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Comparison of 2D and 3D materials on membrane modification for improved pressure retarded osmosis (PRO) process

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ABSTRACT

Pressure retarded osmosis (PRO) is a sustainable process that convert Gibbs free energy to osmotic energy by mixing two solutions of different salinities. The main challenges in the design of PRO membranes are obtaining a membrane with high water permeability and low salt permeability but also very high mechanical strength because the PRO process involves high pressure on the draw solution. Commercially available RO membranes with potential utility in a PRO system exhibit a high salt rejection rate but low water permeability and mechanical stability. Surface modification is a promising strategy for tuning the fundamental properties of the membranes (e.g. hydrophilicity, surface charge and thickness) that can improve the filtration performance of the membranes. The coating layer can also improve the mechanical stability of the membranes. Therefore, in this work, various types of modification materials were applied to the commercial available RO membranes to enhance their performance.

With the assistance of hydrophilic materials (e.g. polydopamine – PDA), filtration performance of the membranes can be increased through membrane modification by 2D materials with high charge intensities (e.g. polyelectrolytes and graphene oxides) and by 3D mesoporous materials (e.g. zeolites), which increases the thickness of the membrane that can be beneficial in mechanically reinforcing the membrane. In this work, we modified commercial RO membrane with PDA, polyelectrolytes, graphene oxide and zeolites (ZSM-5). Improved filtration performance (increased water permeability and maintained salt permeability) of the modified membrane was observed. Tensile tests showed enhanced mechanical strength of the modified membranes, especially following 3D zeolites modification (up to 35 % of higher tensile strain was reported). Interestingly, a lower concentration of PDA (2 mg/mL) and zeolites resulted in higher mechanical strength of the modified membranes. Such results were likely due to a more homogenous coating layer when a low modifier concentration was applied. The thin and uniform layer can better absorb energy when membranes are under high pressure.

1. Introduction

The world is currently facing a severe threat posed by climate change, driven mainly by burning fossil fuels (York and Bell, 2019; Falkner, 2016). However, even though awareness of a climate change is broadly spread, in 2017 the global emissions increased by 1.7 % (Gielen et al., 2019; Taylor et al., 2016). Therefore, to reach the global goals for reduction of greenhouse gases, new renewable technologies need to be

developed (Mohanty, 2012; Østergaard et al., 2020). Over the past decade there has been a 16.2 % annual increase in renewable energy output, mainly electricity generation from solar or wind driven installations (York and Bell, 2019; Timilsina, 2021). However, those technologies face issues connected with environmental conditions, meaning they are not available 24 h per day, hence they are not able to produce energy at a constant rate. As a result, new energy vectors have to be explored to improve the production and efficiency of renewable

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energy. A novel method of generating renewable energy is to harvest the naturally occurring process through which energy is generated when salt water and fresh water are mixed. This energy is produced by osmotic pressure and can be collected (Kim et al., 2015). One application where natural osmosis occurs is when a river (fresh water) flows into the ocean (salty water) and produces Gibbs energy of mixing (Helfer et al., 2014). It is estimated that the potential salinity gradient energy (i.e. mixing fluids with different salt concentrations) on a global scale is 647 GW (SALINITY GRADIENT ENERGY TECHNOLOGY BRIEF, 2014). One of the methods for energy harvesting from this process is pressure retarded osmosis (PRO) using membranes. Due to osmotic pressure differences, fresh water will pass to the salt side and the volume will be increased. This increase in volume can then be used to drive a turbine to generate energy (AlZainati et al., 2021). A major benefit of PRO compared to traditional renewables is continuous production (Feinberg et al., 2013; Chung et al., 2015).

