



# Long-term stability of cellulose membranes in spent deep eutectic solvent used in the recovery of lignin from lignocellulosic biomass

Vadim Ippolitov · Ikenna Anugwom ·  
Mika Mänttari · Mari Kallioinen-Mänttari

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**Abstract** Deep eutectic solvents (DESs) are a novel class of solvents that can be used to fractionate biomass compounds. However, their sustainability depends strongly on their recyclability. In previous research, it was seen that membrane filtration with commercial cellulose membranes (RC70PP and Ultracel 5 kDa) might be a solution for purification of spent deep eutectic solvent (DES) that has been used in lignin extraction (Choline Chloride: Lactic Acid 1:10 molar ratio) from woody biomass. This DES is, however, very acidic (pH 1.3), which can have detrimental effects on the longevity of the membrane. In a previous study, the time that the membranes were exposed to the spent DES was relatively short. This study aims to increase knowledge of how cellulose

membranes withstand spent DES over longer time periods of up to 8 weeks. The results show that cellulose membranes are quite stable under exposure to spent DES in terms of pure water flux and PEG retention for up to 4 weeks. After 8 weeks, the RC70PP membrane demonstrated an increase in pure water permeability of 45% and a noticeable decrease in PEG retention. Surface characterization revealed, however, that the chemical structure of the cellulose membranes changed already after 2 weeks of exposure prior to any changes in pure water permeability were observed. Experimentally revealed esterification of cellulose membrane by Lactic Acid of DES led to more negative charge of the exposed samples compared to their references. This esterification was accompanied by hydrolysis that removed amorphous parts and increased the crystallinity of the membrane.

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V. Ippolitov (✉) · I. Anugwom · M. Mänttari ·  
M. Kallioinen-Mänttari  
Department of Separation Science, LUT School  
of Engineering Science, LUT University, Lappeenranta,  
Finland  
e-mail: Vadim.Ippolitov@lut.fi

I. Anugwom  
e-mail: Ikenna.Anugwom@lut.fi

M. Mänttari  
e-mail: Mika.Manttari@lut.fi

M. Kallioinen-Mänttari  
e-mail: Mari.Kallioinen-Manttari@lut.fi

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## Introduction

Deep eutectic solvents (DESs) are a novel class of sustainable solvents (Kaoui et al. 2023). DESs consist of a hydrogen bond acceptor (HBA) – typically, quaternary ammonium salt – and a hydrogen bond donor (HBD) such as an amide, an alcohol, or a carboxylic

acid (Smith et al. 2014; Marcus 2019b). The properties of DESs can be tuned and are dependent on the nature and ratios of their constituents (Omar and Sadeghi 2021). Common advantageous properties of DESs are their safety, low-toxicity, non-volatility, thermal stability, non-flammability and biodegradability (Y. Liu et al. 2018; Mbous et al. 2017). DESs can be used in a variety of fields including, for example, as reaction media in biomass and biodiesel processes, for metal electrodeposition and electropolishing, and in applications related to nanotechnology (Marcus 2019a). Interest in biomass delignification with DESs has increased recently (Cassoni et al. 2023; Lu et al. 2022; Fernandes et al. 2021; Chen, Ragauskas, and Wan 2020; Malaeké et al. 2018) as a part of efforts to gain deeper understanding on sustainable biomass treatment and a DES comprising a mixture of choline chloride and lactic acid at a molar ratio of 1:10 has been seen to be an efficient solvent for delignification (Jablonský et al. 2015).

Sustainable recovery of DES is an important prerequisite for the successful implementation of DES usage on an industrial scale. A recent review of DES recovery and recycling techniques by Isci and Kaltschmitt (2021) noted that anti-solvent addition is a common and easy method for recovery of DES. The method consists of two stages. First, hydrogen bonding between the macromolecular fractions dissolved in the DES and the DES constituents is disrupted by the introduction of anti-solvent. The disruption of the hydrogen bonding network leads to precipitation of compounds extracted from the biomass. Subsequently, following removal of the precipitated compounds, the anti-solvent is separated from the system by evaporation (Isci and Kaltschmitt 2021). However, study of anti-solvent addition for DES recovery has consistently found a decrease in DES efficiency with each recovery cycle (Kim et al. 2018; Cheng et al. 2022; Zhong et al. 2022; Mankar et al. 2022). In biomass delignification at an industrial scale, this efficiency drop would necessitate the continuous addition of fresh DES.

Water is a common anti-solvent for lignin precipitation from spent DES (Isci and Kaltschmitt 2021). According to Smink et al. (2020), higher water-to-DES ratio leads to higher lignin recovery. However, the need for large volumes of water and continuous fresh DES addition to the system would increase total capital investment costs due to increased distillation

equipment costs (Zhao et al. 2022; Kulas et al. 2021). Effective spent DES recycling processes that noticeably reduce anti-solvent addition to the system are thus required.

One technique in the area of spent DES recycling that has recently gained increased interest is membrane filtration (Gholami et al. 2022; Ippolitov et al. 2022; Liang et al. 2023; Roy et al. 2023). The interest in the usage of membranes is most probably because membrane filtration offers the possibility of DES purification without phase change and because the purification level can be tailored via the choice of membrane. However, it has been found that the filtration capacity is low due to the high viscosity of spent DES (e.g., choline chloride: lactic acid at 1:10 has viscosity of 154 mPa·s at 25°C) (Ippolitov et al. 2022), although it should be noted that membrane filtration of DES can be facilitated by dilution with solvents (e.g., water, ethanol or acetone) (Gholami, Schuur, and Roy 2022; Liang et al. 2023; Roy et al. 2023). In our previous research, spent DES viscosity was decreased via ethanol addition, which enabled effective filtration with ultrafiltration membranes at a temperature of 45°C (Ippolitov et al. 2022).

To the best of our knowledge, most published research on membrane filtration of DES has been done with synthetic polymer-based membranes (Gholami, Schuur, and Roy 2022; Liang et al. 2023; Roy et al. 2023). Our approach in this work was to use cellulose membranes because the cellulose fraction stays in solid form in the recovery of lignin from wood biomass and it was thought that cellulose might thus be a resistant material for membranes in the treatment of spent DES. This assumption is supported by work by Majová et al. (2017), where cellulose was found to be insoluble in a choline chloride: lactic acid DES of any ratio at 60°C. In our previous paper, it was seen that the commercial cellulose membrane RC70PP withstood exposure to spent DES over the short term (3 weeks) (Ippolitov et al. 2022). However, spent DES prepared from choline chloride and lactic acid is very acidic (pH 1.3) and the membrane used in the recycling process is consequently exposed to extreme conditions beyond manufacturers' typical recommendations for cellulose membranes. There is, thus, a need to increase knowledge about the stability of the membranes in conditions found with spent DES. The goal of this study was to increase understanding of how long-term exposure

of cellulose membranes to spent DES diluted with ethanol influences their properties and performance. The experiments examined both commercial cellulose membranes and a lab-made cotton-based cellulose membrane to enable understanding of the effect of the DES exposure on different cellulose-based matrices.

