

High-Flux, Porous and Homogeneous PVDF/ Cellulose Microfiltration Membranes

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Abstract

Low hydrophilicity of membranes is probably the biggest concern in membrane filtration since it increases the costs for water treatment. Conversely, application of hydrophilic biopolymers (such as cellulose) is limited because of its complex and crystalline structure. Enabling the widely use of the most common biopolymer in nature is crucial to improve the performance of water treatment, especially in terms of membrane sustainability. Here, we study the effect of cellulose dissolution in the synthesis of homogeneous PVDF/cellulose membranes. Although only partial dissolution was achieved for studied samples, adding cellulose to the membranes greatly improved their water flux. Besides, the porous structure obtained after partial solvent removal indicates the WF (and consequently the pore size) may be tailored according to the membrane production method. Therefore, the homogeneous cellulose microfiltration membranes studied here may have potential for water treatment considering their high-water flux and low complexity to produce.

1. Introduction

Water is considered a finite resource essential for life that is distributed around earth. Nevertheless, 97% is represented by non-potable seawater and, from the remaining freshwater, most is entrapped as ice glaciers thus virtually inaccessible (Wang et al. 2017). This issue was even of more interest in Israel due to the low availability of freshwater resources in this semi-arid country located in the middle east. Therefore, the water shortage along with the exponential population growth after Israel's independence turned essential for the technological development to fulfill population demands. The first desalination plant in the country was opened in the late 90s which, along with other reuse and preservation practices (wastewater treatment, water conservation, etc.), enabled Israel's self-sustainability and commercialization of water surplus to neighbor countries (Weinglass 2015; IMFA 2018).

The first milestone within water treatment technology was the development in the 60s of desalination membranes of different types from which derivatized cellulose ones (cellulose acetate) stood out, presenting over 90% salt rejection (Loeb & Sourirajan 1963; 1964). Over the years, new materials have been used to improve water treatment efficiency even further and to overcome the limitations of cellulose acetate membranes, especially the pH stability and rejection (Voicu et al. 2015). One of these materials is polyvinylidene fluoride (PVDF), which is considered an ideal polymer in water treatment for its improved mechanical, chemical and thermal stability (Razzaghi et al. 2014).

Nevertheless, the hydrophobic behavior of neat PVDF results in membranes with low water flux and rejection, which affects membrane efficiency in industrial scale. One alternative to overcome these drawbacks without compromising their stability is to mix PVDF with more hydrophilic materials, such as nanocellulose (Bai et al. 2012; Lalia et al. 2014; Lv et al. 2018; Zhang et al. 2017). However, none of these methods could accomplish cellulose dissolution when used along with other polymers; yet these were only able to disperse the cellulose within the membranes. This is due to its complex and crystalline

structure that makes it insoluble in most organic solvents (Hu, et al. 2018; Ishii et al. 2008; Zhang et al. 2014).

From the most common dissolution methods, the non-aqueous ones seem to be the most appropriate because water hinders the synthesis of PVDF membranes (Xiong et al. 2014; Xu et al. 2013). The well-studied LiCl/DMAc dissolution method can be a good alternative since it was reported to generate stable dissolved cellulose solutions for over an year (Dupont 2003). It consists in the heat activation of cellulose to allow fibers swelling in DMAc, followed by the interaction of LiCl between cellulose hydroxyl groups, thus leading to its dissolution (Ishii et al. 2008; Zhang et al. 2014).

Here, the effect of nanocellulose in PVDF membranes water flux is studied. To the best of our knowledge, no other study attempted to dissolve nanocellulose for water treatment membranes. The PVDF/nanocellulose porous membranes were prepared through partial solvent evaporation, followed by phase-inversion, using different types of cellulose (pristine, cellulose nanocrystals and cellulose nanofibers). The performance of the membranes was evaluated according to their water flux and their structure was characterized by SEM.

2. Material And Methods

2.1 MATERIAL

Bleached Eucalyptus Pulp (BEP) (obtained from Suzano Papel e Celulose, Brazil) was used as raw material to prepare the cellulose nanocrystals (CNC) by acid hydrolysis and the nanofibers (CNF) by defibrillation. Microcrystalline cellulose (Avicel, PH 101) was acquired from Sigma-Aldrich (Saint-Louis, USA) and used without modification as a blank. Polyvinylidene fluoride (PVDF), with an average molecular weight of 500,000, and the N, N-dimethylacetamide (DMAc) (38840, lot BCBW9878) were also acquired from Sigma-Aldrich.

2.2 METHODS

2.2.1 Preparation of cellulose nanofibers (CNF) and nanocrystals (CNC)

Based on the method described in Morais et al. (2013), BEP CNC and Avicel CNC were produced with minor modifications, as follow. Both sources (Avicel and BEP) were added into H₂SO₄ (60% m/m) at 1:20 (w/v) and stirred at 45 °C for 30 min. Then, the solids were washed thoroughly with distilled water and filtered to remove residual acids and dissolved sugars. The solids were resuspended in water and sonicated in a Sonics (Sonics & Materials, inc.) Vibra-Cell VCX 130 (Newtown, USA) at an 80 % power input for 10 min to disperse cellulose aggregates. The colloidal suspensions were dialyzed in tap water to neutral pH for at least 5 days using D9527-100 ft. dialysis tubing membranes from Sigma-Aldrich (St. Louis, USA). To produce the CNF, BEP was soaked at 1% in 2 L distilled water, dispersed using a lab mixer and ground in a MKCA 6-2J super mass collioder, Masuko Sangyo (Kawaguchi, Japan) for 3 cycles.

The colloidal suspensions (Avicel CNC, BEP CNC and BEP CNF) were spray-dried in an Elettronica Veneta MDS/EV spray-dryer (Motta di Livenza, Italy). This step was necessary since LiCl/DMAc-assisted dissolution of cellulose is sensitive to the presence of water and to avoid aggregation of nanocrystals. The procedure for producing both CNC and CNF is represented in Fig. 1.

2.2.3 X-ray diffractometry (XRD)

The X-ray diffractogram patterns were obtained in an X-ray Diffractometer X XRD 700 (Shimadzu, Japan) using Cu-K α radiation ($k = 1.5418 \text{ \AA}$), 40 kV and 20 mA. The scattered radiation was detected in the angular range of 5-40° ($2q$), with a scanning speed of 2° min⁻¹ ($2q$) and a step of 0.02° ($2q$). Segal crystallinity index was calculated according to Eq. (1) (Segal et al. 1959):

$$\text{Crystallinity index} = \frac{(I_{200} - I_{am})}{I_{200}} \quad (1)$$

where I_{200} refers to the maximum intensity due to reflections of the planes (200) around 23° and I_{am} to the amorphous contribution, at the minimum intensity between 15° < $2q$ < 23° (at approximately 18° ($2q$)) (French and Santiago Cintrón 2013). Prior to the crystallinity index calculation, the diffractograms were smoothed in the software OriginPro 8, using the Savitzky–Golay method (50 points) and a second order polynomial function. The baseline correction was performed by subtracting a straight line between the points of least intensity in the range of $2q$ of 5° and 40°, as previously proposed by Agarwal et al. (2018).

2.2.4 Cellulose dissolution

All cellulose samples (Avicel, Avicel CNC, BEP CNC and BEP CNF) and LiCl were previously dried at 70 °C in a JSR JSVO-60 T vacuum oven (Gongju city, South Korea) for at least 24 h to remove residual moisture, which could affect the dissolution efficiency. The dissolution method was based on Hu et al. (2018) and Ishii et al. (2008), using the cellulose to DMAc/LiCl ratio (w/w) of 3/97. First, each of the dried cellulose samples was mixed with DMAc, heated to 150 °C and stirred for 1 h. Heating the DMAc just below its boiling point is crucial for cellulose activation and consequent dissolution since it allows the penetration of the solvent and swelling of the fibers (Dupont 2003). Next, the temperature was decreased to 100 °C and LiCl was added to the system. The amount of LiCl was that necessary to reach 8 wt% LiCl in DMAc. After complete dissolution of the salt (at least 30 min stirring), the temperature was decreased to 50 °C and the solution was stirred for at least 16 h. Afterwards, the solution was let to stand at room temperature for 24 h and the cellulose was considered dissolved if the final solution became clear.

