surrounding area, these nuclei continue to grow until the polymer concentration at their boundaries becomes so high that solidification occurs (the demixing process is completed). The demixing process rate influences the membranes morphology. Instantaneous demixing often results in the formation of macrovoids in membrane structure, while in the case of slow demixing, a denser structure will be obtained [36].

The morphological difference caused by MMCC inclusion is mainly attributed to the fact that hydrophilic modified microcrystalline cellulose accelerates the velocity of water diffusion into the casting solution [37]. Also, interaction between MMCC and PES leads to easier and faster diffusion of DMSO molecules from the polymer matrix to the coagulation bath [38]. It can be concluded that in the

Fig. 5. DSC thermograms of membranes embedded with different MMCC contents.

Fig. 6. SEM micrographs of the surface of PES-0 (a), PES-0.5 (b), PES-1 (c) and PES-3 (d) membranes.

presence of MMCC (< 3 wt%), the thermodynamic instability of solution, and consequently, the diffusional exchange rate of DMSO solvent and water non-solvent increases during the demixing process which intensifies the instantaneous solidification [39]. The reverse trend for PES-3 can be attributed to the increase in the viscosity of the membrane solution at 3 wt% MMCC concentration which can hinder the exchange between solvent and nonsolvent and consequently, smaller pore size is achieved.

3.5. AFM analysis

Table 4 presents the surface roughness parameters of the membranes, expressed in terms of mean roughness (S_a), root mean square of the Z data (S_q) and mean difference between the highest peaks and lowest valleys (S_z) which were obtained from AFM images at scan size of $10\ \mu\text{m} \times 10\ \mu\text{m}$ and by using Nova v.1.26.0.1443 for Solver software. According to this table, the order of increasing roughness was: 0 wt% < 0.5 wt% < 1 wt% < 3 wt%, confirming that all membranes incorporated with MMCC had higher roughness compared to neat PES. The results from AFM analysis are consistent with the morphologies observed by SEM images. Similar results have been obtained in the case of polylactic acid composites reinforced with oil palm biomass MCC and reported by Mohamad Haafiz et al. (2013) [40].

The hydrophilicity of MMCC leads to an acceleration in the ratio of solvent outflow and nonsolvent inflow of the polymer system. Therefore, the composites containing less than 3% MMCC had larger pore size and rougher surface. At 3%, MMCC tend to agglomerate

through interfacial hydrogen bonds formation, due to the omnipresence of interacting hydroxyl groups of cellulose and amine groups of metformine HCl. The formed agglomerates cause that the increasing trend in roughness continues at this concentrations. A higher roughness results in poor antifouling efficacy because of fouling accumulation in the rough membrane valleys but the increased porosity and hydrophilicity of the membrane surface due to the introduction of hydrophilic MMCC, causes an increase in the membrane permeability. Therefore, the solid materials adsorbed on the composite membrane can be removed more easily by the shear forces of a hydraulic backwashing, and the fouling created by them can be classified in the category of reversible fouling [41].

Fig. 8 shows the two and three-dimensional surface AFM images for PES-0 and PES-3 as the membranes with the lowest and the highest roughness, respectively. In these images, the color brightness represents the vertical dimension of the membrane. The highest points of the membrane surface are indicated as light areas and the valley or membrane pores are presented as dark regions.

3.6. Surface area and pore size determination

Brunauer-Emmett-Teller (BET), Langmuir and Barrett-Joyner-Halenda (BJH) isotherms were plotted and the data extracted from these three plots were collected and summarized in Table 5. The surface area (a_s) was obtained by the BET method in the relative pressure range of 0.05 to 0.3. The obtained values for a_s ($21.67\text{--}24.14\ \text{m}^2\ \text{g}^{-1}$) were similar to those reported by Gohari et al. (2018) for polyethersulfone membranes filled with modified

Fig. 7. SEM micrographs of the cross section of PES-0 (a), PES-0.5 (b), PES-1 (c) and PES-3 (d) membranes; S: surface, B: bottom.

alumina nanoparticles ($20.6\text{--}35.6\text{ m}^2\text{ g}^{-1}$) [38]. The total pore volume was determined by the nitrogen absorbance value at $P/P_0 = 0.99$. The absorption on the external surface was assumed negligible in comparison with the absorption in the pores.

Fig. 9 shows the nitrogen adsorption-desorption isotherms. According to IUPAC classifications, all investigated nanocomposites exhibited type IV isotherms, showing the mesoporous nature of the materials, and type H_3 hysteresis loops.

