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Nanocellulose in polyvinylidene fluoride (PVDF) membranes: Assessing reinforcement impact and modelling techniques

Seren Acarer-Arat^{a,*}, Mertol Tüfekci^{b,c,**}, İnci Pir^d, Neşe Tüfekci^a

^a Department of Environmental Engineering, Istanbul University-Cerrahpaşa, Avcilar, Istanbul 34320, Turkey

^b Centre for Engineering Research, University of Hertfordshire, Hatfield, Hertfordshire AL10 9AB, United Kingdom

^c School of Physics, Engineering and Computer Science, University of Hertfordshire, Hatfield, Hertfordshire AL10 9AB, United Kingdom

^d Istanbul Technical University, Faculty of Mechanical Engineering, Gumussuyu, Istanbul 34437, Turkey

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ABSTRACT

In this study, polyvinylidene fluoride (PVDF)-based nanocomposite membranes reinforced with cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF) were fabricated using the phase inversion method. The effects of 0.5 wt% and 1 wt% CNC and CNF on structural, mechanical, and filtration properties were examined. Membranes reinforced with 1 wt% CNF exhibited the highest distilled water flux, increasing from 445.91 to 476.17 L/m².h, and showed improved antifouling ability and higher total organic carbon (TOC) removal compared to unreinforced membranes. Mechanical properties were modelled using five numerical methods, with finite element and Mori-Tanaka models showing the best agreement with experimental data. Modelling results indicated that finite element and Mori-Tanaka methods were the most accurate in predicting the modulus of elasticity. The reinforcement significantly enhanced the membranes' performance in terms of flux recovery, fouling resistance, and mechanical strength, making this a novel interdisciplinary investigation of nanocomposite membranes focusing on both mechanical and filtration capabilities.

1. Introduction

Polymeric membranes are selective materials used in water and wastewater filtration applications. Today, polymeric membranes are widely used in water, wastewater, and solid waste leachate filtration applications [1,2]. The low cost and easy production of polymeric membranes compared to ceramic membranes bring polymeric membranes to the forefront of filtration applications [3]. Polyvinylidene fluoride (PVDF) is a frequently preferred polymer in membrane production due to its membrane-forming properties, easy solubility in organic solvents used in membrane production (such as dimethylformamide (DMF), dimethylsulphoxide (DMSO), dimethylacetamide (DMAc) and N-methyl-2-pyrrolidone (NMP)), superior thermal stability, flexibility, stability against UV radiation, high mechanical strength and superior chemical stability against corrosive chemicals [4, 5]. PVDF membranes are employed in filtration applications, including microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) [4-7]. Fouling of polymeric membranes in the filtration process and flux reduction following membrane fouling are common problems in the filtration process with membranes. In recent years, researchers have incorporated various nanomaterials into the membrane structure to modify the surface properties of polymer matrix membranes [8,9], increase their flux performance [8,10-12], improve their mechanical properties [12–15], separation performance [15,16], and improve their fouling resistance performance [8,10,15]. Nanocellulose is defined as a material of cellulose origin with at least one dimension in the nanometer range [17]. The small size, high specific surface area, high stiffness, sustainability, environmental friendliness, and non-toxicity of nanomaterials derived from cellulose [18,19] make them ideal materials for nanocomposite membranes used in water filtration applications. Cellulose nanocrystals (CNCs) are cylindrical rod-like structures with high crystallinity [18]. CNCs are obtained from the source by acid hydrolysis or enzymatic hydrolysis [20]. Cellulose nanofibrils (CNFs) are another type of nanocellulose produced by chemical or enzymatic pretreatment and mechanical fibrillation [21]. CNCs and CNFs, which are hydrophilic nanomaterials, also have high modulus of elasticity and tensile strength [22]. Recent studies have demonstrated that the incorporation of nanocellulose (CNC and CNF) into different polymeric membrane

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^{*} Corresponding author.

^{**} Corresponding author at: Centre for Engineering Research, University of Hertfordshire, Hatfield, Hertfordshire AL10 9AB, United Kingdom. *E-mail addresses:* acarerseren@gmail.com (S. Acarer-Arat), m.tufekci@herts.ac.uk (M. Tüfekci).

matrices results in alterations to the membrane morphology [23,24], improvements in mechanical properties [24,25], increases in flux performance [23–25], improvements in fouling resistance [26] and improvements in separation performance [23,26].