2.2.5 Synthesis of PVDF membranes

The membranes were produced by Sourirajan-Loeb method (a.k.a. phase inversion) (Loeb and Sourirajan 1963) with the modifications as follow. PVDF and different amounts of each dissolved cellulose source (Avicel, Avicel CNC, BEP CNC or BEP CNF) were added to reach the final concentration of cellulose into the casting solution of 1%. During preliminary studies, it was decided to use a polymer to solvent ratio of

15:85 (m/m) since higher amounts of polymers could lead to high viscosity gels, which hindered the pouring and casting to make the membranes. The PVDF powder was added into DMAc, heated to 60 °C and stirred at 200 rpm until completely dissolved. Only then, the dissolved cellulose (in DMAc) was added to the casting solution and stirred until obtaining a homogeneous solution. The importance of dissolution on the membranes properties was also checked by using the same cellulose sources. For this, each cellulose source (in powder) was directly mixed with PVDF dissolved in DMAc to make PVDF/cellulose blends without the cellulose pre-dissolution step.

To prepare the membranes, around 1.5 mL of each casting solution (PVDF, DMAc and dispersed/dissolved cellulose) was poured onto individual glass plates and smeared using a Sheen 1107/80/1 casting knife (Ho Chi Minh, Vietnam) at a 120 mm gap size between the plate and the knife. The casted membranes were then immersed into a distilled water bath (around 20 °C) to allow the remaining solvent (DMAc) migration to water. Partial solvent evaporation influence on the membrane properties and structure was also investigated in additional trials as it can induce the formation of sponge-like pores rather than finger-like structures by reducing solvent-nonsolvent exchange (Guillen et al. 2011). Therefore, the casted solutions were previously heated in a vacuum oven drier (National Appliance Co. USA) at 75 °C until dry (around 11 min). The relative humidity (RH) was recorded during the tests and it ranged from 10-15 %. Then, the membranes were immersed in distilled water, as usual, and the detached membranes (with or without partial solvent evaporation) were washed under flowing distilled water and kept immersed in distilled water filled flasks until further analysis.

2.2.6 Scanning electron microscopy (SEM)

The SEM analyzes were performed using a TESCAN Vega-II (Brno, Czech Republic) equipment which was configured with 20 mm reading scale and 10 kV tension. For surface analysis, small pieces of the membranes were cut and clued on carbon tape. For cross-section, small pieces of the membranes were frozen and snapped in liquid nitrogen and supported in SEM stubs using a G 302 PLANO GmbH quick-drying conductive silver glue (Wetzlar, Germany). Then, the samples were metalized with gold and analyzed in an electron detector.

2.2.7 Water flux (WF)

The efficiency of membranes according to their water flux was measured using the dead-end filtration system represented in Bussi et al. (2018). Briefly, distilled water was added to system and the membranes were maintained under water at a constant pressure (3 bar) for at least 2 h to reach their equilibrium. Then, the membranes WF was measured from 1 to 10 bar. The measurements were conducted in triplicate for each type of membrane.

2.2.8 Statistical analysis

For statistical analysis, analysis of variance (ANOVA) and Tukey's test were employed to compare samples average at a 95% confidence level ($p < 0.05$) using Statistica 13.3 software (StatSoft, Inc, Tulsa,

OK, USA).

3. Results And Discussion

3.1 XRD

As expected, the partial removal of the amorphous portion from cellulose increased the crystallinity index of BEP CNC (~88%) compared to BEP CNF (~79%) (Fig. 2). The higher crystallinity index of Avicel CNC (~90%) compared to BEP CNC (88%) is due to the higher purity of Avicel (in terms of cellulose content) since it consists in pure cellulose rather than a mix of cellulose and hemicellulose in BEP (Malucelli et al. 2018).

3.2 Cellulose dissolution

Cellulose is usually dissolved using the LiCl/DMAc system in concentrations up to 3%, even for high molecular weight cellulose (Hu et al. 2018; Jing et al. 2007). However, the molecular weight of wood pulp tends to be much higher than pure cellulose. Therefore, complete dissolution is only achieved by reducing the cellulose and LiCl/DMAc ratio. In earlier studies, Sjöholm et al. (2000) could only dissolve bleached and unbleached wood pulp using much lower amounts of sample (around 0.5% bleached wood pulp in total solution). Consequently, BEP CNF was only partially dissolved using this same ratio (0.5/ 99.5 cellulose/LiCl and DMAc) since higher cellulose content resulted in cellulose agglomerates and a viscous hazy solution. The minimum amounts of cellulose (in respect of its source), LiCl, DMAc and their ratio used in the partial dissolution tests are represented in Table 1.

Table 1 – Required concentration of cellulose from different sources, LiCl and DMAc to ensure its partial dissolution.

Sample	Cellulose % (m/m)	LiCl % (m/m)	DMAc % (m/m)	Cellulose to LiCl/DMAc ratio
Avicel	3	8	89	3/97
Avicel CNC	2	8	90	2/98
BEP CNC	2	8	90	2/98
BEP CNF	0.5	8	91.5	0.5/99.5

BEP – bleached eucalyptus pulp; CNC – cellulose nanocrystals; CNF – cellulose nanofibers.

These results suggest that the size and composition of the fibers have a higher influence than the crystallinity index towards cellulose dissolution (Isogai and Atalla 1998). Although the influence of cellulose crystallinity in dissolution is a controversial aspect (Parviainen et al. 2014; Ramos et al. 2011), it appears that dissolution is only complete if decrystallization and disentanglement are combined (Ghasemi et al. 2017). BEP CNF have a much more complex structure than their respective nanocrystals (BEP CNC – after acid hydrolysis) since it is basically composed of interchained cellulose and around

15% hemicellulose (Malucelli et al. 2018). Therefore, the lower availability of cellulose and the higher degree of polymerization in BEP CNF (as suggested by its apparent high viscosity) explains their low dissolution ability (only 0.5% cellulose in total solution). On the other hand, dissolution was facilitated using cellulose with low degree of polymerization (such as Avicel) or after acid hydrolysis (Avicel CNC or BEP CNC). The removal of amorphous domains by acid hydrolysis probably improved the susceptibility of cellulose for dissolution (Lu and Hsieh 2010).

3.3 Membranes preparation

Because of the low dissolution ability of BEP CNF, it was not possible to make 1% BEP CNF membranes while maintaining DMAc, PVDF and LiCl concentrations constant (the maximum concentration possible was 0.25% BEP CNF in total solution). Therefore, it was decided not to include these membranes in the water flux and surface/ cross-section characterization studies. The amount of each component used to produce the membranes is shown in Table 2.

Table 2 – Procedure to prepare the PVDF and cellulose (Avicel, Avicel CNC and BEP CNC) membranes with or without partial solvent evaporation.

Membranes	PVDF %	DMAc %	Dispersed cellulose %	Dissolved cellulose %	Solvent evaporation?
PVDF/ cellulose blends	15	75	10	-	No
Blank PVDF	15	85	-	-	No
PVDF + cellulose	15	84	-	1	No
Blank PVDF	15	85	-	-	Yes
PVDF + cellulose	15	84	-	1	Yes

BEP – bleached eucalyptus pulp; CNC – cellulose nanocrystals.