Even though PRO is a promising concept, the technology faces some economic and technical barriers which are mainly due to the cost of the membranes. To make the process economically viable the price of membranes must be reduced (SALINITY GRADIENT ENERGY TECH-NOLOGY BRIEF, 2014; Mark, 2014; Mulder and Mulder, 1996; Cui and Muralidhara, 2010). Presently, commercially accessible reverse osmosis (RO) membranes, specifically the conventional thin film composite (TFC) membranes, demonstrate commendable salt rejection capabilities, making them potentially suitable for maintaining elevated salinity levels in the draw solution within a PRO system. However, their application in the PRO process is impeded by two primary challenges: low water permeability and insufficient mechanical stability. This is critical as the power density in the PRO system hinges on both the permeate flux and the mechanical pressure applied (Shi et al., 2021). To overcome these hurdles, a promising avenue involves surface modification through the incorporation of additional layers. This strategic enhancement, as detailed in literature (Zornoza et al., 2011), holds the potential to augment the water permeability and bolster the mechanical stability of RO membranes, thereby rendering them more amenable for utilization in the PRO process. The extra coating layers on the membrane surface should not alter the asymmetric membrane structure significantly, i.e. the membrane should still maintain a porous thick support layer and a dense active layer that is selective to transport. The hydrophilic and mechanically stable coating layers act as an additional attachment that helps to increase the permeability and robustness of the membrane.

Under alkaline conditions, dopamine can self-polymerize to a homogenous and hydrophilic polydopamine (PDA) coating layer on the membrane surface. PDA has multiple nucleophilic and electrophilic reactive groups that allows it to bind to a surface, while other reactive groups can bind to a different compound (Liebscher, 2019). Therefore, PDA can enhance the water permeability of the modified membrane (Drever et al., 2013; Yang et al., 2018). In addition, 2-dimensional (2D) materials such as polyelectrolytes (PE) and graphene oxide (GO) have attracted wide attention due to their unique physicochemical properties (Lipton et al., 2020). These materials are charged compounds that are able to alter the surface charge density of a membrane and influence Donnan exclusion, which can be exploited for the removal of target ions. The layer-by-layer (LbL) assembly utilizes the natural force of the 2D materials (e.g. electrostatic interactions, hydrogen bonding, metalorganic coordination, charge-transfer interactions and molecular interactions) to form multiple coating layers on the membrane surface (Lipton et al., 2020). The multiple charged modification layers introduce higher energy barriers for ion transport, which can increase the salt rejection of the membrane (Sigurdardottir et al., 2020). Moreover, the porous structure of the PE layers allows high water permeability and thus the membrane can maintain high filtration performance. Thanks to a high mass-to-charge ratio, the GO sheets can form thin and homogenous coating layers on the membrane surface and nanochannels between the GO sheets allow extremely fast water transport (Hu and Mi,

2014).

The other promising option is to use the nanoporous properties of 3dimention (3D) materials, such as zeolites, for membrane modification (Algieri and Drioli, 2021). Zeolites possess a uniform pore structure and high chemical stability (Zhou et al., 2015). They are characterized by a three-dimensional morphology that creates a relatively open structure comprising pore openings and channel systems. The sizes of pores are in the range of 4.1 to 7.4 Å (Klier, 2005). Such a small pore structure has the ability to work as a molecular sieve and discriminate between molecules by size (Rangnekar et al., 2015). Because of the ordered hexagonal structure (Song and Yan, 2008), zeolites possess high mechanical stability and have also been proven to increase the mechanical stability of the membrane (Mahdi and Tan, 2016; Wang et al., 2019). An enhancement of the membrane modulus of elasticity by up to 40 % was reported when a composite membrane was incorporated with zeolites (Nigiz et al., 2015). The mesoporous structure of the zeolites modification layer can increase the total filtration surface of the membrane and thus increase water permeability (Sakai et al., 2019). There are different options for binding zeolites to the surface of the membrane (Zhou et al., 2015). Due to the high adhesion capacity, dopamine can adhere to various surfaces. Under aerobic and alkaline conditions, dopamine can oxidize and polymerize through deprotonation and intermolecular Michael addition. The resultant PDA layer usually functions as a versatile platform for a secondary reaction, for example, to link to zeolites (Liu et al., 2013).

Mechanical stability is one of the main parameters that we have focused on due to how crucial this property is for achieving a required PRO working principle. Material strength under tension can be characterized by yield strength (YS) and ultimate tensile strength (UTS). Yield strength, the stress at which plastic deformation of a material starts, while useful for materials such as metals where there is a distinct elastic response followed by a distinct plastic response, is less useful for viscoplastic polymers where their entire response is plastic flow of varied degree. Ultimate tensile strength, the peak stress sustained before failure, as well as breaking strain, the strain at which the material fails, are both more useful metrics. These two values are also proxies for the area under the measured stress-strain curve, which describes the amount of energy the material is capable of absorbing.