The incorporation of nanomaterials into polymeric membranes has been extensively researched to enhance their mechanical, thermal, and antifouling properties for water filtration applications. Recent studies have shown that integrating nanocrystalline cellulose (NCC) and cellulose nanowhisker (CNW) into poly (D-lactic acid) (PDLA) membranes significantly improves their mechanical and thermal properties, with the best results observed at 1 wt% loading of CNW, achieving water permeability of 41.92 L/m².h at pressures of 0.1-0.5 MPa [27]. This demonstrates the potential of CNW-filled PDLA membranes in water filtration. Polyethersulfone (PES)-based membranes have also been enhanced with graphene oxide (GO) and sulfonic acid-functionalised GO, showing up to five-fold improvement in tensile strength and enhanced dispersion within the matrix due to strong interfacial adhesion via hydrogen bonding and dipole-dipole interactions [28]. Similarly, CNC additions to PES membranes have resulted in significantly increased dye solution flux and enhanced antifouling properties due to the hydrophilic nature of CNCs [29]. In the field of carbon-based nanomaterials, multi-wall carbon nanotubes (MWCNTs) incorporated into aromatic polyamide (PA) membranes have improved both mechanical properties and pollutant rejection rates, although with a slight in permeability [30]. Additionally, decrease hallovsite nanotube-ferrihydrite (HNT-HFO) incorporated into PES mixed matrix membranes has resulted in enhanced water flux and antifouling properties, achieving a pure water flux of up to 640.82 L/m².h and a flux recovery ratio exceeding 98 % after washing [31]. Research on CNCs blended with inherently hydrophobic PES membranes has shown increased porosity, zeta potential, and hydrophilicity, leading to improved NOM removal and fouling resistance [23]. Moreover, polyacrylonitrile (PAN) membranes reinforced with fumed silica (FS) have demonstrated enhanced porosity, water flux, and mechanical rigidity, particularly under wet conditions, making them suitable for robust water filtration applications [12]. Iron oxide (Fe₃O₄) nanoparticles have been effectively used to enhance the hydrophilicity and antifouling properties of polymeric membranes, addressing the sustainability of clean water supply [32]. Titanium dioxide (TiO₂) nanoparticle incorporation into PES/CA membranes has further improved desalination performance, increasing both water flux and salt rejection, thus highlighting the multifunctionality of these nanocomposite membranes [33]. The advancements in membrane technology underscore the significant role of nanomaterials in enhancing polymeric ultrafiltration membranes' characteristics and separation performance [34]

In this study, the effect of CNC (0.25 and 0.5 wt%), CNF (0.25 and 0.5 wt%), and CNC-CNF (0.5 wt%) on the properties and performance of membranes containing 20 wt% PVDF and 5 wt% polyvinyl pyrrolidone (PVP) is investigated. Currently, nanomaterials such as CNC and CNF are not widely used in the preparation of UF membranes for water treatment. In this study, for the first time, the effect of different ratios of CNF (0.5 and 1 wt%), CNC (0.5 and 1 wt%) and CNC-CNF (0.5 wt%) on the morphology, roughness, crystallinity, mechanical properties, water flux performance, surface water treatment performance (TOC removal performance) and antifouling ability of flat sheet PVDF-based membranes produced by phase inversion method is presented. In addition, for the first time in the literature, the mechanical properties of nanocellulosereinforced nanocomposite PVDF-based membranes were predicted via five different modeling methods, and the success of the modeling methods in predicting the real (experimental) mechanical properties of nanocomposite PVDF-based membranes was presented. This investigation uniquely examines how varying the concentration and type of nanocellulose affects the structural, mechanical, and filtration characteristics of the resulting membranes. Moreover, the mechanical properties derived from tensile tests of the produced membranes (experimental results) were modelled using five distinct methods: the

Mori-Tanaka mean-field homogenisation method, finite element method, Halpin-Tsai method, self-consistent scheme method and Voigt-Reuss method. For the first time, this study predicts the modulus of elasticity or the limit values of the elasticity modulus of nanocellulosereinforced nanocomposite membranes using these five different modelling techniques. This multi-faceted approach provides a comprehensive understanding of the mechanical behaviour of nanocellulosereinforced membranes under various modelling frameworks. Membranes operated under pressure must possess enhanced mechanical properties to maintain their mechanical integrity and ensure a longer service life. By demonstrating that the mechanical properties of membranes can be predicted numerically before the actual production of nanocomposite membranes, this study offers valuable insights for membrane production studies. Researchers and engineers can leverage these findings to design membranes with tailored mechanical properties, thereby improving their durability and performance in practical applications.