The visual aspect of the membranes was similar despite the partial solvent evaporation used for some of the samples. It was interesting to observe that the surface of the membranes was very homogeneous even for those containing partially dissolved cellulose. In preliminary studies using dispersed cellulose (rather than dissolved cellulose), the PVDF membranes were very heterogeneous with several surface micropores (showing low mechanical strength) and variable thickness. These results corroborate with those obtained by Lv et al. (2018) in which large CNC agglomerates resulted in several pores/ defects specially on the membranes' surface. To overcome the limitations in using dispersed cellulose membranes (PVDF/ cellulose blends), a deeper investigation on PVDF + dissolved cellulose membranes was conducted in this study since this is a much more homogeneous system (and scalable, in terms of reproducibility) than the first.

3.4 Scanning electron microscopy (SEM)

All PVDF/ cellulose blends had a heterogeneous surface aspect, because of the low compatibility between cellulose (hydrophilic) and PVDF (hydrophobic) (Figs. 3-5). The addition of cellulose resulted not only in the formation of agglomerates on blends surface but also in the thickness increase of the membranes. However, this did not compromise the WF probably because the addition of cellulose improved the hydrophilicity of the PVDF membranes (Lv et al. 2018).

Although it was difficult to determine the actual size and extension of the membranes surface pores, however, it was clear that the immersion precipitation technique resulted in the formation of vertical channels. This kind of membranes present lower mechanical strength because of the “finger-like” structures formed during the quick solvent exchange after immersion in a coagulation bath (distilled water) (Lv et al. 2018).

After cellulose partial dissolution and solvent evaporation (DMAc), the membranes structure drastically changed. This was confirmed by the formation of dense membranes (Figs. 6-8), yet with a clear surface (due to complete cellulose dissolution), in contrast to the PVDF/ cellulose blends (Figs. 3-5). Besides, solvent evaporation created several surface pores (Kim et al. 2016) ranging from 300-400 nm (in diameter) that probably contributed to the high WF and, therefore, suggesting the formation of microfiltration membranes (Hankins and Singh 2016).

3.5 WF

The PVDF and cellulose blends (dispersed cellulose) had similar WF to other studies that used mainly cellulose nanocrystals to improve the hydrophilicity of PVDF membranes (Bai et al. 2012; Lalia et al. 2014; Lv et al. 2018). The use of cellulose greatly increased the WF of the membranes, especially in that using pure cellulose (Avicel + PVDF), suggesting an increase in their hydrophilicity (Fig. 9). Also, the use of both partially dissolved nanocellulose sources (Avicel CNC and BEP CNC) resulted in a much more compact membrane as suggested by their lower WF (compared to PVDF + Avicel).

Next, it was decided to evaluate the influence of cellulose dissolution (Fig. 10) and partial solvent evaporation (Fig. 11) on the membranes WF. An intense decrease on membranes' WF was observed after cellulose dissolution, suggesting the formation of a much more homogeneous membrane (compared to PVDF and cellulose blends) and free of agglomerates and large pores derived from cellulose particles.

The partial solvent removal is capable of modifying the pore pattern in membranes by forming porous structures rather than “finger-like” voids and smaller surface pores (Guillen et al. 2011). Therefore, it is clear that the thermal pretreatment and cellulose dissolution contributed to generating porous and homogeneous high-flux membranes (Fig. 11) that could be a potential method to produce microfiltration membranes, considering these have in general WF over 500 L/m²h (Han et al. 2016; Meng et al. 2018; Mu et al. 2010).

4. Conclusion

The partial dissolution of cellulose had a great impact over the WF of membranes, thus suggesting its role in the formation of much more compact and homogeneous membranes for water treatment which is somewhat difficult using polymers blends or similar. Besides, the porous structure obtained after partial solvent removal indicates the WF (and consequently the pore size) may be tailored according to the membrane production method. Therefore, the homogeneous cellulose microfiltration membranes studied here may have potential for water treatment considering their high-water flux and low complexity to produce.

Declarations

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Conflicts of interest/Competing interests

Not applicable.

Availability of data and material

Not applicable.

Code availability

Not applicable.

Consent to participate

All authors consented in the development of the work described in this manuscript comprising writing, discussion, data interpretation or both.

Consent for publication

All authors consented in the final version of the manuscript prior to submission.

Compliance with Ethical Standards

All authors agreed there was no potential conflicts of interest in the development of this work. The research developed here did not include any human participants and/ or animals, therefore, none informed consents were considered during the development of this work.

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Figures

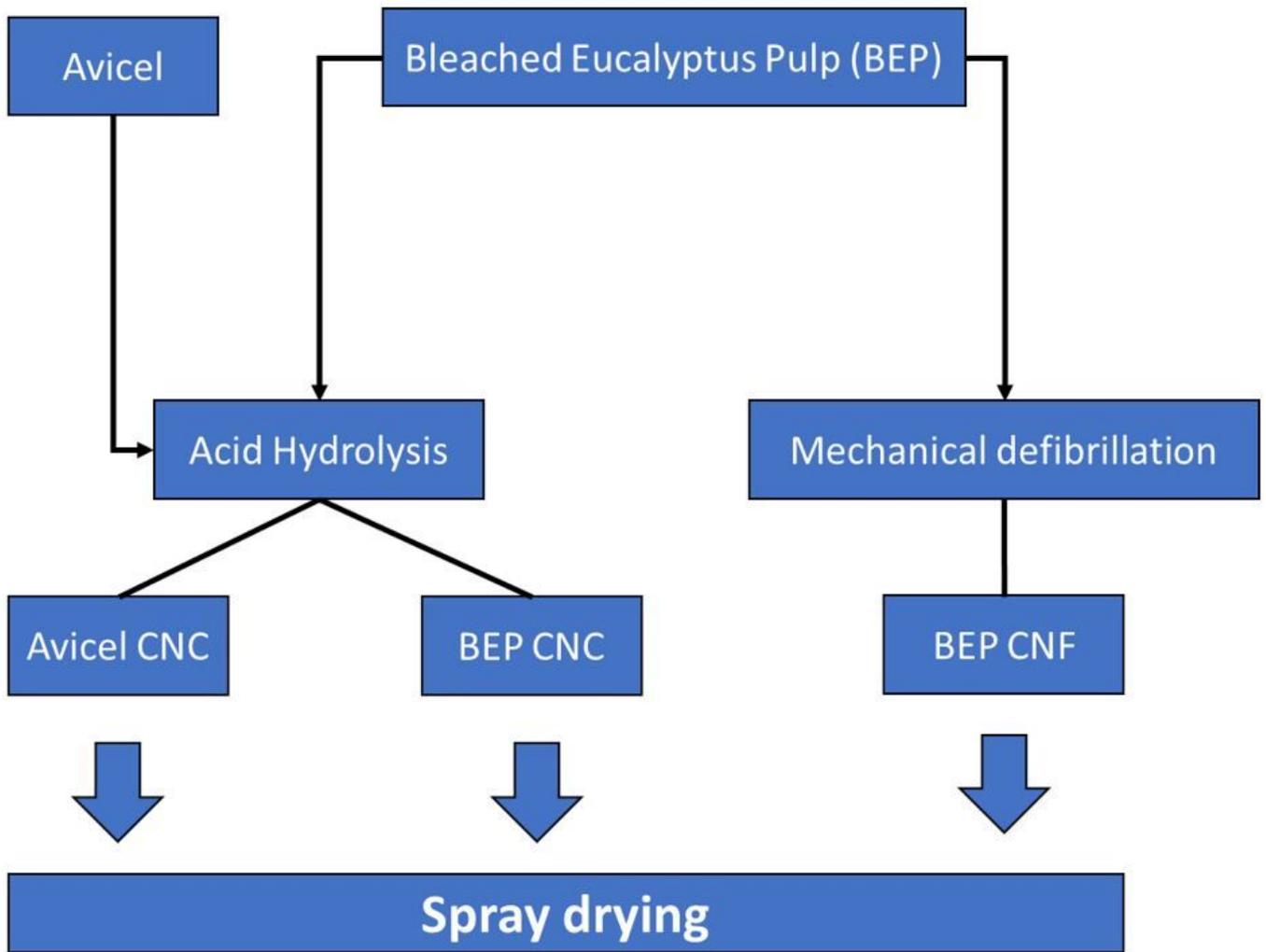


Figure 1

Steps for the preparation of spray-dried Avicel and BEP CNC and BEP CNF. BEP – bleached eucalyptus pulp; CNC – cellulose nanocrystals; CNF – cellulose nanofibers.