Enhancing commercially available reverse osmosis membranes becomes instrumental for scaling up pressure retarded osmosis applications, especially given the absence of dedicated PRO membranes in the market. The innovative coating materials such as PDA, PE, GO, and zeolites mentioned earlier offer a versatile toolkit for tailoring the properties of these commercial membranes. Through strategic application, these materials can fine-tune membrane characteristics in various ways, thereby optimizing their performance within the PRO process. In this work, we demonstrate successful membrane modification strategies with 2D (poly cation - poly(diallyldimethylammonium chloride) PDADMAC, polyanion - poly(methacrylic acid) PMAA and GO), and 3D materials (zeolites - ZSM-5). The 2D materials were assembled via LbL on the active layer on the PDA modified membrane surface. Zeolites and PDA were co-deposited on the active as well as the support side of the membrane. As far as we are aware this is the first time zeolites have been used to modify a commercial membrane in order to increase membrane water permeability and mechanical stability. Membrane performance was investigated by testing the water and salt permeability of an RO filtration system, and membrane stability was examined by tensile tests.

2. Materials and methods

2.1. Materials

The chemicals used – NaOH (Honeywell), Tris-HCl (Sigma-Aldrich), NaCl (Sigma-Aldrich), Dopamine-HCl (Sigma-Aldrich), PDADMAC (Sigma-Aldrich), PMAA (Sigma-Aldrich), GO (Sigma-Aldrich), ZSM-5 zeolite (NIST) – were all of analytical grade and were used without any additional pretreatment. Commercially available membranes were purchased from Alfa Laval.

2.2. Methods

Commercially available Alfa Laval RO-99 membrane was chosen for modification with PDA, PEs, GO and zeolites. Properties of the membrane are shown in Table 1.

Flat sheet membranes were cut into squares (80 mm \times 80 mm) and activated in a 0.03 % NaOH solution for 60 min at 60 °C. The activated membranes were washed thoroughly with Milli Q water and then mounted in a self-assembled mold of 6×6 cm surface area for the following modifications.

2.2.1. Membrane modification

2.2.1.1. Modification with 2D materials via LbL assembly. The layer-bylayer mythologies are modified from the previous studies that utilized PS or GO as the coating materials (Sigurdardottir et al., 2020; Kulkarni et al., 2010). The active layer of the RO membranes was coated with 2 mg/mL PDA (in Tris-HCl buffer, pH 8.5) for 7 h. The LbL modification of PE or GO multi-bilayers (BLs) was initiated by the deposition of PDADMAC solution by exposing the PDA coated membrane to 10 mL of PDADMAC solution for 10 min. Next, the PDADMAC solution was removed and the PDA coasted membrane was subjected to two 5-min rinsing cycles (10 mL of 0.5 M NaCl) to remove any loosely adsorbed PDADMAC. Subsequently, 10 mL of 20 mM PMAA solution (or 0.01 mg/ mL of GO solution in 0.5 M NaCl) was applied to the membrane for 10 min, followed by two 5-min NaCl solution rinsing cycles. The above six steps concluded fabrication of the first BL. Subsequent BLs were fabricated in the same manner as described to obtain membrane with 1 BL, 3 BLs and 5 BLs. After modification, the membranes were annealed by immersion in 2 M NaCl solution for 30 min.

2.2.1.2. Modification with 3D zeolites materials. The 3D material methods are modified from the previous studies that utilized dopamine and zeolites as the coating materials (Zhou et al., 2015). ZSM-5 zeolites were mixed with Tris-HCl buffer solution (50 mM, pH 8.5) and the mixture was sonicated (Hielscher UP400ST) for 15 min to ensure no agglomeration of zeolite particles. In the meantime, different concentrations of polydopamine were obtained by mixing polydopamine hydrochloride solution and Tris-HCl buffer. Zeolites were added to the PDA solution, mixed and poured onto the RO membranes that were placed inside the molds. The membranes were coated with the solution and placed on a shaker (Heidolph Duomax 1012) for a given amount of hours. Afterwards, the molds were drained of liquid and modified membranes were dried in an oven for 2 h at 50 °C. The membranes were then stored in Milli-Q water until further analysis. The modification strategies are summarized in Fig. 1.