2. Materials and methods

2.1. Materials

Powdered PVDF (average molecular weight ~534,000 Da) was purchased from Sigma-Aldrich. Powdered PVP (average molecular weight 40,000 Da), used to increase the porosity of the membranes, was also purchased from Sigma-Aldrich. DMF, used as the solvent, was purchased from Carlo Erba. CNF in powder form (width: 10–20 nm and length: 2–3 μ m) and CNC in powder form (width: 10–20 nm and length: 300–900 nm) were obtained from Nanografi Turkey. All chemicals were used as purchased without further purification or processing.

2.2. Production of flat sheet membranes

All PVDF based flat sheet membranes were produced using the nonsolvent-induced phase inversion method. Membrane casting solutions were prepared according to the compositions shown in Table 1. To produce nanocellulose (CNC, CNF, CNC-CNF) reinforced PVDF-based membranes, the required amount of solvent (DMF) was added to glass bottles and stirred at 60 °C using a heated magnetic stirrer (Wisd, MSH20A). Then, CNC, CNF, or CNC-CNF was added to the solvent and stirred at high speed for 10 minutes to homogeneously disperse the nanomaterials. Next, 5 wt% PVP and 20 wt% PVDF were added to the solution. The solution was stirred at 60 °C for 48 hours to obtain a homogeneous mixture. The same experimental conditions used for the preparation of the casting solution of PVDF-based membranes were applied to the preparation of casting solutions for nanocellulosereinforced nanocomposite PVDF-based membranes.

To remove air bubbles from the well-mixed membrane casting solutions, the solutions were degassed using an ultrasonic water bath (Weightlab Instruments) for 30 minutes at 25 °C. The composition of the membrane casting solutions is presented in Table 1. Subsequently, the solutions were spread as a liquid film on a dry glass plate with a thickness of 200 μ m using a casting knife (TQC Sheen, VF2170–261). Immediately afterward, the glass plate was immersed in a water bath containing distilled water at 25 °C. The polymers solidified due to the

Composition of membrane casting solutions.

Membrane	PVDF (wt%)	PVP (wt%)	DMF (wt%)	CNC (wt%)	CNF (wt%)
PVDF	20	5	75	-	-
PVDF/CNC/0.5	20	5	74.5	0.5	-
PVDF/CNC/1	20	5	74	1	-
PVDF/CNF/0.5	20	5	74.5	-	0.5
PVDF/CNF/1	20	5	74	-	1
PVDF/CNC-CNF	20	5	74.5	0.25	0.25

liquid-liquid exchange between the solvent in the liquid film (DMF) and the non-solvent in the water bath (distilled water). The front and back surfaces of the membranes produced by the non-solvent-induced phase inversion method were thoroughly washed with distilled water to remove impurities. The membranes were stored in distilled water in glass containers with lids.

2.3. Hansen solubility parameters and Flory-Huggins interaction parameter

The affinity between membrane components can be estimated by the solubility parameter (δ). The Hansen total solubility parameter (δ t) was calculated using Eq. 1 [35].

$$\delta t = \sqrt{\delta d^2 + \delta p^2 + \delta h^2} \tag{1}$$

where, δh , δp and δh represent dispersion, polar and hydrogen bonding interactions, respectively

The affinity between polymer and solvent (PVDF-DMF and PVP-DMF), the affinity between polymers and non-solvent (water) (PVDF-water, PVP-water) and the affinity between solvent and non-solvent (DMF-water) were investigated using Eq. 2, Eq. 3 and Eq. 4 respectively.

$$\Delta \delta_{P-S} = \sqrt{\left(\delta d, P - \delta d, S\right)^2 + \left(\delta p, P - \delta p, S\right)^2 + \left(\delta h, P - \delta h, S\right)^2} \tag{2}$$

$$\Delta \delta_{P-NS} = \sqrt{\left(\delta d, P - \delta d, NS\right)^2 + \left(\delta p, P - \delta p, NS\right)^2 + \left(\delta h, P - \delta h, NS\right)^2}$$
(3)

$$\Delta \delta_{S-NS} = \sqrt{\left(\delta d, S - \delta d, NS\right)^2 + \left(\delta p, S - \delta p, NS\right)^2 + \left(\delta h, S - \delta h, NS\right)^2}$$
(4)

where P, S and NS represent polymer solvent and non-solvent (water) respectively.