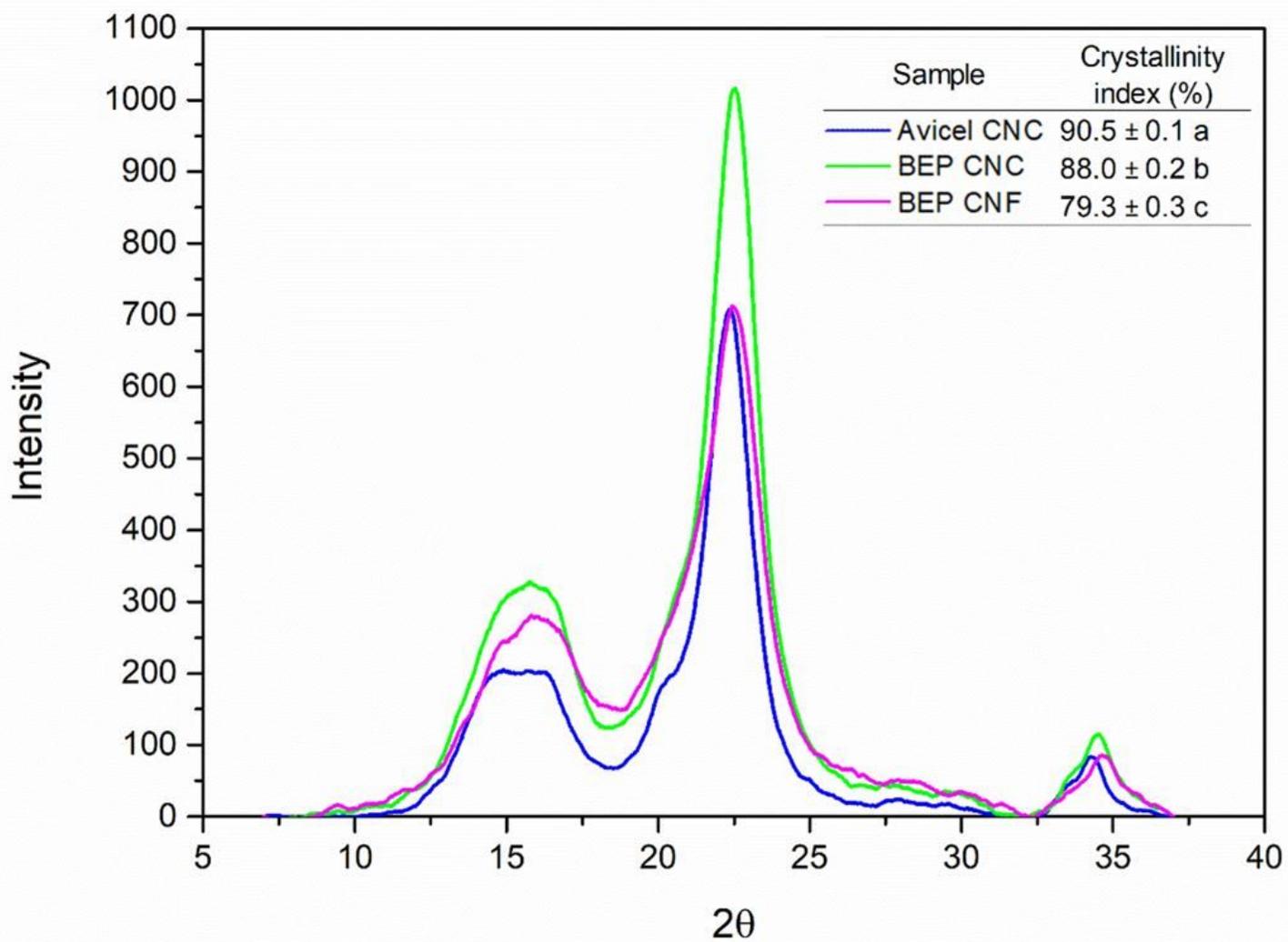


Figure 2

XRD patterns and crystallinity index of cellulose from different sources. Averages followed by the same letters do not differ statistically by Tukey's test ($p < 0.05$).

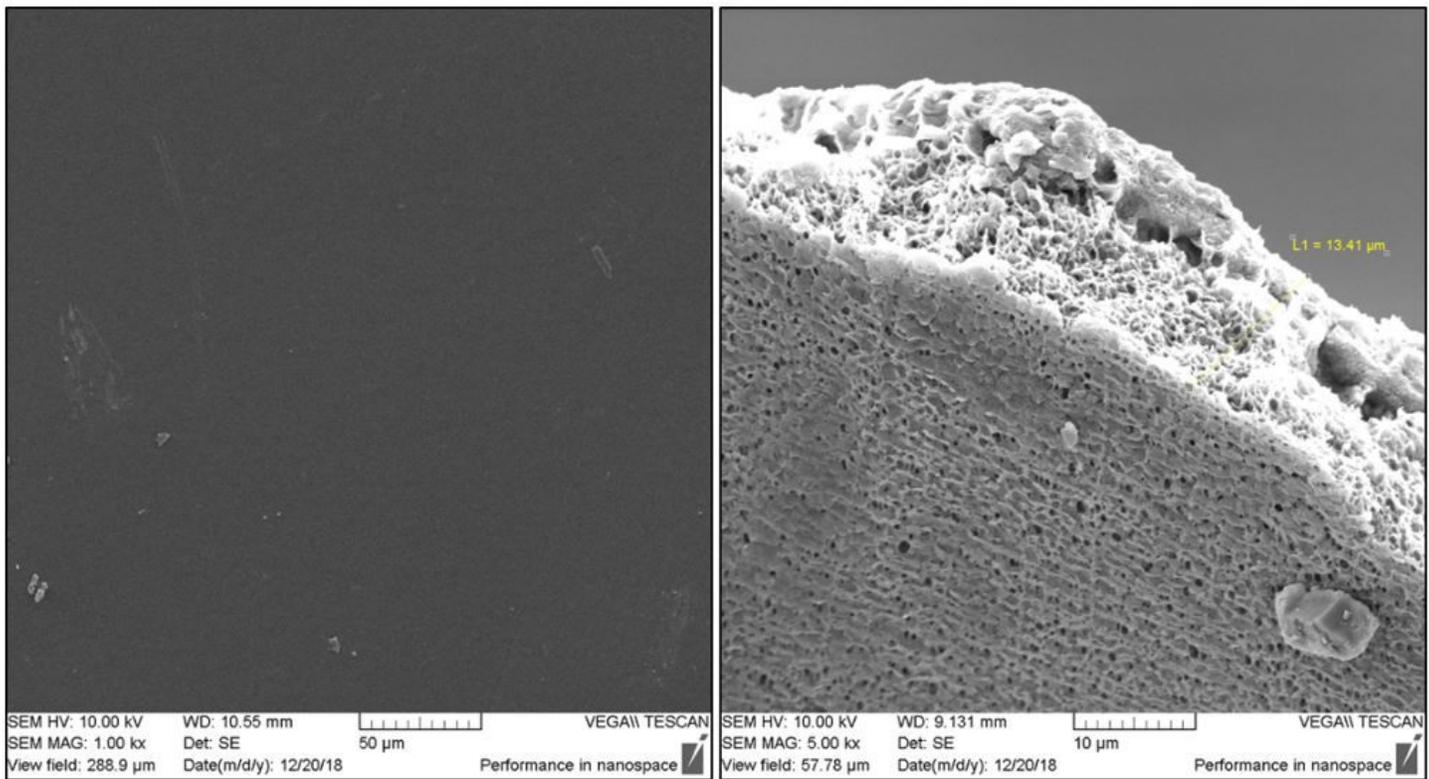


Figure 3

Surface (left – 1 kx) and cross-section (right – 10 kx) micrographs of Blank PVDF membrane.