## Materials and Methods

### 2.1. Spent DES preparation

The DES used in this study was prepared using lactic acid (LA, 85% purity, Sigma-Aldrich, Germany, CAS-No: 50–21-5) and choline chloride (ChCl, 99% purity, Sigma-Aldrich, Germany, CAS-No: 67–48-1). The spent DES was produced in a process in which lignin was dissolved from air-dried birch chips (*Betula pendula*) provided by a local wood mill using heated DES ( $T=120^{\circ}\text{C}$ ). Prior to lignin dissolution, the chips (typically  $25\text{--}35\times 0\text{--}25\times 2.5\text{--}6$  mm,  $L\times W\times T$ ) were milled to 1 mm size using a hammer mill. The results of our previous paper (Ippolito et al. 2022) demonstrated that the viscosity of the spent DES has to be decreased before the spent DES can be filtered with membranes. Viscosity of 60 vol% spent DES in ethanol (ETAX A, 99.9% purity) solution is by 88% lower compared to spent DES alone. Thus, 60 vol% spent DES solution was used for all stability experiments performed in this study.

### Membranes

Three different membranes are studied in this research – two commercial membranes and one lab-cast membrane. The commercial membranes used in this study are introduced in Table 1.

The regenerated cellulose acetate of the RC70PP membrane should be understood as regenerated cellulose that was obtained by incomplete deacetylation

of cellulose acetate. Thus, the material still contains some small amount of acetate groups.

The lab-made membrane (henceforth “cotton-based membrane”) was fabricated from 100% cotton bed sheet according to the procedure described by Lopatina et al. (2021). The cotton sheet was preliminary cut into approximately  $1.5\times 1.5$  cm pieces and used directly without any pretreatment. A mixture of ionic liquid – 1-ethyl-3-methylimidazolium acetate ([Emim][OAc], 95% purity, CAS-No: 143314–17-4, Iolitec Ionic Liquids Technologies GmbH) and DMSO (99.7% purity, CAS-No: 67–68-5, Merck KGaA, Darmstadt, Germany) was used to prepare the membrane casting solution. 5 wt.% solution of cellulose in [Emim][OAc]-DMSO was prepared by stirring cotton textile shreds overnight under constant heating in an oil bath at  $90^{\circ}\text{C}$ . The obtained casting solution was homogenous. Flat-sheet membranes were cast on nonwoven polypropylene/polyethylene carrier material Viledon® Novatexx 2484 ( $60\text{ L}/(\text{s}\cdot\text{m}^2)$  air permeability, Freudenberg, Germany). Freshly cast membrane sheet was immediately immersed in a coagulation bath consisting solely of pure water at  $0^{\circ}\text{C}$ . The sheet was left in the bath overnight.

### Stability experiments

All membranes were exposed to 60 vol% spent DES in ethanol for periods of 2 weeks and 4 weeks at  $45^{\circ}\text{C}$  and 200 rpm shaking. An exposure for 8 weeks was also set up but only for RC70PP. Three parallel measurements were done for each type of membrane. The exposure experiment was carried out in sealed Duran bottles.

Pure water permeability (PWP) and PEG retention were measured for all the studied membrane samples in crossflow cells to get an understanding of the influence of the spent DES exposure on membrane performance. The membranes were compacted prior to the

**Table 1** Characteristics of the RC70PP membrane (Alfa Laval) and the Ultracel UF Discs 5 kDa membrane (Millipore)

Membrane Type	Material	MWCO value, kDa	Recommended maximum operating temperature, $^{\circ}\text{C}$
RC70PP	Regenerated cellulose acetate	10	60
Ultracel 5 kDa	Regenerated cellulose	5	50

first PWP and retention measurements. Membrane compaction and permeability conditions were chosen for each membrane individually (Table 2).

Although the cell dimensions are different for the experiments with the RC70PP membrane, crossflow velocity was kept at a constant level of 2 m/s for all the studied membranes throughout the whole measurement process.

Polyethylene glycol (PEG) of different molecular weights was used as model compounds in measurement of the retention of the membranes. PEGs of the following approximate molecular weight – 600 Da, 1000 Da, 3000 Da, 4000 Da, 6000 Da, 8000 Da, 12,000 Da, 35,000 Da – were purchased from Merck KGaA (Darmstadt, Germany; CAS-No: 25322–68–3). PEG retention was measured at three different pressures for each membrane. The PEG sizes in the mixtures and the pressures used in PEG retention measurement were selected individually for each membrane (Table 3).

PEG content in feeds, permeates and retentates was analysed by performing size-exclusion chromatography (SEC) in a HPLC unit with a PolySep-GFC-P 3000 LC column (300×7.8 mm) and PolySep-GFC-P Guard column (35×7.8 mm). Both columns are manufactured by Phenomenex.

Membrane retentions were calculated from measured peak areas obtained using HPLC software. Each

peak corresponded to a particular PEG compound. Membrane retention was calculated using Eq. (1):

$$R = \left(1 - \frac{2 \cdot A_p}{A_f + A_r}\right) \cdot 100 \quad (1)$$

where  $A_p$ ,  $A_f$  and  $A_r$  are the areas of the peak that represent a particular PEG compound in the permeate, feed and retentate respectively.

#### Surface characterization of the membranes

Prior to surface characterization, pure water was filtered through all studied membranes until permeate's conductivity got equal to feed's conductivity. Membrane surface charge was measured with a SurPASS Electrokinetic Analyzer (Anton Paar GmbH, Graz, Austria) using an adjustable gap cell method and using 0.001 M KCl solution as a background electrolyte. The final value of the zeta potential was calculated automatically by SurPASS software based on the Helmholtz-Smoluchowski equation.

Possible chemical changes of the membrane as a result of exposure to spent DES were assessed using ATR-FTIR (attenuated total reflection – Fourier transform infrared) spectroscopy. The analysis was performed with an FTIR spectrometer (PerkinElmer Inc.) equipped with a universal attenuated total reflectance (ATR) module. Each sample was analyzed

**Table 2** Pure water permeability measurement conditions for the RC70PP, Ultracel 5 kDa and the cotton-based membranes

Membrane type	Filtration equipment	Compaction procedure	Temperature, °C	Range of pressures, bar
RC70PP	crossflow with cell dimensions 22.5×2×0.1 cm	30 min at 3.5 bar	35	1.0, 2.0, 3.0
Ultracel 5 kDa	crossflow with cell dimensions 5.2×2×0.1 cm	30 min at 4.5 bar	35	2.2, 3.0, 4.0
Cotton-based membrane	crossflow with cell dimensions 5.2×2×0.1 cm	30 min at 4.5 bar	35	2.2, 3.0, 4.0

**Table 3** PEG retention measurement conditions for the RC70PP, Ultracel 5 kDa and cotton-based membranes

Membrane type	Crossflow equipment, cell dimensions	Temperature, °C	PEG compounds, kDa	PEG mixture solution concentration, ppm	Range of pressures, bar
RC70PP	22.5×2×0.1 cm	35	1, 4, 8, 12	400	1.0, 2.0, 3.0
Ultracel 5 kDa	5.2×2×0.1 cm	35	0.6, 1.5, 3.0, 6.0	400	2.2, 3.0, 4.0
Cotton-based membrane	5.2×2×0.1 cm	35	4, 8, 12, 35	400	2.2, 3.0, 4.0

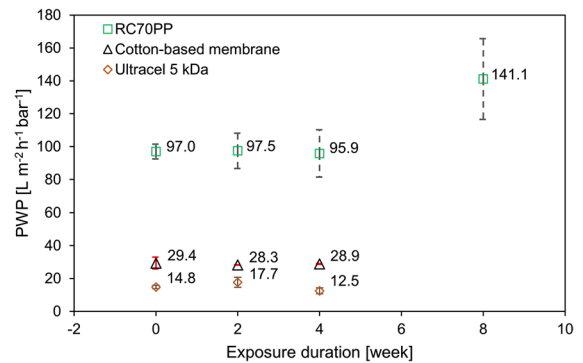
at five different points in the wavenumber range of 4000–400  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ . Four scans were carried out with a data interval of 1  $\text{cm}^{-1}$  in absorbance mode. All spectra underwent ATR, baseline corrections and normalization.