In the studies, the miscibility of various polymer-polymer blends has been extensively investigated [36–39]. In this study, the Flory-Huggins Interaction Parameter (χ) was calculated based on Hansen solubility parameters to estimate the solvent miscibility of each polymer in the polymeric membrane casting solution. The miscibility of the polymers with DMF was evaluated using Eq. 5 [40]

$$\chi_{1,2} = \frac{Vr}{RT} (\delta 1 - \delta 2)^2 \tag{5}$$

where $\delta 1$ and $\delta 2$ are the solubility parameters of the polymer and solvent. V is the molar volume of the solvent. R is the ideal gas constant and T is the temperature.

2.4. Surface morphology of CNC and CNF

The morphology of powdered CNC and powdered CNF was examined by scanning electron microscopy (SEM, Philips XL 30S FEG). Before SEM analysis, CNC and CNF were coated with gold for 90 seconds in a coating device (Quorum SC7620) at 10 mA. The surface morphology of CNC and CNF was examined at low (500x) and high (2000x) magnifications.

2.5. Viscosity of membrane casting solutions

The viscosity of the casting solutions of the membranes was measured with a viscometer at 22° C. Before measuring the viscosity of the membrane casting solutions, the viscometer was calibrated with distilled water.

2.6. Scanning electron microscopy

The membranes were dried at room temperature for 48 hours to examine their surface morphology by SEM (Philips XL 30S FEG). The surfaces of the membrane samples were placed in a coating device (Quorum SC7620) and coated with gold at 10 mA for 90 seconds. Surface views of the membranes were examined at 20000x magnification. The surface views of the "fouled-cleaned" membranes after filtration were also examined by SEM (Philips XL 30S FEG). The same coating procedures applied to the clean membrane samples were used for the fouled-cleaned membrane samples. The surface views of the fouledcleaned membrane samples were examined by SEM at 5000x and 20000x magnifications.

2.7. Atomic force microscopy

Atomic force microscopy (AFM, Digital Instruments Nanoscope IV) was used to examine the surface morphology of the membranes in more detail and to determine the roughness values. A silicon nitride (Si3N4) probe (Bruker) was used for AFM analysis, which was conducted in contact mode. Membrane samples of $5 \times 5 \ \mu m^2$ were scanned. The roughness of all membranes was determined by examining three roughness parameters: average roughness (R_a), root-mean-square roughness (R_{rms}), and the average of the five highest and five lowest points on the membrane surface (R₂).

2.8. X-ray diffraction spectroscopy

X-ray diffraction patterns of the membranes were analysed by an X-ray Diffractometer (XRD, Bruker D8 Advance). XRD patterns of the membranes were analysed at 40 kV and 40 mA in a device equipped with Cu K α ($\lambda = 1.54$ Å) radiation. XRD patterns of the membranes were recorded at diffraction angles ranging from $2\theta = 3-70^{\circ}$.

2.9. Water content

To determine the water content of the membrane samples, the samples were placed in aluminium weighing dishes and dried in an oven (Nuve EN 500) at 45°C for 60 hours. The weights of the dried membrane samples were determined with a precision balance (Precisa XB 220 A). The dried membranes were then immersed in distilled water using tweezers. After 30 seconds, the membranes were removed from the water and excess water was immediately removed using blotting paper. The wet weights of the membranes were then determined with a precision balance (Precisa XB 220 A). The water content of the membranes was calculated using Eq. 6 [41]. Water content experiments were performed three times for each membrane.

$$Water \ content(\%) = \frac{W_w - W_d}{W_w} x100$$
(6)

where $W_w\left(g\right)$ and $W_d\left(g\right)$ are the wet and dry weights of the membranes respectively.

2.10. Porosity and average pore size

The porosity of the membranes was determined by the gravimetric method using the Eq. 7 [42].

$$P = \frac{m_w - m_d}{A t\rho} x \quad 100 \tag{7}$$

where m_w and m_d are the wet and dry weights (g) of the membrane, respectively. A is the membrane area (cm²), t is the membrane thickness (cm), and ρ represents the density of water (0.998 g/cm³). P represents the porosity of the membrane (%). After calculating the porosity, the average pore size (rm) of the membranes was calculated using the Guerout-Elford-Ferry equation which is given below (Eq. 8) [35].

$$rm = \sqrt{\frac{(2.9 - 1.75P) \times 8\eta lQ}{P \times A \times \Delta P}}$$
(8)

where η is the viscosity of water (8.9 ×10⁻⁴ Pa.s), l is the membrane thickness (m), Q is the permeate volume per unit time (m³/s), A is the

effective membrane area (m²) and ΔP is the operating pressure (0.3 MPa).