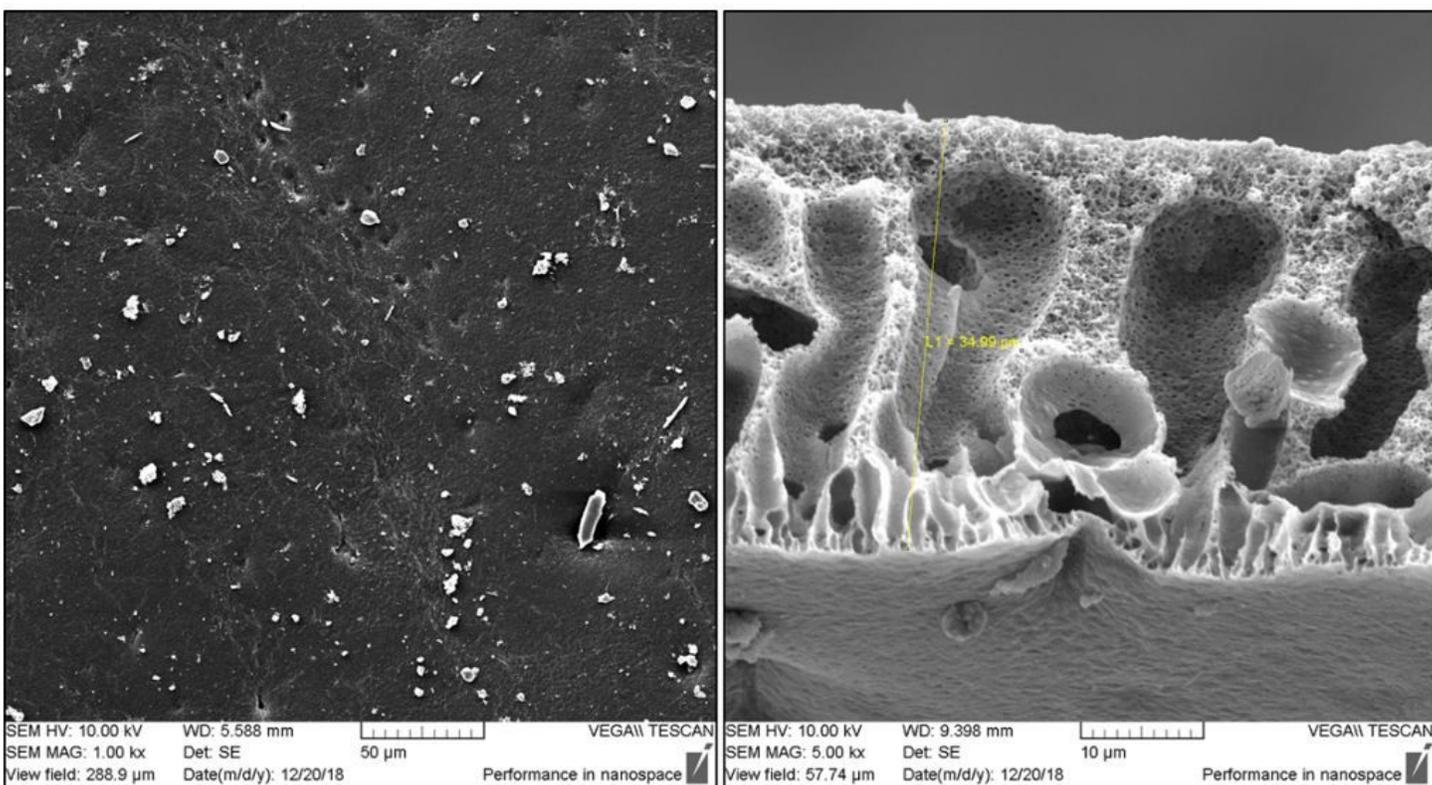


Figure 4

Surface (left – 1 kx) and cross-section (right – 10 kx) micrographs of PVDF + Avicel membrane (dispersed cellulose).

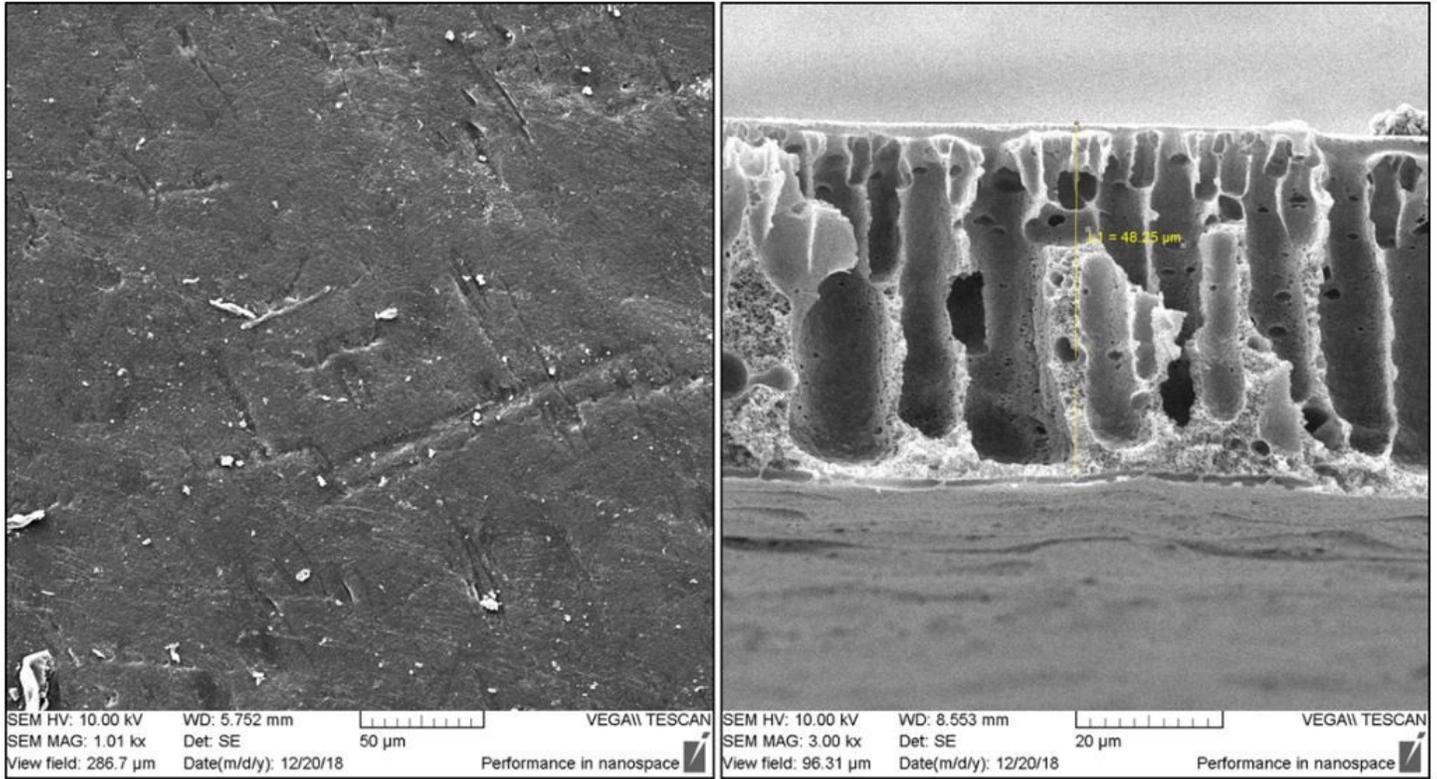


Figure 5

Surface (left – 1 kx) and cross-section (right – 10 kx) micrographs of PVDF + Avicel CNC membrane (dispersed cellulose). CNC – cellulose nanocrystals.