To examine changes in the crystallinity of the cellulosic skin layer, XRD (X-ray diffraction) patterns of the membranes before and after spent DES exposure were recorded with a Bruker D8 Advance X-ray diffractometer. The samples were scanned in the range of  $2\theta = 10^\circ - 50^\circ$  at  $25^\circ\text{C}$  with  $\text{Cu } \alpha$  radiation ( $\lambda = 0.1540 \text{ nm}$ ). XRD was performed only for the RC70PP and cotton-based membranes because their skin layers are easily detachable from the support, unlike the skin layer of the Ultracel 5 kDa membrane. Crystallinity indexes (CrI) of the analyzed samples were determined by the Segal peak height method (Segal et al. 1959). The calculation followed the Eq. (2):

$$CrI = \frac{I_{tot} - I_{am}}{I_{tot}} \cdot 100 \quad (2)$$

where  $CrI$  – crystallinity index,  $I_{tot}$  – intensity around  $2\theta \approx 22^\circ$ ,  $I_{am}$  – amorphous intensity around  $2\theta \approx 13.5^\circ$ .

Cellulose degree of polymerization (DP) was identified using a method in which the cellulose was diluted in a 1 M solution in water of copper(II)-ethylene-diamine (CED) complex (purchased from Acros Organics; CAS-No.: 14552–35-3). DP measurement of cellulose skin layer samples was based on the procedure described by Bu et al. (2019) with the exception of lower cellulose concentration, where 1.2–1.4 g/L was implemented instead of 3–4 g/L. Briefly, dry skin layers of the RC70PP membrane and cotton-based membrane were dissolved in 1.0 M CED solution. Later the relative viscosities of the cellulose/CED solutions were measured with a Ubbelohde-type viscometer at  $30^\circ\text{C}$ . DP calculations were done using the Staudinger-Mark-Houwink equation (Gruber and Gruber 1981).



**Fig. 1** Pure water permeabilities of the RC70PP, Ultracel 5 kDa and cotton-based membrane before and after exposure to spent DES measured at  $35^\circ\text{C}$  and crossflow velocity 2 m/s

## Results and Discussion

### Comparison of membrane performance

#### Pure water permeability

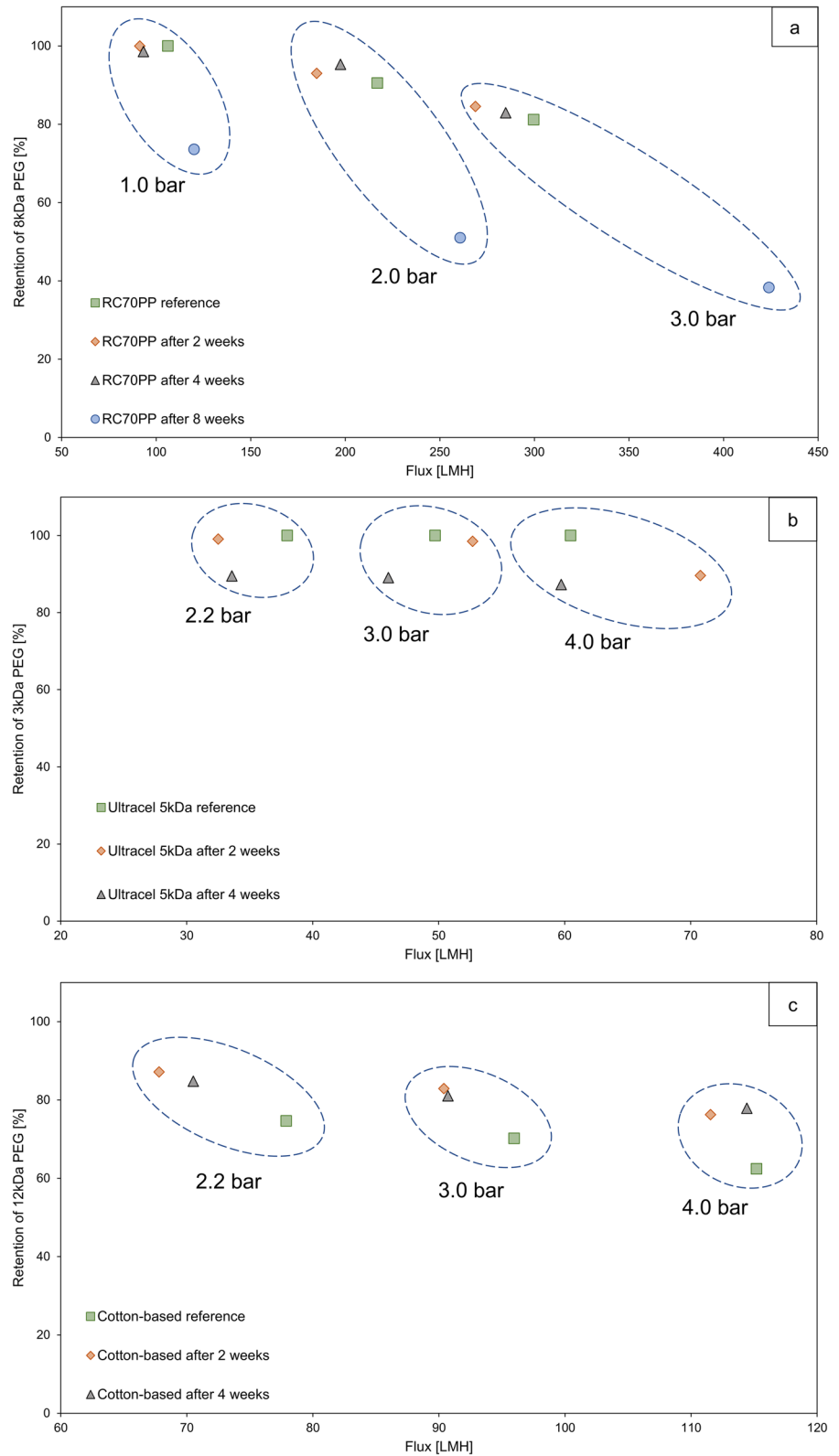
PWP results for the RC70PP, Ultracel 5 kDa and cotton-based membrane before and after exposure to spent DES in ethanol are presented in Fig. 1.

Permeabilities of all the membranes in Fig. 1 remain relatively unchanged for exposure of up to 4 weeks. For example, the PWP of the RC70PP membrane drops only by roughly 1% compared to the reference after a 4-week exposure. Nevertheless, after 8 weeks of exposure the membrane loses its flux stability and a substantial PWP increase of 45% can be seen. The RC70PP membrane, which has the highest flux of the membranes studied, also shows an increase in standard deviation with time. It would appear that pieces of the RC70PP membrane from different parts of the sheet experience the exposure differently. Changes in the PWP of the cotton-based membrane after a 4-week exposure to spent DES are small (under 2% PWP decrease). The Ultracel 5 kDa membrane demonstrates minor fluctuations during the DES exposure period.