2.11. Zeta potential of membranes

The zeta potentials of the membranes at pH 8 were measured by SurPASS, Anton Paar GmbH using 500 mL of 1.0 mM KCl feed solution. Since the pH of the surface water filtered through the membrane was about 8, the zeta potential of the produced membranes at pH 8 was analyzed.

2.12. Water flux performance

Water flux tests of the membranes were conducted using a dead-end filtration system (Tin Mühendislik). The pure water and lake water flux performances of the clean membranes were determined in the dead-end system. Additionally, the pure water fluxes of fouled membranes after the filtration process with lake water were determined. Terkos Lake water in Istanbul, Turkey was utilised in the lake water filtration studies. Table 2 shows the physico-chemical properties of Lake Terkos as reported in recent studies. To determine the pure water fluxes of the membranes, circular samples with a diameter of 5 cm were cut from the membranes to fit the filtration cell. The cut samples were placed in the filtration cell of the dead-end system. Afterward, the magnetic apparatus, which ensures the mixing of the water to be filtered through the membrane, was placed into the filtration cell, and the cell was filled with 300 mL of distilled water. Then, the filtration system was tightly locked by connecting a hose with one end connected to nitrogen gas. Pure water or lake water was continuously stirred in the filtration cell placed on the magnetic stirrer (JKI). Pure water or lake water was filtered through the membrane by pressurising with nitrogen gas. The filtered pure water or lake water (permeate) was collected in a glass beaker on a precision balance (AND EJ-610). The precision balance was connected to a computer and time-weight values were recorded for each membrane for 15 minutes, every 60 seconds, using WinCT-RSWeight software. All flux tests were performed at 3 bar. The flux values of the membranes were calculated using the numerical values transferred to the computer and the effective area of the membrane in Eq. 9 [43].

$$J = \frac{V}{A \quad x \quad \Delta t} \tag{9}$$

where J is flux (L/m².h), V is permeate volume (L), A is membrane area (m^2) and Δt is time (h).

2.13. Fouling resistance of membranes

The total fouling ratio (R_t), reversible fouling ratio (R_r), irreversible fouling ratio (R_{ir}), and flux recovery ratio (FRR) of the membranes were calculated using the values obtained from flux tests to determine the resistance of the membranes against fouling. The R_t , R_r , R_{irr} , and FRR values of the membranes were calculated using the following equations (Eqs. 10–13) [46].

Table 2	
Physico-chemical properties of Lake Terkos.	

	Unit	[44]	[45]
pН	-	7.85	7.74
Conductivity	μS/cm	432	344
Alkalinity	mg CaCO ₃ /L	105	-
Total Hardness	Mg CaCO ₃ /L	126	-
Turbidity	NTU	4.40	1.20
TOC	mg/L	4.81	-
DOC	mg/L	-	6.58
UV ₂₅₄	cm^{-1}	0.15	0.13

*TOC: total organic carbon, DOC: dissolved organic carbon, and UV_{254} : UV absorbance of the sample at 254 nm.

$$R_t(\%) = \frac{J_{w1} - j_{lake}}{j_{w1}} \quad x \quad 100$$
(10)

$$R_r(\%) = \frac{j_{w2} - j_{lake}}{j_{w1}} \quad x \quad 100$$
(11)

$$R_{ir} \quad (\%) = \quad \frac{j_{w1} - j_{w2}}{j_{w1}} \quad x \quad 100 \tag{12}$$

$$FRR(\%) = \frac{j_{w2}}{j_{w1}} \times 100$$
 (13)

where J_{wI} represents pure water flux of clean membranes (L/m².h), J_{lake} represents Terkos Lake water flux of clean membranes (L/m².h), J_{w2} represents pure water flux of fouled membranes (Terkos Lake water filtered membranes) physically cleaned by immersion in distilled water for 15 minutes (L/m².h)

2.14. Experimental determination of mechanical properties

The mechanical properties of the membranes were determined by tensile tests. Tensile tests were performed with Shimadzu AG-IS 50 kN universal testing machine. First, the dimensions of each membrane sample were measured with a caliper and micrometer. The elasticity modulus (Young's modulus), tensile strength, and elongation at break values of the membranes were determined from the stress-strain curves of the membranes obtained at the end of the tensile test. The elasticity modulus of the membranes was calculated from the slopes of the elastic deformation regions of the stress-strain curves. Tensile test experiments were performed three times for each membrane.