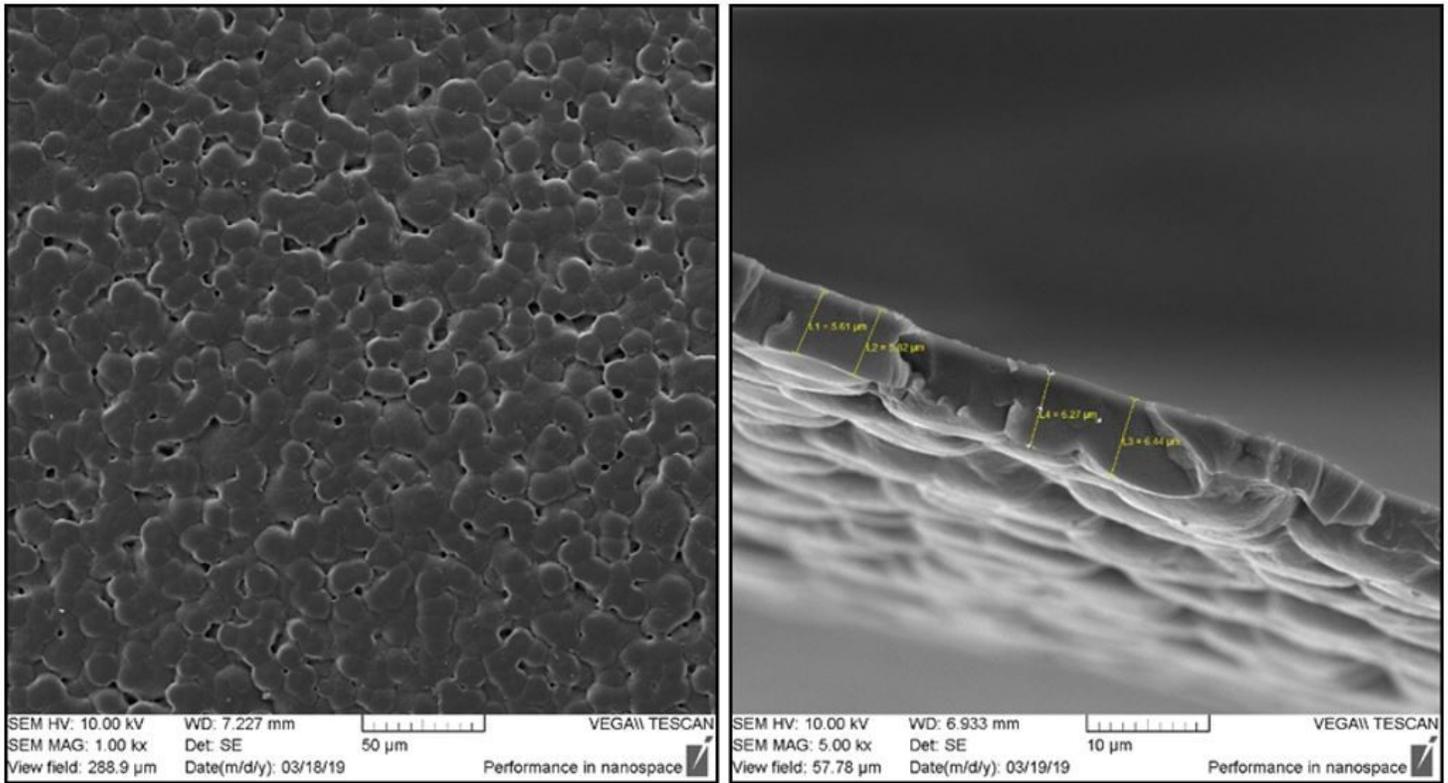


Figure 6

Surface (left – 1 kx) and cross-section (right – 10 kx) micrographs of Blank PVDF membrane after partial solvent evaporation in oven drier.

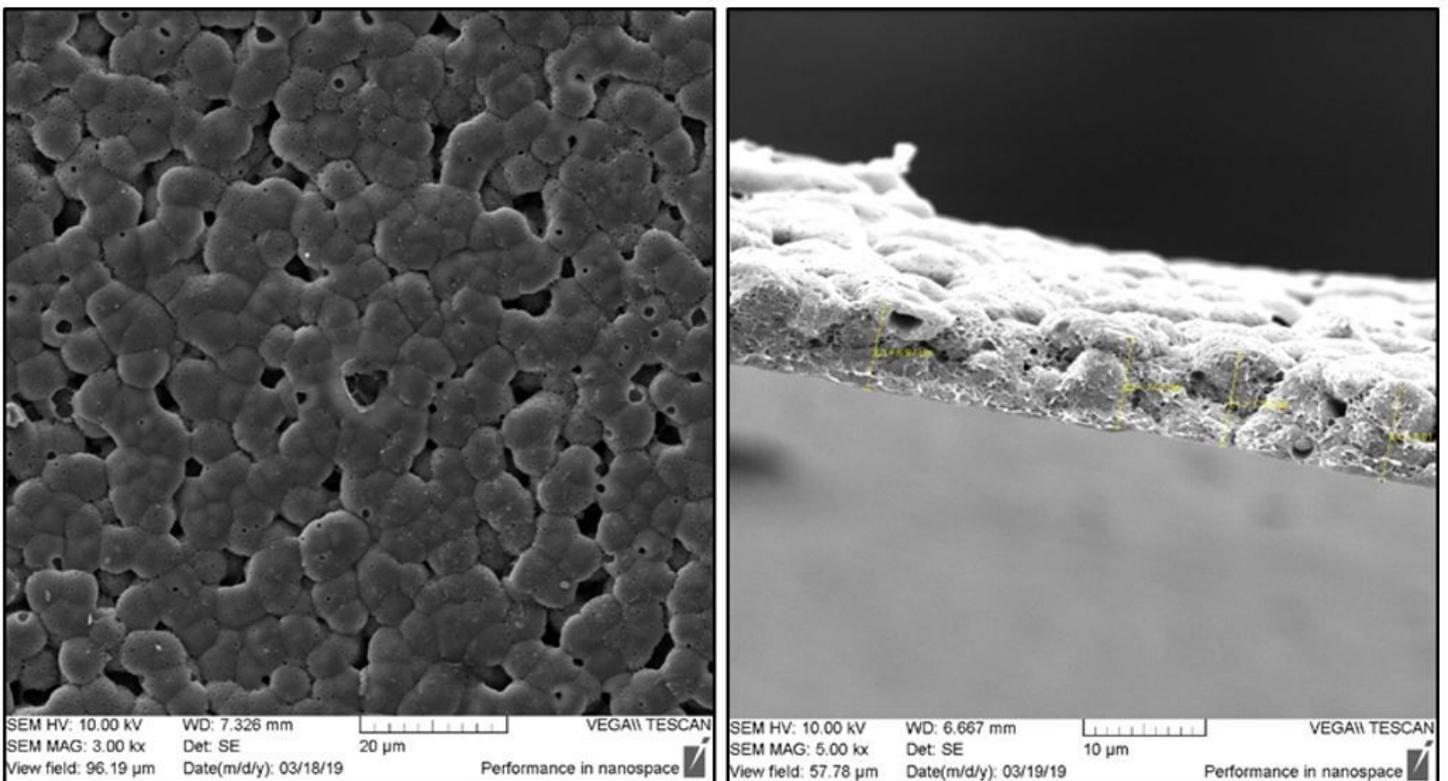


Figure 7

Surface (left – 1 kx) and cross-section (right – 10 kx) micrographs of PVDF + Avicel membrane (dissolved cellulose) after partial solvent evaporation in oven drier.