#### PEG retention

Figure 2 presents PEG retentions for the tested membranes at three different flux values. It can be noted that Fig. 2 shows retentions of the second biggest PEG of the PEG mixtures, namely 8 kDa for RC70PP,

**Fig. 2** Retentions vs Flux before and after spent DES exposure: (a) 8 kDa PEG for the RC70PP membrane, (b) 3 kDa PEG for the Ultracel 5 kDa membrane, and (c) 12 kDa for the Cotton-based membrane



3 kDa for Ultracel 5 kDa and 12 kDa for Cotton-based. As stated earlier, a unique PEG mixture was used for each membrane type. Charts containing full data on PEG retention at different pressures can be found in the Appendix.

It can be seen in Fig. 2a that retention values of the 8 kDa PEG decrease with flux growth for the RC70PP membrane. The reference, the 2-week membrane and the 4-week membrane have close to each other values of retention and flux. The 8-week sample demonstrates much lower retention and higher flux than the membrane samples that undergo shorter exposure. As mentioned earlier, only the RC70PP membrane was tested for 8 weeks of spent DES exposure.

The 3 kDa PEG retention values of the Ultracel 5 kDa membrane (Fig. 2b) demonstrate good stability regardless of flux for up to 4 weeks. Nevertheless, it can be seen that exposure to spent DES reduces the membrane's retention.

The retention pattern of the cotton-based membrane is quite similar to that of the RC70PP membrane. Indeed, retention of the 12 kDa PEG decreased with increase in flux. Interestingly, retentions of the exposed pieces were slightly higher than those of the reference.

The fluxes and PEG retentions show that the membranes remain stable in spent DES solution for at least 4 weeks.

#### Material characterization of the membranes before and after spent DES exposure

The clearest change in membrane charge following exposure to spent DES can be seen in the RC70PP and cotton-based membranes (Fig. 3a and 3c), where DES exposure made the membrane surface more negatively charged. Unlike the other membranes, the Ultracel 5 kDa membrane did not become significantly more negatively charged after exposure.

The spent DES in the experiments is from hardwood treatment and is diluted with ethanol. Hence, the solution is a complex mixture of DES, ethanol, and a variety of dissolved and suspended organic compounds of lignin and hemicellulose origin. The influence of the latter compounds on the membrane morphology can be identified by comparing IR spectra of the RC70PP membrane, exposed to pure DES in ethanol, with the same membrane, exposed to spent DES in ethanol. This comparison, presented in Fig. 4,

reveals that the spectra of both membrane samples are almost identical. The spectra differ from the spectrum of the reference RC70PP, indicating that changes on the surface of the membrane during the exposure are caused solely by cellulose-DES interactions.

Liu et al. (2021) conducted research where cellulose was immersed in choline chloride – lactic acid (1:9 molar ratio) DES and kept in the solvent for 3 h with heating in the range 50–100°C. As a result, monoesters and cross-linked diesters formed on the surface of the cellulose (S. Liu et al. 2021). As this research studies a very similar DES with lower heating conditions but longer exposure period, there are grounds to hypothesize that the cellulose membranes studied in this work were also esterified.

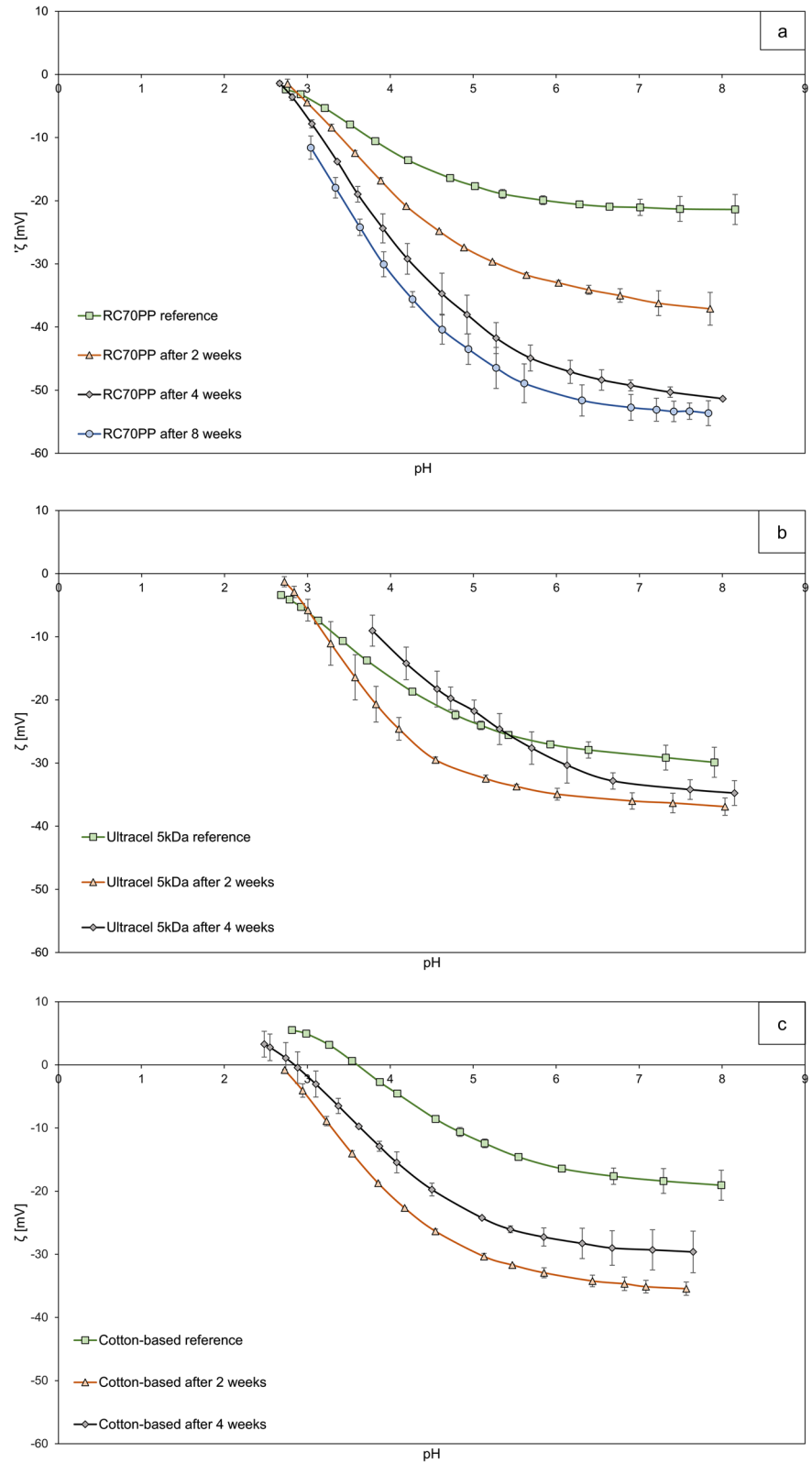
The most evident sign of esterification that can be detected with FTIR is appearance of the C=O vibration band. This band lies in the range 1690–1810  $\text{cm}^{-1}$  and is absent in the spectrum for pure cellulose. (Pavia et al. 2001) FTIR spectra of the exposed and reference membranes can be compared to reveal the appearance of the carbonyl group and changes in the cellulose peaks of the DES-exposed pieces. Typical IR bands for cellulose are presented in Table 4.

Comparison of the RC70PP spectra before and after exposure to spent DES (Fig. 5) reveals the following changes: the gradual increase in intensity with exposure time of the peak at 2885  $\text{cm}^{-1}$  shows slow growth in the number of aliphatic hydrocarbon groups, and the noticeable increase of the peak in the area 1753–1733  $\text{cm}^{-1}$  suggests an increase in the number of carbonyl groups. It is interesting that after 8 weeks in spent DES the carbonyl group peak decreased almost to the reference value.