3.7. Porosity determination

The results of porosity measurements are listed in Table 6. Consistent with the microscopic observations, composites filled with 0.5 and 1% MMCC were more porous compared to PES-0 membrane. The description used to interpret the results of the roughness obtained by AFM can also be applied to the interpretation of porosity findings. The obtained values in the present work were within the reported range

(~14% to ~47%) for a proton exchange membrane consisting of PES, PVP and SiO_2 solid spheres (10 wt% to 50 wt%) [42].

3.8. Surface hydrophilicity

The contact angle between the membrane surface and water can express the hydrophilic character of the membrane. A lower contact angle implies that the membrane has higher hydrophilic characteristics. Higher hydrophilicity along with lower roughness values can result in better antifouling properties and also, higher water flux of the mixed matrix membranes. According to Fig. 10 and Table 7, the water contact angle (WCA) decreased in the presence of MMCC and PES-1 exhibited the lowest value. Therefore, it can be concluded that the incorporation of hydrophilic MMCC containing a great amount of hydroxyl groups improved the hydrophilic nature of the PES membrane. Similar observation was made by Qu et al. (2010) in the case of PES membrane loaded with unmodified MCC [5].

Compared to the neat PES membrane, the surface energy of composites increased and reached its maximum value at 1% MMCC concentration. Our results are in agreement with those of Qu et al. (2010) [5].

3.9. Mechanical properties

Fig. 11 reports TS and EB values, extracted from the stress-strain curves for the PES membrane and composites filled with various concentrations of MMCC. The observed improvement in tensile strength of many composites loaded with micro/nano cellulose may be attributed to the reinforcement effect and homogeneous dispersion of this

Table 4

Mean roughness (S_a), root mean square of the Z data (S_q) and mean difference between the highest peaks and lowest valleys (S_z).

Membrane	S_a (nm)	S_q (nm)	S_z (nm)
PES-0	10.08	12.97	52.95
PES-0.5	18.57	23.69	95.25
PES-1	23.22	30.86	130.52
PES-3	32.29	41.62	199.06

Fig. 8. Two (left) and three (right) dimensional surface AFM images for PES-0 (top) and PES-3 (bottom).

high-strength filler in the host matrix. Chemical compatibility between the membrane constituents (the filler and the matrix) plays a critical role in this even distribution and also, in the adhesion between them [43]. The more particles are in contact with the polymer, the higher is a probability of interaction. The large contact area allows an efficient stress transfer between both materials which in turn improves the stiffness and strength. On the other hand, the tensile fracture of the membrane can result from the destruction of intermolecular sintering joints and porosity is the decisive factor that inversely influences the number of junction zones. So, the pores are preferred nucleation sites for fatigue cracks and the failure process is initiated from the voids. Therefore, an increase in porosity should

have an adverse effect on the fracture strength for all dense brittle materials.

In the present work, the differences between TS and EB values are within the limits of the standard deviations, therefore, it can be concluded that the strength and elongation at break remain constant by MMCC addition and by increasing its concentration from 0.5 to 3%. This is probable that reinforcement effect of MMCC on TS is counteracted by the weakening effect of higher porosity in composites compared to neat PES. A similar result has been reported by Mathew et al. (2013). They evaluated the effect of incorporating MCC on the morphological, thermal and mechanical properties of polylactic acid (PLA) as a matrix. There was no significant change

Table 5
Parameters extracted from BET, Langmuir and BJH plots.

Membrane	BET plot			Langmuir plot		BJH plot		
	V_m [cm ³ (STP) g ⁻¹]	$a_{s,BET}$ [m ² g ⁻¹]	Total pore volume ($p/p_0 = 0.990$) [cm ³ g ⁻¹]	V_m [cm ³ (STP) g ⁻¹]	$a_{s,Lang}$ [m ² g ⁻¹]	V_p [cm ³ g ⁻¹]	$r_{p,peak}$ (Area) (nm)	a_p [m ² g ⁻¹]
PES-0	5.1397	22.370	0.2253	5.1998	22.632	0.2262	1.29	22.452
PES-0.5	5.2001	22.633	0.2296	5.2006	22.635	0.2309	1.29	23.413
PES-1	5.5468	24.142	0.2309	5.4022	23.513	0.2335	1.29	27.379
PES-3	4.9794	21.673	0.1928	4.9101	21.371	0.1943	1.29	23.029

Fig. 9. BET adsorption/desorption isotherms for membranes loaded with 0% (a), 0.5% (b), 1% (c) and 3% (d) MMCC.

in strength values for the composites when compared to neat PLA film [44].