2.2.2. Permeability measurements

Before any measurement of performance parameters, the membranes were compacted to avoid any large offsets in the flux. For compaction, the membranes were placed in a measuring cell (Sterlitech) under the controlled temperature of 20 °C (adjusted by a chiller from PolyScience) at 60 bars (achieved by a hydraulic pump from WASHGUARD® SST) for

 Table 1

 Alfa Laval RO-99 commercial membrane parameters.

Variable	Properties
Active layer	Polyamide
Support layer	Polyethersulfone
Non-woven back layer	Polyester
pH-range	3–10
Membrane thickness	150 µm



Fig. 1. 2D and 3D modification strategies of the study.

1 h, and possible leaks were inspected (see Fig. 2). All the membranes in the test had their active layer facing the water or salt solution. Water permeability was measured at 20, 40 and 60 bars in an RO membrane test cell (methods modified from the previous study (Li et al., 2019). Salt permeability was measured by utilizing an aqueous solution of salt (3.5 wt% NaCl which gave 30.8 bar osmotic pressure). The system was left to run for 40 min at 40 bars to ensure all piping was filled with brine solution. The permeate was collected in the permeate side of the system and the collected samples were used to measure the conductivity of the solution to obtain salt permeability calculations. The salt concentrations from the measured conductivities were calculated by relating conductivity to ion mobility with Eq. (1):

$$C = \frac{\sigma}{q_{Na}^+ \bullet \mu_{Na}^+} \bullet \frac{1}{N_A} \tag{1}$$

where, C is the concentration (mol/m³), σ is the conductivity (S/m) (1 μ S/m = 0.0001 S/m), q_{Na}^+ is the charge of the sodium ion (1.6 \cdot 10 $^{-19}$ C), μ_{Na}^+ is the mobility of the sodium ion (5.19 \cdot 10 $^{-8}$ m²/V·s) and N_A is the Avogadros number (6.023 \cdot 10 23 mol $^{-1}$).

The key parameters, water permeability and salt permeability, are calculated from the following equations:

$$J_w = A(\Delta \pi - \Delta P) \tag{2}$$

$$J_s = B(C_D - C_F) \tag{3}$$

where, J_w is water permeating flux, A is water permeability, $\Delta \pi$ is osmotic pressure difference, ΔP is hydraulic pressure difference, J_s is the salt permeating flux, B is salt permeability, C_D and C_F are the concentration of the solute in the draw and feed side, respectively.

2.3. Characterization

The surface morphology of the pristine and modified membranes as well as their cross sections were inspected by Scanning Electron Microscopy (SEM) (Prisma E-SEM, Thermofisher Scientific) operated at an accelerating voltage of 5–10 kV. EDX analysis coupled with SEM was used to identify chemical composition at the membrane surface. Two EDX analytical tools were applied: 1) spectrum and 2) spectral imaging.



Fig. 2. PI-diagram of the RO setup.

The change of the membrane surface chemistry was analysed by FT-IR Spectrometer Invenio-S (Bruker) to compare the modified membranes with the pristine unmodified structures. Electrokinetic potential between the membrane surface and dispersed solutes (zeta potential) was measured by Electrokinetic Analyzer SurPASS 3 (Anton Paar). Zeta potential is used as an indicator of membrane surface charge, which is a dominating factor in solute rejection. The hydrophilicity of the membrane surface was determined by determining the water contact angle (sessile drop technique) using an optical tensiometer (Attension Theta Lite, Biolin Scientific). The concentration of salt in the permeate side after the salt permeability test was calculated from conductivity measurements made using a Seven Excellence pH/Ion/Conductivity meter S975-K (Mettler Toledo).