Unlike the RC70PP membrane, the Ultracel 5 kDa membrane (Fig. 6) did not contain any carbonyl groups in the reference piece. A considerable increase in intensity of the carbonyl group (1734  $\text{cm}^{-1}$ ), noticeable increase in intensity of the C–O and C–O–C vibrations (1160  $\text{cm}^{-1}$  and 1040  $\text{cm}^{-1}$ ), slightly increased intensity in C–H aliphatic vibrations (2890  $\text{cm}^{-1}$ ) and decreased intensity of the O–H group (3350  $\text{cm}^{-1}$ ) can be observed after exposure to spent DES in ethanol.

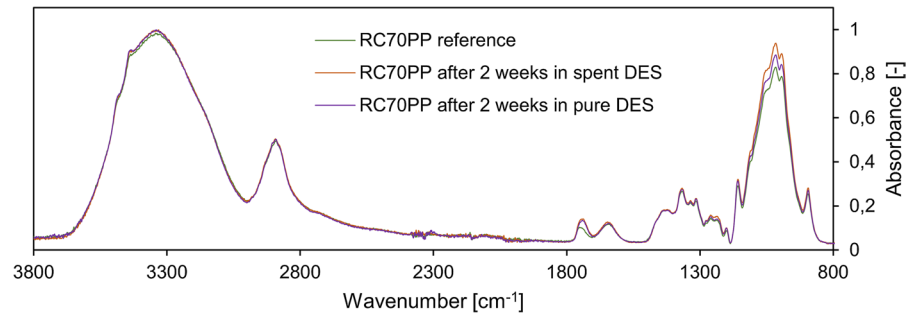
In the FTIR spectra of the cotton-based membrane (Fig. 7), a reduction in intensities is observed at almost all the wavenumbers of interest except the carbonyl peak at 1728  $\text{cm}^{-1}$ . This peak increased

**Fig. 3** Zeta potential curves before and after spent DES exposure: (a) the RC70PP membrane, (b) the Ultracel 5 kDa membrane, and (c) the cotton-based membrane





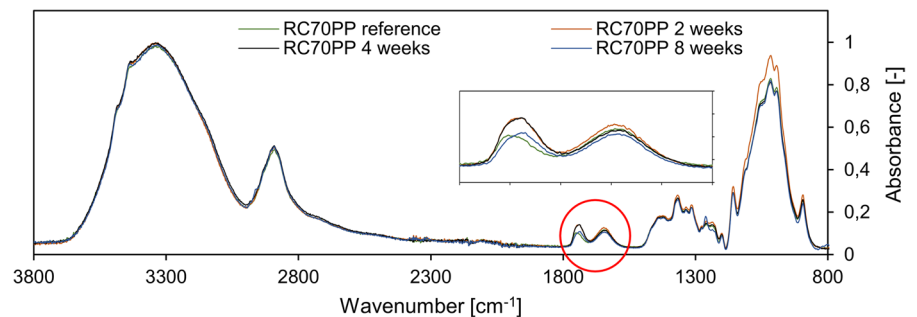
**Fig. 4** FTIR spectra of RC70PP membrane samples exposed for 2 weeks to spent DES and pure DES



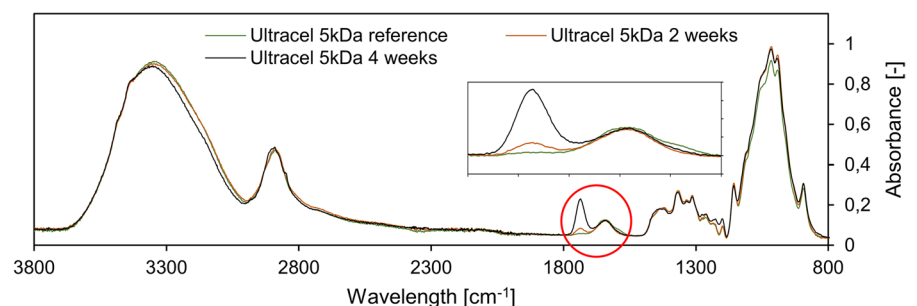
**Table 4** Common IR band ranges for cellulose which is a skin layer material in the RC70PP, Ultracel 5 kDa and cotton-based membranes

Band area, $\text{cm}^{-1}$	Chemical bond vibration	Reference
~3400	Hydroxyl O–H stretching	(R. Sun, Sun, and Tomkinson 2004)
~2900	Stretching vibrations of C–H group	(R. Sun, Sun, and Tomkinson 2004)
~1640	Bending of absorbed water	(R. Sun, Sun, and Tomkinson 2004)
~1370	Hydroxyl O–H bending	(J. X. Sun et al. 2004a, b)
~1160	C–O stretching in cellulose	(J. X. Sun et al. 2004a, b)
~1040	C–O–C pyranose ring skeletal vibration	(J. X. Sun et al. 2004a, b)
~890	$\beta$ -glucosidic linkages between the sugar units	(Gupta, Madan, and Bansal, n.d.)

**Fig. 5** FTIR spectra of the RC70PP membrane before and after exposure to spent DES solution



**Fig. 6** FTIR spectra of the Ultracel 5 kDa membrane before and after exposure to spent DES solution

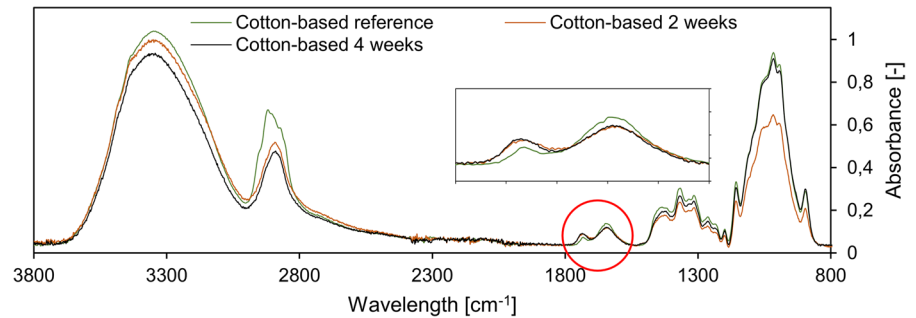


slightly after a 2-week exposure, and grew further after 4 weeks of exposure.