4. Conclusion

FTIR analysis showed that a suitable level of molecular compatibility was achieved based on the interfacial matrix-filler interactions through hydrogen bonds formation between functional groups of PES and PVP and hydroxyl groups of MMCC. The addition of MMCC enhanced the glass transition temperature, total porosity, Brunauer–Emmett–Teller surface area, and hydrophilicity of the membranes. Although the thermal stability decreased in the presence of MMCC, the thermograms showed that the weight loss of the composite membrane was limited at temperatures lower than 300 °C, indicating that they can meet all the requirements for different membrane applications. Two main stages

Fig. 10. Contact angle versus time for different membranes.

Table 6
porosity percentage for membranes filled with various amounts of MMCC.

Membrane	Porosity (%)
PES-0	40.54
PES-0.5	47.31
PES-1	48.90
PES-3	38.97

Table 7
Contact angle and surface energy for membranes with different MMCC contents.

Membrane	Contact angle (°)	Surface energy (mN.m ⁻²)
PES-0	77.85	88.12
PES-0.5	67.45	100.72
PES-1	66.19	102.19
PES-3	71.6	95.78

Fig. 11. Tensile strength and elongation at break for membranes filled with 0, 0.5, 1 and 3% MMCC.

of weight loss were observed in the TGA curves for the pure PES membrane because of thermal degradation of PVP and PES. The additional stage in the case of composites is attributed to MMCC decomposition. No statistically significant change was observed in the mechanical properties of the membrane by MMCC inclusion.

CRediT authorship contribution statement

Fatemeh Rafieian: Conceptualization; Methodology; Software; Validation; Formal Analysis; Data curation; Writing –original draft; Writing – Review & Editing; Visualization.

Mohammad Mousavi: Writing – Review & Editing; Supervision; Project administration.

Alain Dufresne: Writing – Review & Editing; Supervision.

Qingliang Yu: Resources; Writing – Review & Editing; Supervision; Funding acquisition.

Acknowledgements

The authors are grateful to the Built Environment Department (TU/e, Netherlands) and Iran National Science Foundation for the financial support of this research project # 95001134.