2.3.1. Tensile tests

Tensile tests were performed on a Zwick/Roell Z030 universal test machine. Test coupons were 6 cm \times 0.6 cm for all modified membranes and the pristine membrane controls. 1 cm of each end of the test coupon was gripped in the machine, leaving a 4 cm \times 0.6 cm test area. The non-woven layer was always oriented with its fibers running in the direction of elongation. All tests were performed at a strain rate of 0.1 s⁻¹. The tensile test stretched the material until it failed, producing a curve of induced force vs. applied elongation. The tensile strength and failure strain were calculated by Eqs. (4) and (5), respectively:

$$\sigma = \frac{F}{A} \tag{4}$$

$$\varepsilon = \frac{L - L_0}{L_0} \tag{5}$$

where, F is the force experienced during the test, A is the cross-sectional area of the coupon, L is the coupon length at a point in time, and L_0 is the original length of the coupon. The width of each coupon was measured using calipers, and the thickness was assumed to be the 150 μ m nominal value for this particular membrane. Values for the ultimate tensile strength and failure strain were extracted and compared. For each modality, 3 specimens were tested.

3. Results and discussion

3.1. Filtration performance of different modification strategies

Different modification strategies resulted in different water and salt permeability. The PE modified membrane showed slightly higher water permeability (1-BL and 3-BL) in comparison to the pristine membrane (Fig. 3A) and in general had lower salt permeability (Fig. 3B). This result could be attributed to the loose structure of the PE BLs that did not add extra resistance for the water molecules to pass through. In contrast, the multiple PE BLs increased the energy barriers for the ions thus resulting in lower salt permeability (Sigurdardottir et al., 2020). For the PE and GO modified membranes, improved water permeability was observed (Fig. 3C) but the modified membranes were also characterized by higher salt permeability (Fig. 3D). The PDADMAC/GO interlayer nanochannels built above the membrane allowed higher molecular transport and therefore increased throughput was observed (Liu et al., 2023).

Moreover, a series of experiments was performed to study the effects of concentrations of PDA and zeolites and their influence on membrane performance (mainly water and salt permeability values). To this end, a range of concentrations between 2 mg/mL and 20 mg/mL for both PDA and zeolites was examined. The modifications were applied on the active layer and support layer of the membranes (Table 2).

Fig. 3E shows that the PDA+zeolites modification on the active layer improved the water permeability of the membranes and higher salt permeability was observed (Fig. 3F). The results could be attributed to higher hydrophilicity of PDA and to structural expansion due to the zeolites, which resulted in a larger surface area and further led to an increase in water and salt permeability (Zhang et al., 2016) (i.e. the additional zeolites increased the filtration surface area of the membrane so the membrane allowed more solute to pass through (Zhang et al., 2016). However, the same modification on the support layers showed different results. Lower water permeability and salt permeability were observed when the modifications were conducted on the support layer. This result could be due to the porous structure of the support layer, and the PDA and zeolites might have been entrapped into the pores of the support - much larger than the pores of the active layer - and caused pore blocking (Arena et al., 2011), which resulted in lower water and salt permeability. The morphology change of the support layer was observed after modification (Fig. 7) - the coating materials entrapped into the pours on the support layer which can be the cause of the decrease of water and salt permeability (Fig. 3E and F).

Fig. 4 summarizes water permeability and salt permeability among the membranes. High water permeability and low salt permeability is desired, therefore the membrane results found at the right upper corner of the Figure indicate higher filtration performance. For the PE modified membranes, 1 BL of PDADMAC/PMAA exhibited the highest performance, and the 3-BL modification also showed improved filtration behavior (Fig. 4A). Similarly, the 1-BL of PDADMAC/GO modification showed significant improvement regarding both water and salt permeability. Interestingly, increasing the number of BLs (e.g. the 5-BL modification of PDADMAC/PMAA or PDADMAC/GO) did not further improve the filtration performance of the membranes. The results indicate that PE or GO materials can efficiently enhance the performance of the membranes, and that the number of BL in these cases played a less significant role in increasing overall filtration performance. These results are consistent with membrane charge alternation (Fig. 6) surface charge of the membrane changed significantly after1 BL of



Fig. 3. Water permeability of different membranes: (A) PDA+PDADMAC/PMAA modified membranes, (C) PDA+PDADMAC/GO modified membranes, and (E) PDA+zeolites modified membranes. Salt permeability of different membranes: (B) PDA+PDADMAC/PMAA modified membranes, (D) PDA+PDADMAC/GO modified membranes, and (F) PDA+zeolites modified membranes. (Note: figure E and F show the results of the active layer modified membranes – blue columns and support layer modified membranes – red columns).