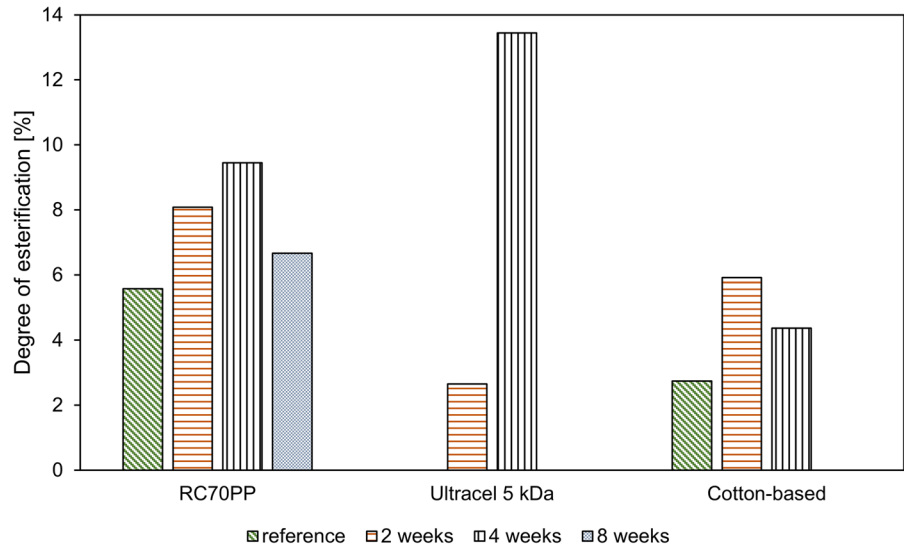
To summarize, the FTIR results support our esterification hypothesis as the appearance of carbonyl

group vibration can be seen in all membrane pieces exposed to spent DES in ethanol. It is possible to approximately calculate the degree of esterification based on knowledge of the height of the carbonyl

**Fig. 7** FTIR spectra of the cotton-based membrane before and after exposure to spent DES solution



**Fig. 8** Approximate degree of esterification of the reference samples and samples exposed to spent DES in ethanol of the RC70PP, Ultracel 5 kDa and cotton-based membranes



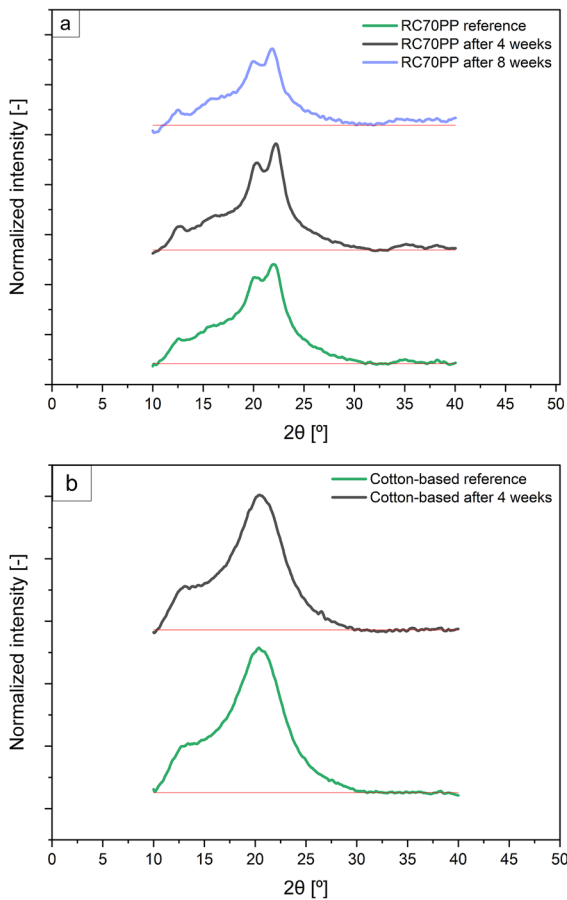
peak of cellulose acetate with known acetylation degree (39.7 wt% acetyl). The approximate degree of esterification of all the studied membranes (reference and DES solution exposed pieces) is presented in Fig. 8.

Figure 8 shows that in the case of the RC70PP and the cotton-based membranes, esterification steadily increases, reaches a maximum value, and then decreases. The decrease in the degree of esterification of samples exposed to DES solution for a longer period might be a signal of the start of degradation. The growth of the degree of acetylation of the Ultracel 5 kDa membrane starts from 0% and changes abruptly.

Cellulose is a semi-crystalline biopolymer. In other words, it consists of both crystalline and amorphous regions. Changes in their ratio (i.e., the crystallinity index) can indicate cellulose degradation. XRD spectra can reveal possible allomorph changes as well as help in calculation of the crystallinity index (CrI).

The X-ray diffraction patterns of the skin layers of the RC70PP membrane and the cotton-based membrane before and after DES exposure are presented in Fig. 9 (a, b). As mentioned earlier, XRD was not performed for the Ultracel 5 kDa membrane because its skin layer is not detachable from the support layer.

Figure 9a shows the X-ray spectra of unexposed and exposed RC70PP samples. Three typical diffraction peaks appeared at approximately  $2\theta = 13.0^\circ$ ,  $20.5^\circ$  and  $22.0^\circ$  for (1–10), (110) and (020) lattice planes of cellulose II. Interestingly, the barely noticeable presence in the reference diffractogram of the (002) reflection ( $2\theta = 16.0^\circ$ ) becomes clearer in the 8-week sample. This trend might be connected to a growing random orientation of cellulose II crystallites in the membrane. The cotton-based membrane samples also showed a cellulose II pattern having two main peaks at approximately  $2\theta = 13.0^\circ$  and  $20.5^\circ$  for (1–10) and (110) lattice planes. (French 2014) Despite the fact



**Fig. 9** XRD curves: (a) the RC70PP membrane (reference, after 4-week exposure, after 8-week exposure); and (b) the cotton-based membrane (reference, after a 4-week exposure)

**Table 5** Crystallinity indexes of the RC70PP and cotton-based membranes in fresh condition and after exposure to spent DES solution

Membrane name	Crystallinity index, %
RC70PP reference	76
RC70PP after 4 weeks	83
RC70PP after 8 weeks	89
Cotton-based reference	66
Cotton-based after 4 weeks	71

that both membranes belong to the same cellulose allomorph, their diffractograms differ by the peak  $22.0^\circ$  for (020) plane. Apparently, the cotton-based

membrane's diffractogram can be recognized as amorphous pattern (French 2020).

CrI calculations for the RC70PP and cotton-based membranes are presented in Table 5. The CrI values in Table 5 were calculated based on the method described by Segal et al. (1959).

For both membranes, the main peaks of the X-ray diffractograms of the membranes exposed to DES solution are the same as their references, indicating that no rearrangement to other cellulose allomorphs occurred (Sirviö et al. 2016). At the same time, the CrI values (Table 5) suggest an increase in crystallinity of the DES-exposed samples with time. In other words, long exposure to DES solution was removing amorphous regions from both kinds of cellulose membranes.

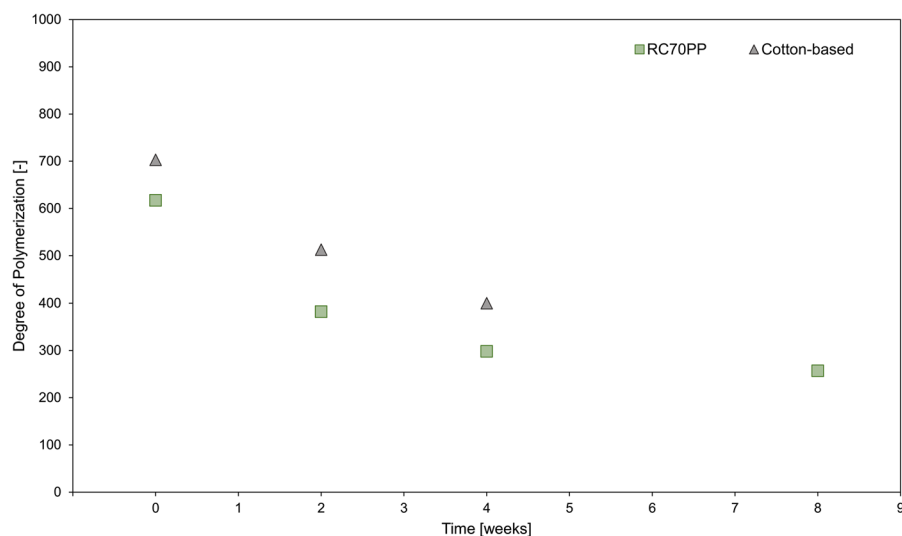
The degree of polymerization (DP) results (Fig. 10) show changes in cellulose chain length. Both membranes undergo cellulose chain reduction with time of exposure. The reduction is more dramatic for the RC70PP membrane – 52% and 43% of chain length reduction respectively after 4 weeks of exposure to spent DES.