2.15. Modelling of nanocellulose reinforced polymeric membranes

The success of different numerical modelling methods in predicting the mechanical properties of membranes allows for the determination of the results closest to the real values among the methods. Modelling the mechanical behaviour of membranes with numerical approaches enables the examination of the mechanical behaviour of membranes under load and the determination of the nanomaterial type and nanomaterial ratio that contribute to the increased mechanical strength of the membrane. In this study, the mechanical properties of PVDF-based nanocomposite membranes were modelled by five different numerical approaches: the Mori-Tanaka mean field homogenisation method, finite element method, self-consistent scheme method, Voigt-Reuss method, and Halpin-Tsai method. The modulus of elasticity, which is an indicator of the stiffness of the membranes, was estimated using these five different numerical methods. The Mori-Tanaka mean field homogenisation method and finite element method were performed in the Digimat-MF and Digimat-FE sections of Digimat software, respectively.

To create finite element models in Digimat software, geometries



Fig. 1. Cubic RVE generated for CNC and CNF reinforced PVDF based membrane in finite element approach.

called cubic representative volume elements (RVE) containing stochastically distributed and sized nanoparticles (CNC and CNF) were created. Fig. 1 shows an image of the generated RVE. The edge length of the RVE was chosen to be at least five times the diameter of the largest cavity that actually represents the nanomaterial. It is assumed that the reinforcing materials (CNC, CNF, or CNC-CNF) in the RVEs are homogeneous and randomly distributed in the PVDF matrix. The RVEs formed in the finite element approach are assumed to be isotropic. The generated geometries were divided into tetrahedral elements. Table 3 shows the values entered into the program for modelling the membranes by the finite element approach in Digimat-FE software. In estimating the modulus of elasticity of the membranes using the finite element method, the experimental results obtained from the tensile test for the modulus of elasticity of the polymeric membrane matrix (PVDF/PVP) were introduced into the program. For nanocellulose reinforcements, the modulus of elasticity, density, and Poisson's ratio were entered into the software as 80 GPa, 1.5 g/cm³, and 0.25, respectively. The aspect ratio was entered as 60-100 and 85-130 for CNC and CNF, respectively. The computer specifications on which the finite element method analyses were performed are as follows: Processor: Intel(R) Xeon(R) Gold 6230 R CPU @ 2.10 GHz (104 CPUs), ~2.1 GHz, Memory: 262144MB RAM, Video Card: NVIDIA RTX A5000.

Modelling of the mechanical properties of membranes using the Mori-Tanaka mean-field homogenisation approach was carried out in the Digimat-MF (mean-field) section of Digimat software. In the Mori-Tanaka homogenisation approach, the polymeric matrix (PVDF/PVP) is assumed to have linear elastic behaviour, a homogeneous structure, and an isotropic structure. Similarly, the reinforcement materials (CNC and CNF) are also assumed to exhibit linear elastic behaviour and a homogeneous and isotropic structure. The reinforcement materials are assumed to be randomly distributed in the membrane matrix. Finally, in the Mori-Tanaka homogenisation approach, CNC, CNF, and CNC-CNF reinforced nanocomposite membranes are assumed to be isotropic and exhibit linear elastic behaviour. In the calculation of the modulus of elasticity of the membranes by the Mori-Tanaka homogenisation method, the data entered into the programme for the finite element method were used. For the modulus of elasticity of the polymeric membrane matrix (PVDF/PVP), the experimental results obtained from the tensile test were introduced into the programme. For nanocellulose reinforcements, the modulus of elasticity, density, and Poisson's ratio were entered into the software as 80 GPa, 1.5 g/cm³, and 0.25, respectively. The aspect ratio was entered as 60-100 and 85-130 for CNC and CNF, respectively.