References

- [1] N. Singh, G. Nagpal, S. Agrawal, Water purification by using adsorbents: a review, *Environ. Technol. Innov.* 11 (2018) 187–240.
- [2] M. Ghangrekar, P. Chatterjee, Water Pollutants Classification and its Effects on Environment, Carbon Nanotubes for Clean Water, Springer, 2018 11–26.
- [3] S.A. Al-Saydeh, M.H. El-Naas, S.J. Zaidi, Copper removal from industrial wastewater: a comprehensive review, *J. Ind. Eng. Chem.* 56 (2017) 35–44.
- [4] K. Khulbe, T. Matsuura, Removal of heavy metals and pollutants by membrane adsorption techniques, *Appl Water Sci* 8 (1) (2018) 19.
- [5] P. Qu, H. Tang, Y. Gao, L. Zhang, S. Wang, Polyethersulfone composite membrane blended with cellulose fibrils, *BioResources* 5 (4) (2010) 2323–2336.
- [6] F. Rafieian, J. Simonsen, The effect of carboxylated nanocrystalline cellulose on the mechanical, thermal and barrier properties of cysteine cross-linked gliadin nanocomposite, *Cellulose* 22 (2) (2015) 1175–1188.
- [7] X. Yu, S. Tong, M. Ge, L. Wu, J. Zuo, C. Cao, W. Song, Adsorption of heavy metal ions from aqueous solution by carboxylated cellulose nanocrystals, *J. Environ. Sci.* 25 (5) (2013) 933–943.
- [8] A. Rahimpour, M. Jahanshahi, B. Rajaeian, M. Rahimnejad, TiO₂ entrapped nanocomposite PVDF/SPES membranes: preparation, characterization, antifouling and antibacterial properties, *Desalination* 278 (1–3) (2011) 343–353.
- [9] L.M. Munirathnamma, H.B. Ravikumar, Positron lifetime study of PAN-based carbon fiber-reinforced polymer composites, *Polym. Compos.* 40 (S2) (2019) E939–E952.
- [10] B. Malczewska, A. Żak, Structural changes and operational deterioration of the Uf Polyethersulfone (Pes) membrane due to chemical cleaning, *Sci. Rep.* 9 (1) (2019) 422.
- [11] I.G. Sandoval-Olvera, L. Villafañá-López, J.A. Reyes-Aguilera, M. Ávila-Rodríguez, T.A. Razo-Lazcano, M.P. González-Muñoz, Surface modification of polyethersulfone membranes with goethite through self-assembly, *Desalin. Water Treat.* 65 (2017) 199–207.
- [12] A. Jalali, A. Shockravi, V. Vatanpour, M. Hajibeygi, Preparation and characterization of novel microporous ultrafiltration PES membranes using synthesized hydrophilic polysulfide-amide copolymer as an additive in the casting solution, *Microporous Mesoporous Mater.* 228 (2016) 1–13.
- [13] E. Drioli, L. Giorno, *Comprehensive Membrane Science and Engineering*, Newnes, 2010.
- [14] Z. Zuo, L. Song, Y. Yang, Tribological behavior of polyethersulfone-reinforced polytetrafluoroethylene composite under dry sliding condition, *Tribol. Int.* 86 (2015) 17–27.
- [15] N. Phao, Synthesis and application of novel functionalized nanostructured membranes incorporating N-doped CNT supported metal nanoparticles in water treatment, *Procedia Engineering* 44 (2012) 1496–1501.
- [16] Nurmin Bolong, Ahmad Fauzi Ismail, Mohd. Razman Salim, T. Matsuura, Miscibility characteristics of poly (ethersulfone)(pes) hollow fiber membranes with charged-surface modifying macromolecules (csmm) for water separations applications, *Jurnal Teknologi* 49 (2008) 123–132.
- [17] A. Rahma, M.M. Munir, A. Prasetyo, V. Suendo, H. Rachmawati, Intermolecular interactions and the release pattern of electrospun curcumin-poly(vinyl pyrrolidone) fiber, *Biol. Pharm. Bull.* 39 (2) (2016) 163–173.
- [18] P. Vasudevan, S. Thomas, P. Biju, C. Sudarsanakumar, N. Unnikrishnan, Synthesis and structural characterization of sol–gel derived titania/poly (vinyl pyrrolidone) nanocomposites, *Journal of Sol-Gel Science Technology* 62 (1) (2012) 41–46.
- [19] I.M. Alibe, K.A. Matori, H.A.A. Sidek, Y. Yaakob, U. Rashid, A.M. Alibe, M.H.M. Zaid, S. Nasir, M.M. Nasir, Effects of polyvinylpyrrolidone on structural and optical properties of willemit semiconductor nanoparticles by polymer thermal treatment method, *J. Therm. Anal. Calorim.* 136 (6) (2019) 2249–2268.
- [20] N. Vijaya, S. Selvasekarapandian, H. Nithya, C. Sanjeeviraja, Proton conducting polymer electrolyte based on poly (N-vinyl pyrrolidone) doped with ammonium iodide, *International Journal of Electroactive Materials* 3 (2015) 20–27.
- [21] N. Vijaya, S. Selvasekarapandian, G. Hirankumar, S. Karthikeyan, H. Nithya, C. Ramya, M. Prabhu, Structural, vibrational, thermal, and conductivity studies on proton-conducting polymer electrolyte based on poly (N-vinylpyrrolidone), *Ionics* 18 (1–2) (2012) 91–99.
- [22] N. Rajeswari, S. Selvasekarapandian, S. Karthikeyan, H. Nithya, C. Sanjeeviraja, Lithium ion conducting polymer electrolyte based on poly (vinyl alcohol)–poly (vinyl pyrrolidone) blend with LiClO₄, *Int. J. Polym. Mater.* 61 (14) (2012) 1164–1175.
- [23] A. Abdelghany, M.S. Mekhail, E. Abdelrazek, M. Aboud, Combined DFT/FTIR structural studies of monodispersed PVP/gold and silver nano particles, *J. Alloys Compd.* 646 (2015) 326–332.
- [24] N. Soltani, E. Saion, M. Erfani, K. Rezaee, G. Bahmanrokh, G.P. Drummen, A. Bahrami, M.Z. Hussein, Influence of the polyvinyl pyrrolidone concentration on particle size and dispersion of ZnS nanoparticles synthesized by microwave irradiation, *Int. J. Mol. Sci.* 13 (10) (2012) 12412–12427.
- [25] W. El Hotaby, H. Sherif, B. Hemdan, W. Khalil, S. Khalil, Assessment of in situ-prepared polyvinylpyrrolidone-silver nanocomposite for antimicrobial applications, *Acta Phys. Pol. A* 131 (6) (2017).
- [26] H.M. Zidan, E.M. Abdelrazek, A.M. Abdelghany, A.E. Tarabiah, Characterization and some physical studies of PVA/PVP filled with MWCNTs, *Journal of Materials Research Technology* 8 (1) (2019) 904–913.
- [27] M. Behera, S. Ram, Interaction between poly (vinyl pyrrolidone) PVP and fullerene C60 at the interface in PVP-C60 nanofluids—a spectroscopic study, *IOP Conference Series: Materials Science and Engineering*, IOP Publishing 2018, p. 012016.
- [28] D. Baganizi, E. Nyairo, S. Duncan, S. Singh, V. Dennis, Interleukin-10 conjugation to carboxylated PVP-coated silver nanoparticles for improved stability and therapeutic efficacy, *Nanomaterials* 7 (7) (2017) 165.
- [29] B. Sadeghi, M. Sadjadi, A. Pourahmad, Effects of protective agents (PVA & PVP) on the formation of silver nanoparticles, *International Journal of Nanoscience and Nanotechnology* 4 (1) (2008) 3–12.
- [30] A.R. Polu, R. Kumar, H.-W. Rhee, Magnesium ion conducting solid polymer blend electrolyte based on biodegradable polymers and application in solid-state batteries, *Ionics* 21 (1) (2015) 125–132.