Both membranes demonstrate a big drop in DP already after 2-week exposure to spent DES solution. The size of the reduction in the cellulose chain length becomes smaller on further exposure to DES. Generally, such DP pattern is similar to the changes in DP of cellulosic fibers subjected to acid. During acid hydrolysis, glycosidic linkages are, initially, broken fast. As hydrolysis proceeds, it slows down and reaches the so-called “levelling-off” degree of polymerization (LODP). (Palme, Theliander, and Brelid 2016).

## Conclusion

The present work examined the performance stability and alterations in chemical structure of commercial and laboratory-cast cellulose membranes following long-term exposure to acidic 60 vol% spent DES in ethanol. It was found that all the membranes studied, namely RC70PP, Ultracel 5 kDa and a cotton-based membrane, demonstrated only minor changes in pure water permeability (PWP) and PEG retention for up to 4 weeks of DES exposure. After 8 weeks of exposure, PWP of the RC70PP membrane increased by 45%. At the same time, PEG retention decreased

**Fig. 10** Degree of Polymerization of RC70PP and Cotton-based membranes due to exposure to spent DES time



noticeably. The other membranes were tested only for 4 weeks of DES exposure.

It was found that spent DES exposure made the surface of the studied membranes more negatively charged, which suggests that modifications occurred on the surface of the membranes. FTIR spectra of the membranes exposed to DES solution supported this conclusion. Additionally, FTIR spectra of the membranes exposed to the DES solution showed an increase in peak intensities in the area  $1753\text{--}1733\text{ cm}^{-1}$  of the carbonyl group, possibly due to cellulose esterification. An increase in the crystallinity of the exposed samples along with a reduction in cellulose chain length are evidence of a hydrolysis reaction taking place in the membranes during exposure to spent DES.

Changes in the chemical structure of the membranes, seen as more negative surface charge, an increase in carbonyl group IR band intensity, an increase in crystallinity, and a decrease in degree of polymerization, occurred already after 2 weeks of DES exposure. However, noticeable changes in membrane performance became apparent only after 8 weeks of exposure. Thus, alterations in chemical structure of cellulose membranes did not instantly lead to big changes in membrane performance. This finding emphasizes the need for comprehensive characterization experiments in evaluation of membrane stability in addition to monitoring of flux and retention values.

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**Author contributions** V.I. did all experiments, analyses, wrote the main manuscript text and prepared all figures and tables. M.K.-M., M.M. and I.A. were responsible for Conceptualization, Methodology, Supervision and Review of the manuscript. M.K.-M. was also responsible for Project administration and Funding acquisition. All authors read and approved the final manuscript.

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#### Declarations

**Conflict of interest** The authors have no relevant financial or non-financial interests to disclose.

**Ethics approval and consent to participate** Not applicable.

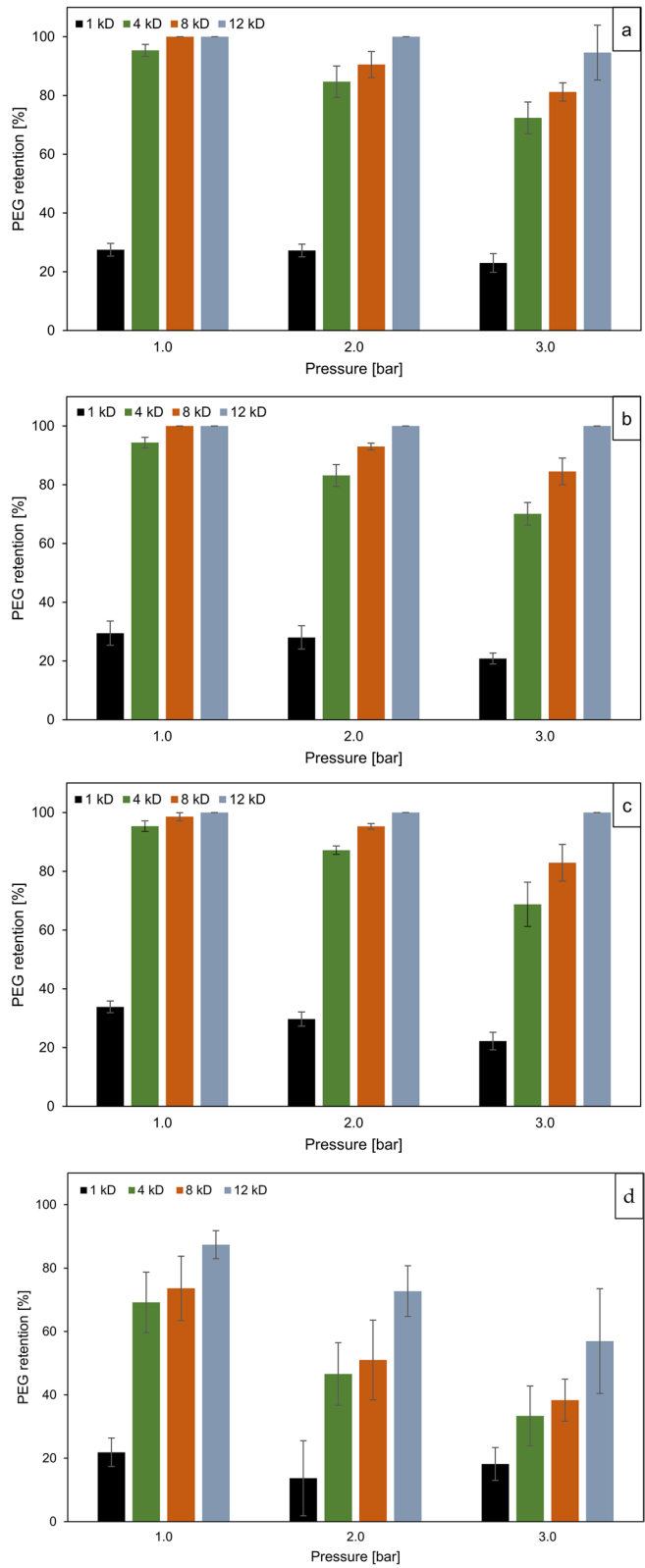
**Consent for publication** Not applicable.