Table 2	
Experimental conditions on active and support layers.	

Active layer	PDA conc. [mg/mL] Zeolite conc. [mg/ mL]	2 2	20 2	2 20	20 20
	Label	CA 2/ 2	CA 20/ 2	CA 2/ 20	CA 20/ 20
Support layer	PDA conc. [mg/mL] Zeolite conc. [mg/ mL]	2 2	20 2	2 20	20 20
	Label	CS 2/2	CS 20/ 2	CS 2/ 20	CS 20/ 20

modification, while addition of further BLs resulted in negligible difference on the membrane surface.

Enhanced water permeability was observed in active layer modifications compared to support layer modifications for PDA+zeolites modified membranes, as illustrated in Fig. 3F. Notably, the CA 20/2 membrane, featuring 20 mg/mL PDA and 2 mg/mL zeolite on the active layer, stood out for its combination of high water permeability and a favorable A/B ratio (Fig. 4B). The larger size of aggregated PDA and zeolite particles prevented them from entering the membrane pores in the dense active layer, mitigating pore blocking. The improved filtration performance of the membranes can be attributed to the heightened hydrophilicity of the coating layer. However, it's worth noting that while the coating materials couldn't penetrate the smaller pores on the active layer, they did enter larger pores from the support side, leading to



Fig. 4. Summary of the water and salt permeability of the pristine and modified membranes.



Fig. 5. Characterization of active layer modified membranes. FITR spectra of (A) PDA+PDADMAC/PMAA modified membrane, (C) PDA+PDADMAC/GO modified membranes, and (E) PDA+zeolites modified membranes. Water contact angle of (B) PDA+PDADMAC/PMAA modified membrane, (D) PDA+PDADMAC/GO modified membranes, and (F) PDA+zeolites modified membranes.



Fig. 6. Zeta potential profiles of (A) PDA+PDADMAC/PMAA modified membranes, (B) PDA+PDADMAC/GO modified membranes.



Fig. 7. SEM images of top views of the A) pristine membrane, B) PDA+PDADMAC/PMMA and C) PDA+PDADMAC/GO modifications on the active layer, D) pristine support layer, E) PDA+zeolite modification on the selective layer and F) PDA+zeolite on the support layer modification. Cross section of the G) pristine membrane, H) PDA+zeolite modification on the selective layer and I) PDA+zeolite modification on the support layer.

partial membrane blockage. This counteracted the otherwise improved water permeability resulting from enhanced hydrophilicity. A similar blockage phenomenon due to PDA modification on the support layer was previously reported in a study (Arena et al., 2011). Consequently, superior outcomes were achieved through active layer modifications.

3.2. Characterization of the membranes

Chemical changes were observed on all the surface modified membranes based on the FTIR spectra (Fig. 5). For the membranes modified by PDADMAC/PMAA or PDADMAC/GO, N-H bonds from PDADMAC were observed in the range $3000-2800 \text{ cm}^{-1}$, even when the modification was terminated by PMAA or GO. The explanation for this result is that the coating layer in these cases was very thin and since PDADMAC is a large molecule possessing abundant N-H bonds, therefore chemical changes due to PDADMAC were observed. This result is consistent with the surface charge alterations (Fig. 6) because PDADMAC is a rather strong and positively charged molecule, and therefore the modified membranes became positive at lower pH. Regarding the GO terminated modification, O-H bonds on the GO flakes were detected at 3300 cm⁻¹ (Fig. 5C). Due to the hydrophilicity of PDA, the surface modified membrane became more hydrophilic and a lower water contact angle was observed (Fig. 5B and D). Moreover, the addition of the PE or GO BLs further decreased the value of the water contact angle. GO flakes are rich in hydroxyl groups and the planar structure of GO resulted in a smooth membrane surface (Fig. 7), therefore PDA+PDADMAC/GO modified membranes had higher water affinity (i.e. a lower water contact angle Fig. 5D).