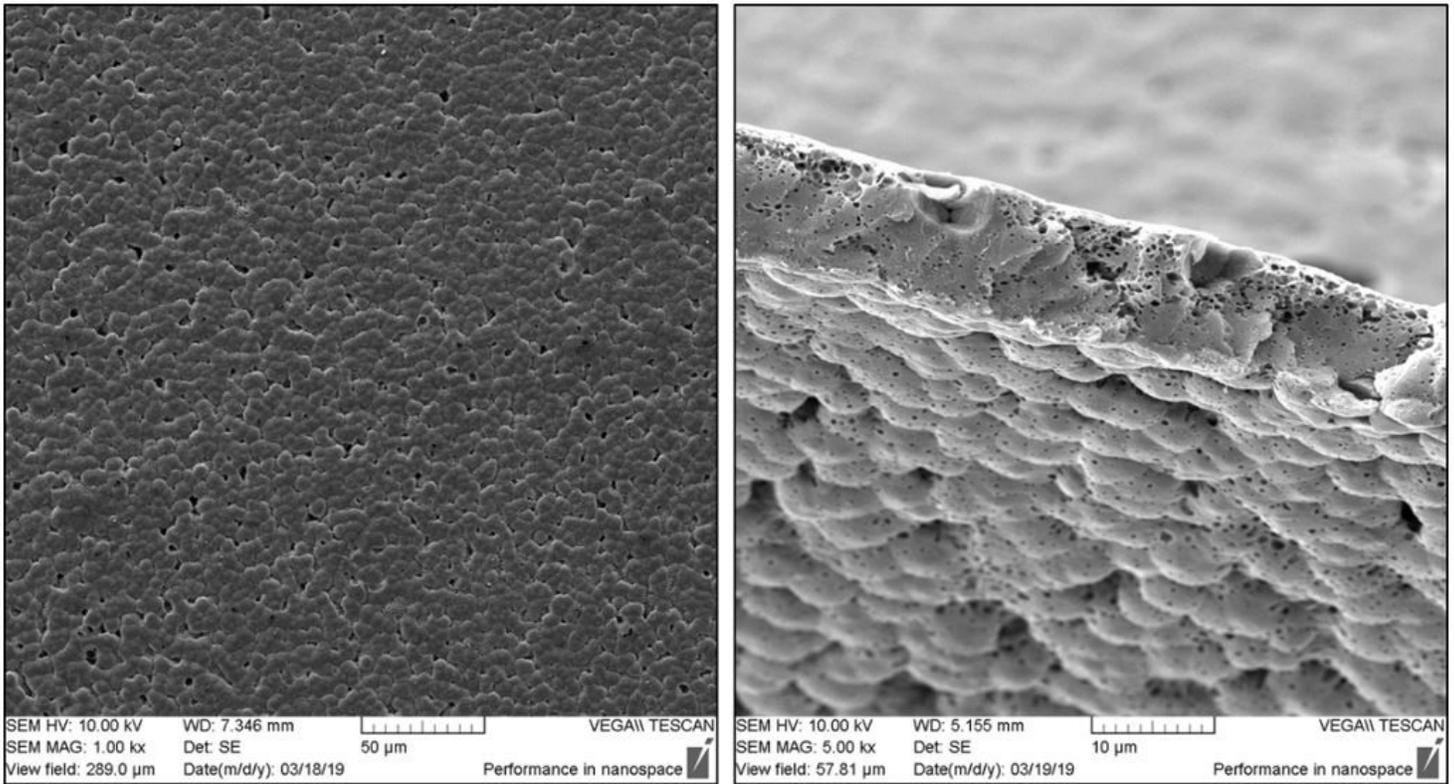


Figure 8

Surface (left – 1 kx) and cross-section (right – 10 kx) micrographs of PVDF + Avicel CNC membrane (dissolved cellulose) after partial solvent evaporation in oven drier. CNC – cellulose nanocrystals.

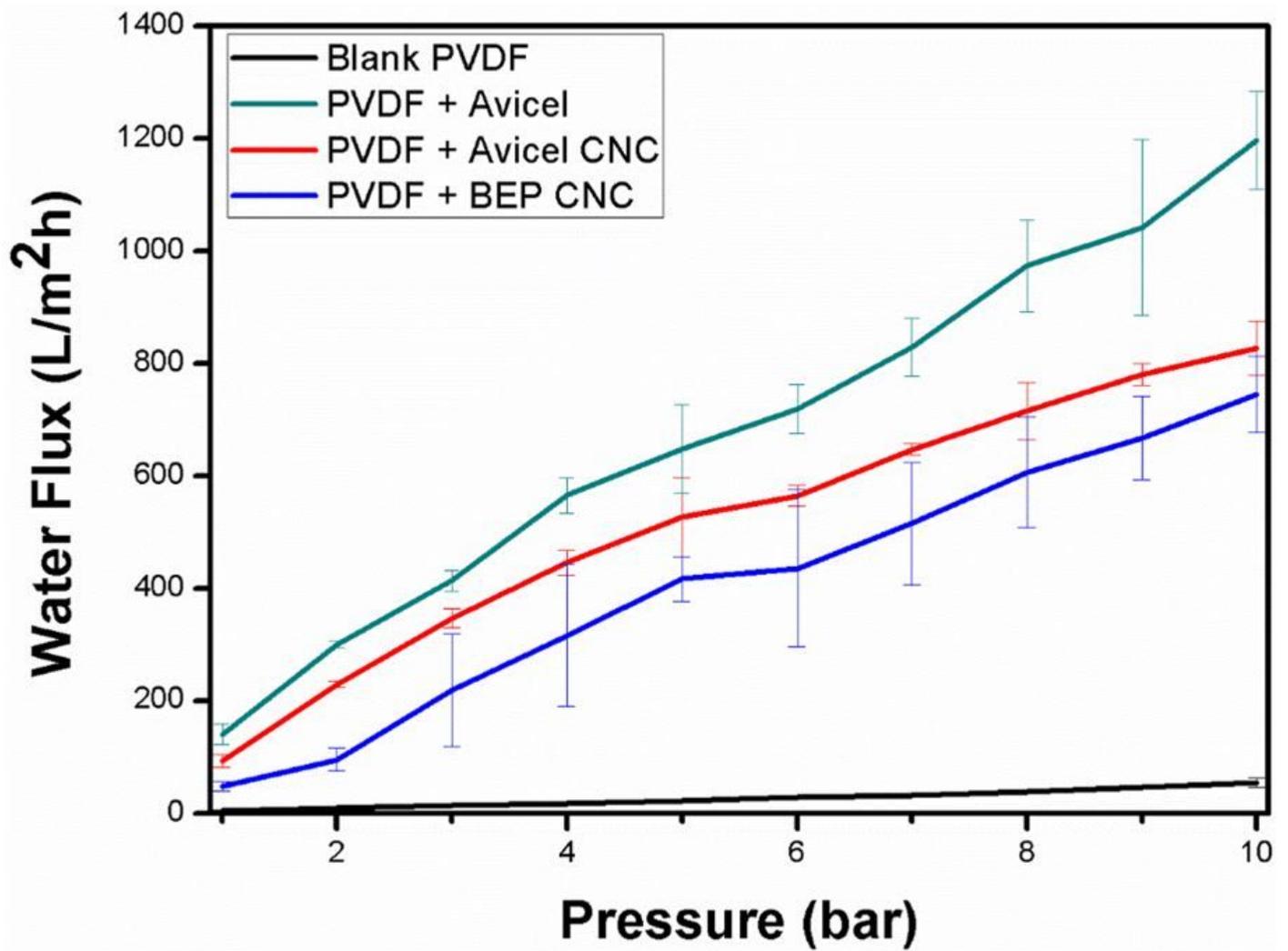


Figure 9

Effect of pressure on the water flux of PVDF and dispersed cellulose blends. CNC – cellulose nanocrystals; BEP – bleached eucalyptus pulp.