**Availability of data and materials** The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

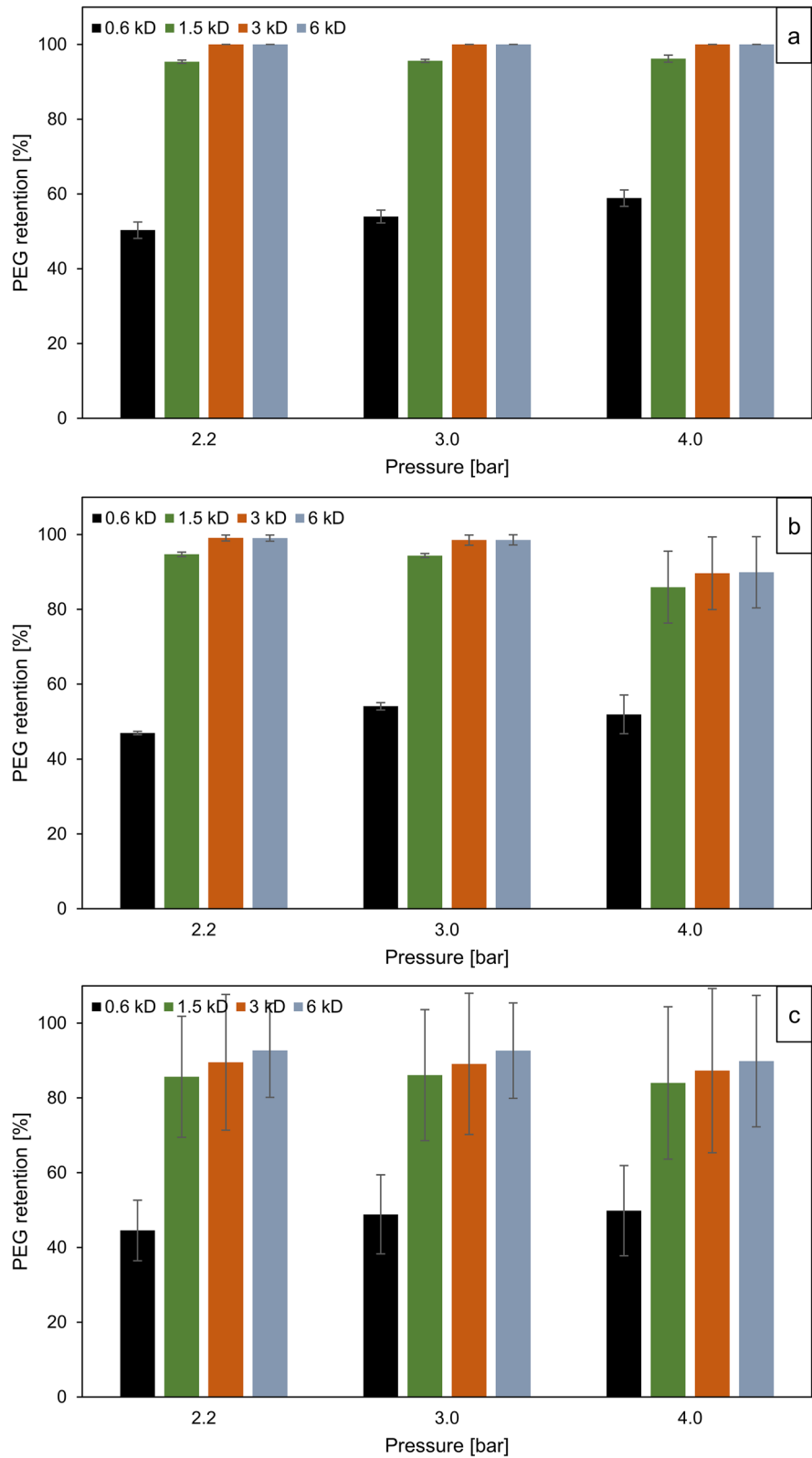
#### Appendix

See Figs. 11, 12 and 13

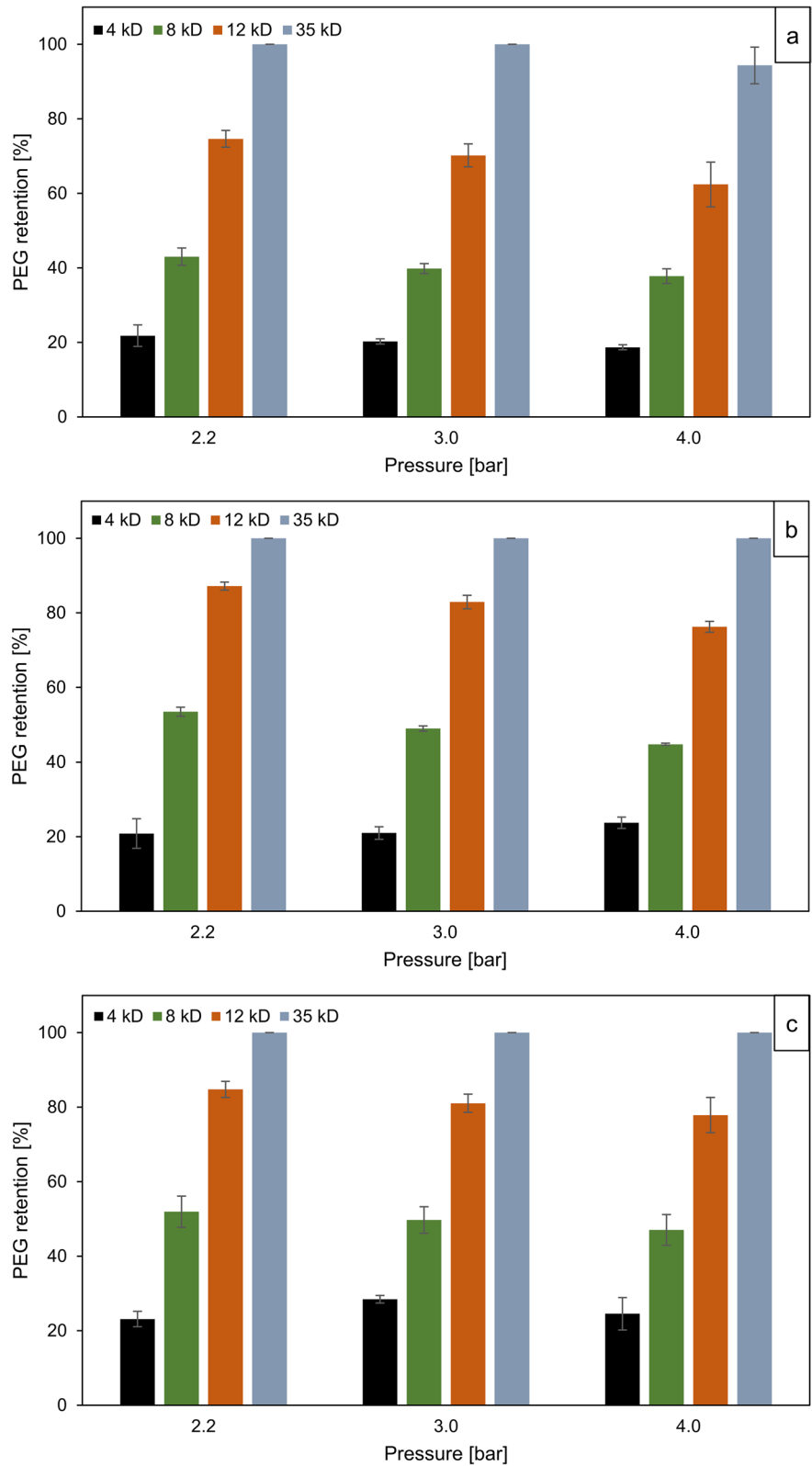
**Fig. 11** PEG retention values of three RC70PP membrane samples: (a) reference; (b) after 2-week exposure to spent DES solution in ethanol; (c) after 4-week exposure to spent DES solution in ethanol, and (d) after 8-week exposure to spent DES solution in ethanol



**Fig. 12** PEG retention values of three Ultracel 5 kDa membrane samples: (a) reference; (b) after 2-week exposure to spent DES solution in ethanol; and (c) after 4-week exposure to spent DES solution in ethanol



**Fig. 13** PEG retention values of three cotton-based membrane samples: (a) reference; (b) after 2-week exposure to spent DES solution in ethanol; and (c) after 4-week exposure to spent DES solution in ethanol



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