For the PDA+zeolites-modified membranes, Si-O bounds from ZSM-5 were observed in the range of 400 cm⁻¹ to 1400 cm⁻¹ (Fig. 5E). Absorbance at 1085 cm⁻¹ has been linked to transverse asymmetric strain bonds between Si-O-Si. There is also the Si-O-Si buckling vibration

at 468 cm⁻¹, which is a characteristic peak for zeolite ZSM-5 (Mukaromah et al., 2019).

The crystalline structure of ZSM-5 and its agglomeration was observed after coating with PDA (Fig. 7). From the SEM image, the size of the crystals is approximately 2 µm (Sakai et al., 2019). The porous structure of ZSM-5 together with higher hydrophilicity of PDA significantly decreased the water contact angle of the modified membranes (Fig. 5F), indicating the much higher water affinity of the modified membrane (from over 45° to around 6°). Zeolites possess porous structure and hence allow water to disperse through the porous layer over a large area on the surface of the membrane (Klier, 2005). This effect of dispersion through ZSM-5 porous channels is coupled with PDA being a hydrophilic compound which would further increase hydrophilicity. The presence of chemical components in a top view on both sides of the membrane (selective and support) was analyzed using EDX based on SEM images, with $5000 \times$ magnification. Considering Figs. S4 and S5 from the Supporting Information for the selective layer and Figs. S6 and S7 for the support layer, the full spectrum shows that the main components of the membrane are C, O, Si, Al and Ag. Carbon and oxygen are the basic elements of a polymeric membrane, which is polyamide for the selective layer and polyethylene terephthalate for the support. Moreover, Si and Al indicate the presence of the ZSM-5 zeolite on both layers since zeolite is an aluminosilicate material. Ag corresponds to the fact that the sample had to be coated with silver before the measurement to make it conductive. Table S2 and S3 show the weight % of each element in the selective and support layer, respectively.

Finally, the measurements conducted on the SEM were divided into two parts: 1) top view of the selective and support layers before and after modification and 2) cross section before and after modification. Fig. 7(A - C) show a clear comparison of a selective layer membrane before and after modifications, where a typical polyamide morphology of a pristine membrane can be appreciated (Fig. 7A), followed by an addition of polyelectrolytes (Fig. 7B) and graphene oxide (Fig. 7C). Fig. 7E shows a selective layer membrane coated with zeolites where typical crystalline zeolitic structure can be observed. Support non-woven layer of the pristine membranes is shown in Fig. 7D, where after modification with zeolites (Fig. 7F) a crystalline structure can be observed in between the non-woven structure. Finally, the cross section of the pristine membrane is shown in Fig. 7G and compared to the membranes coated with zeolites on the selective (Fig. 7H) and support (Fig. 7I) sides. All these techniques prove that the membranes were properly modified for the PRO application.

3.3. Tensile tests

The mechanical properties of the membranes were investigated by tensile tests. The tensile strength of the pristine membrane was 47.22 \pm 0.85 MPa and the elongation strain was 0.100. All the surface modified membranes showed improved tensile strength and failure strain (Table 3), which indicates that the modifications successfully enhanced the mechanical stability to a certain extent. For the 2D materials modification, the PDADMAC/PMAA BLs made the membrane thicker (Sigurdardottir et al., 2020) while the soft PE materials were able to absorb energy when pressure was added to the membrane, thus resulting in higher tensile strength. The PDADMAC/GO BLs improved the tensile strength and failure strain due to a similar mechanism. It is worth noting

Table 3

Comparison of tensile strength and failure strain of pristine and the modified membranes.

Modification	Tensile strength (MPa)	Maximum failure strain
Pristine	47.22±0.85	0.100
PDA+Zeolites	53.33±4.46	0.135
PDA+PDADMAC/PMAA	49.08±2.85	0.132
PDA+PDADMAC/GO	$50.58{\pm}2.20$	0.118

that the 2D materials formed relatively thin layers on the membrane surface, and therefore the addition of thin coating layers can help increase the mechanical stability of the membranes.