- [31] A. Moarefian, H.A. Golestani, H. Bahmanpour, Removal of amoxicillin from wastewater by self-made Polyethersulfone membrane using nanofiltration, *Journal of Environmental Health Science Engineering* 12 (1) (2014) 127.
- [32] I.A. Safo, M. Werheid, C. Dosche, M. Oezaslan, The role of polyvinylpyrrolidone (PVP) as capping and structure-directing agent in the formation of Pt nanocubes, *Nano-scale Advances* 1 (2019) 3095–3106.
- [33] F. Rafieian, M. Mousavi, Q. Yu, M. Jonoobi, Amine functionalization of microcrystalline cellulose assisted by (3-chloropropyl) triethoxysilane, *Int. J. Biol. Macromol.* 130 (2019) 280–287.
- [34] A.K. Agarwal, R.A. Agarwal, T. Gupta, B.R. Gurjar, *Biofuels: Technology, Challenges and Prospects*, Springer, 2017.
- [35] A. Kaushik, M.J.C. Singh, Isolation and characterization of cellulose nanofibrils from wheat straw using steam explosion coupled with high shear homogenization, *Carbohydr. Res.* 346 (1) (2011) 76–85.
- [36] E. Saljoughi, M. Amirilargani, T. Mohammadi, Effect of poly (vinyl pyrrolidone) concentration and coagulation bath temperature on the morphology, permeability, and thermal stability of asymmetric cellulose acetate membranes, *J. Appl. Polym. Sci.* 111 (5) (2009) 2537–2544.
- [37] L. Zhang, G. Chen, H. Tang, Q. Cheng, S. Wang, Preparation and characterization of composite membranes of polysulfone and microcrystalline cellulose, *J. Appl. Polym. Sci.* 112 (1) (2009) 550–556.
- [38] B. Gohari, N. Abu-Zahra, Polyethersulfone membranes prepared with 3-aminopropyltriethoxysilane modified alumina nanoparticles for Cu (II) removal from water, *ACS Omega* 3 (8) (2018) 10154–10162.
- [39] R. Abedini, Enhanced antifouling properties of poly (ethersulfone) nano-composite membrane filled with nano-clay particles, *Polym. Bull.* 76 (4) (2019) 1737–1753.
- [40] M.M. Haafiz, A. Hassan, Z. Zakaria, I.M. Inuwa, M.S. Islam, M. Jawaid, Properties of polylactic acid composites reinforced with oil palm biomass microcrystalline cellulose, *Carbohydr. Polym.* 98 (1) (2013) 139–145.
- [41] S. Ayyaru, Y.-H. Ahn, Fabrication and separation performance of polyethersulfone/sulfonated TiO₂ (PES–STiO₂) ultrafiltration membranes for fouling mitigation, *J. Ind. Eng. Chem.* 67 (2018) 199–209.
- [42] Z. Guo, R. Xiu, S. Lu, X. Xu, S. Yang, Y. Xiang, Submicro-pore containing poly (ether sulfones)/polyvinylpyrrolidone membranes for high-temperature fuel cell applications, *J. Mater. Chem. A* 3 (16) (2015) 8847–8854.
- [43] K.B. Nilagiri Balasubramanian, T. Ramesh, Role, effect, and influences of micro and nano-fillers on various properties of polymer matrix composites for microelectronics: a review, *Polym. Adv. Technol.* 29 (6) (2018) 1568–1585.
- [44] A.P. Mathew, K. Oksman, M. Sain, Mechanical properties of biodegradable composites from poly lactic acid (PLA) and microcrystalline cellulose (MCC), *J. Appl. Polym. Sci.* 97 (5) (2005) 2014–2025.