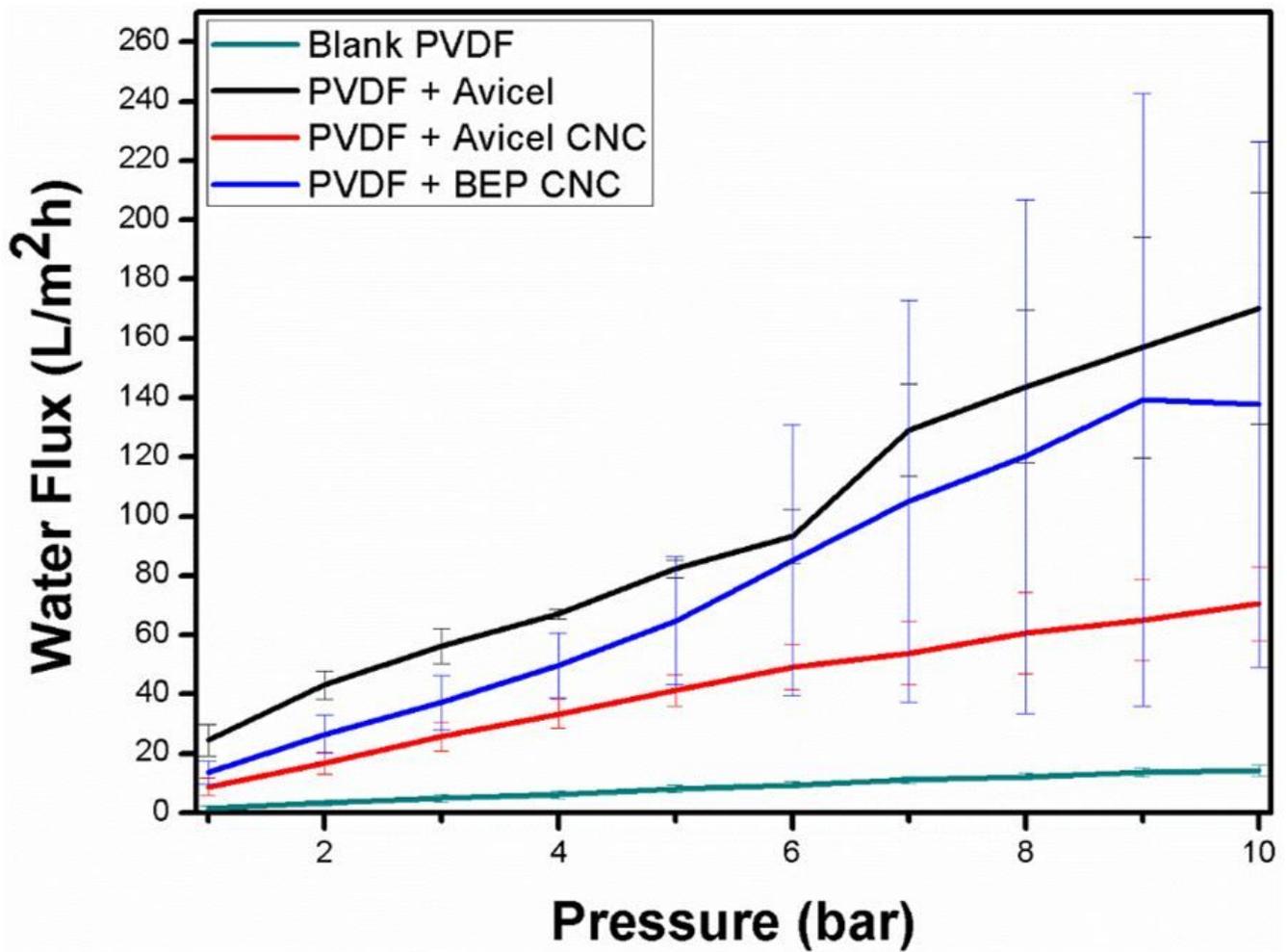


Figure 10

Effect of pressure on the water flux of PVDF and dissolved cellulose membranes. CNC – cellulose nanocrystals; BEP – bleached eucalyptus pulp.

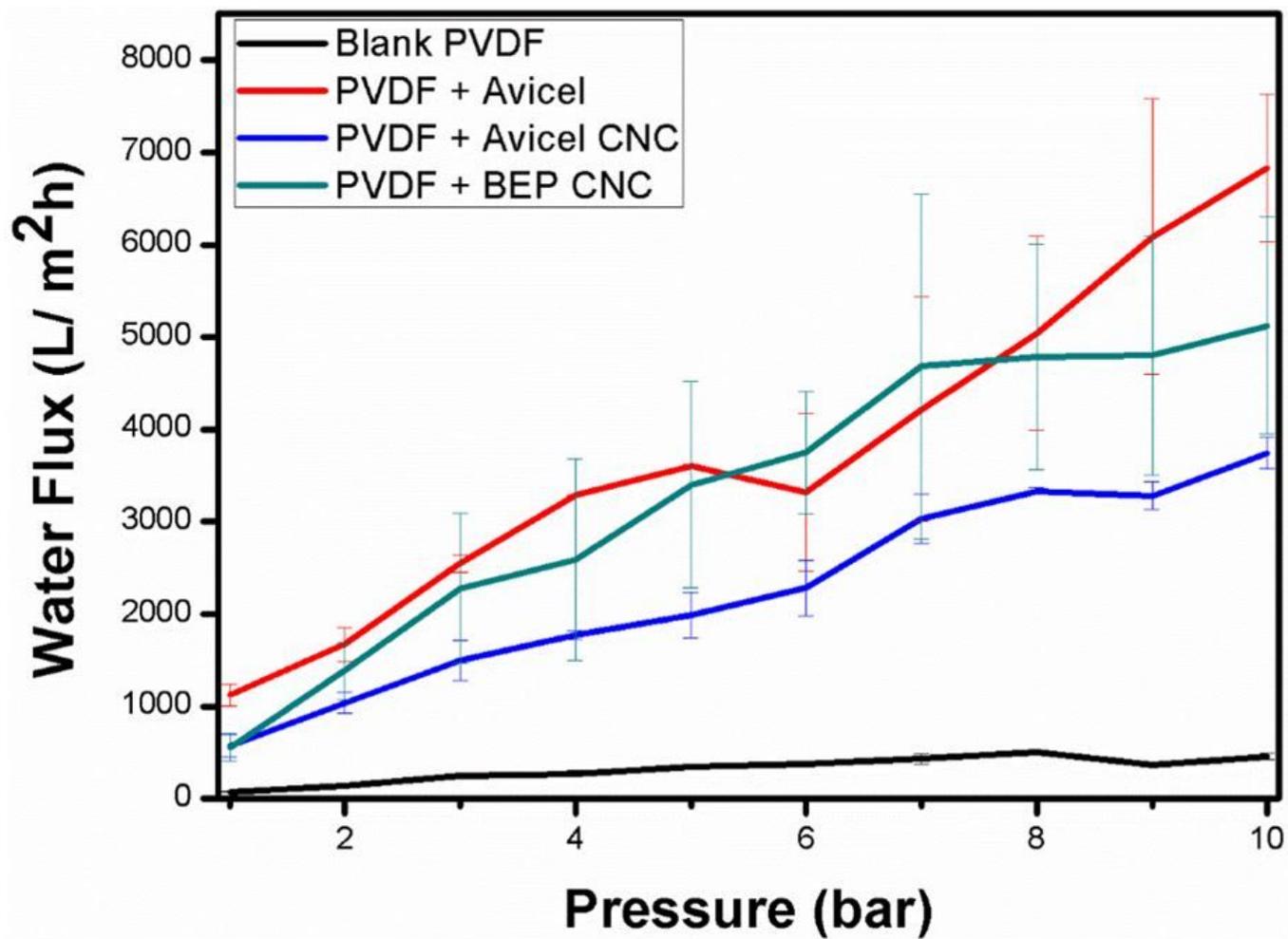


Figure 11

Effect of pressure on the water flux of PVDF and dissolved cellulose membranes (after partial solvent evaporation). CNC – cellulose nanocrystals; BEP – bleached eucalyptus pulp.