Modification with 3D materials (2 mg/mL PDA and 2 mg/mL of ZSM-5) outperformed the other modification strategies and gave even more promising results; the tensile strength of the membrane increased to 53.33 ± 4.46 (MPa), while the tensile strain increased by 35 % (from 0.100 to 0.135, see Table 3 and Fig. 8). This additional mechanical stability of the membrane could be due to polymerization of dopamine and binding with ZSM-5. At pH 8.5, dopamine was oxidized to PDA and C-C bonds among the benzene rings covalently linked the molecules, which enhanced the robustness of the coating layer (Pezzella et al., 2007). Polymerized PDA can adhere to the ZSM-5 particles through intermolecular interactions (e.g. van der Waals forces, or PDA with shorter chains could have formed H-bonds with ZSM-5 (O-H---O or N-H…O)) (Chai et al., 2014), and the coating layer could have attached to the membrane surface via π -stacking (Chen et al., 2018). PDA has been reported to induce crazing resistance and absorb energy during tensile deformation (Jiang et al., 2014), thus leading to greater elongation at failure (i.e. higher failure strain). Interestingly, increasing the PDA concentration (from 2 mg/mL to 20 mg/mL) did not improve the tensile strength of the membranes; 51.25±2.23 MPa of tensile strength and 0.122 of tensile strain were observed on the membrane modified with 20 mg/mL PDA and 2 mg/mL ZSM-5 (Fig. 8). At high concentration, dopamine had the tendency to form free particles. The free particles aggregate through a combination of charge transfer, π -stacking and hydrogen bonding, to form shapeless clusters (Fei et al., 2008; Cheng et al., 2012). Such irregular patterns led to an uneven distribution of the coating layer, thus coating at high PDA concentration did not contribute extra mechanical resistance to the membrane. A lower concentration of PDA is therefore suggested for better control of the modification of the membrane.

The above results imply that a homogenous coating layer of zeolites/ PDA contributed to enhancement of the mechanical stability of the membrane, and thus could be beneficial in developing PRO membranes that require high-pressure resistance in practical applications.

4. Conclusion

Modification with 2D and 3D materials on the membrane selective layer had different influences on the filtration performance of the membranes. Enhanced water permeability and lower salt permeability of the membranes were achieved with the LbL modification of 2D



Fig. 8. Tensile strength and failure strain results for pristine membrane and surface modified membranes.

materials (i.e. PE and GO). The addition of BLs affected the energy barrier of ion transport and therefore higher salt rejection was obtained. A low number of BLs exhibited high filtration performance due to the high charge density of the PE molecules. The strong ionic interactions of the multiple 2D BLs also increased the mechanical strength of the membrane to a certain extent.

In comparison, membranes modified with 3D materials showed improved filtration performance and significant improvements in mechanical strength. Modification of the dense active layer of the membrane improved water permeability and a slight increase of the salt permeability was observed, due to the hydrophilicity of PDA and the larger filtration area of the zeolites. When PDA+zeolites modification was applied on a support layer that has a more porous structure, the modifiers tended to enter the pores and cause blocking which resulted in lower water and salt permeabilities. With PDA+zeolites modification, the active layer is therefore more beneficial in enhancing the filtration performance of the membranes. Additionally, the 3D modification layer on the membrane surface exhibited the highest tensile strength and highest failure strain among all the modified membranes. This result could be due to the modified layer absorbing energy from crazing during tensile stretch testing. An appropriate ratio of PDA+zeolites (i.e. 1:1) that brings about a more homogenous coating layer on the membrane surface contributes most to enhancing the mechanical stability of the membrane. The experimental results indicate that 2D modification efficiently changed the surface properties of the membrane and thus resulted in higher filtration performance, while the 3D modification led to promising enhanced membrane mechanical stability.

CRediT authorship contribution statement

Ziran Su: Conceptualization, Data curation, Investigation, Supervision, Writing – original draft, Writing – review & editing. Magdalena Malankowska: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Supervision, Validation, Writing – original draft, Writing – review & editing. Thomas Marschall Thostrup: . Markus DeMartini: Data curation, Formal analysis, Investigation, Methodology, Validation. Peyman Khajavi: Data curation, Formal analysis, Methodology, Validation. Haofei Guo: Conceptualization, Funding acquisition, Project administration, Supervision. Lars Storm Pedersen: . Manuel Pinelo: Conceptualization, Funding acquisition, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ces.2023.119638.

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