The Voigt model assumes that the strain is constant throughout the composite material and thus provides an upper bound for the modulus of elasticity of the composite membrane, represented as E_{Voigt} . The Voigt model provides an upper bound value for the modulus of elasticity of the composite membrane as it represents the best case of the load-carrying capacity within the material. Conversely, in the Reuss model, the stress is assumed to be constant throughout the composite material, and the

Table 3

Information on modelli	ng of PVDF based	l nanocellulose	reinforced	membranes
using finite element ap	oroach.			

Software	Digimat
Problem	Numerical homogenisation of composite materials
RVE shape	Cube
RVE size	3-5 times the largest particle size
Element type	Tetrahedral
Number of elements	170,000-230,000
Number of analyses per	5
membrane	
Applied load	3 % unit strain
Number of nodes	510,000–690,000
Degrees of freedom	5100,000-6900,000

model provides a lower bound value, denoted as E_{Reuss} . Eq. 14 and Eq. 15 were used to calculate the Voigt upper and Reuss lower values, respectively.

$$E_{\text{Voigt}} = E_f V_f + E_m (1 - V_f) \tag{14}$$

$$E_{\text{Reuss}} = \frac{1}{\frac{V_f}{E_f} + \frac{1 - V_f}{E_m}}$$
(15)

In these equations, E_f and E_m represent the moduli of elasticity of the fibres and matrix, respectively. V_f represents the volume fraction of the fibres in the material.

The self-consistent scheme method extends beyond simple assumptions to meet the need for modelling composites with more complex microstructures. This method aims to more realistically model the microstructural properties of composite materials and their influence on macroscopic elastic properties. Essentially, it treats each phase of the material (reinforcing elements and matrix) as a separate phase that interacts within an overall matrix but is homogeneous in itself. Since the self-consistent scheme method takes into account the interactions between neighbouring particles, it provides consistency, especially for modelling randomly oriented fibres or particle-reinforced composite materials. In this method, a term called the effective modulus of elasticity (E_{eff}) arises and the value of E_{eff} is calculated using Eq. 16.

$$E_{\rm eff} = E_m \left(1 + \frac{3V_f (E_f / E_{\rm eff} - 1)}{1 + V_f (E_f / E_{\rm eff} - 1)} \right)$$
(16)

In this equation, Ef and Em denote the moduli of elasticity of the fibres and matrix, respectively, and Vf represents the volume fraction of the fibres in the material.

The Halpin-Tsai model is one of the methods used to determine the mechanical properties of composite materials. The Halpin-Tsai model is developed to predict the mechanical properties of composite materials based on the properties and geometry of their components. It considers matrix properties, fibre properties, matrix/fibre interfacial interaction, and fibre orientation. In this model, the homogenisation process is performed by considering the elastic properties of the matrix and reinforcing materials and their ratios in the composite material. This model is generally used in the field of composite material design and is useful for determining the mechanical behaviour of fibre-reinforced composite materials and optimising their mechanical properties. Using the Halpin-Tsai numerical approach, the effective longitudinal ($E_{eff,long}$) and effective transverse ($E_{eff,trans}$) moduli of elasticity can be calculated (Eqs. 17 and 18).

$$E_{\rm eff,long} = E_m \left(1 + \frac{\eta_L V_f (E_f / E_m - 1)}{1 - \eta_L V_f (E_f / E_m - 1)} \right)$$
(17)

where E_m , and η_L , are the modulus of elasticity of the matrix, and a parameter related to the aspect ratio of the fibres, respectively.

$$E_{\rm eff,trans} = E_m \left(1 + \frac{\eta_T V_f (E_f / E_m - 1)}{1 - \eta_T V_f (E_f / E_m - 1)} \right)$$
(18)

where, η_{T} is a parameter related to the transverse aspect ratio of the fibres.

3. Results

3.1. Affinity and miscibility of polymers and solvent

The solubility parameter difference between PVDF-DMF and PVP-DMF was 2.42 MPa^{1/2} and 11.24 MPa^{1/2}, respectively. A lower solubility difference indicates that the components are in good compatibility with each other and dissolve well. On the contrary, a higher solubility difference indicates that the dissolution ability between the two components is low, and phase separation will occur. Therefore, DMF was a better solvent for PVDF compared to PVP. The calculated solubility parameter difference for PVDF-water was 33.32 MPa^{1/2} and the high solubility difference revealed that water was a non-solvent for PVDF. The solubility parameter difference for PVP-water (21.96 $MPa^{1/2}$) was higher than the solubility parameter difference for PVP-DMF $(11.24 \text{ MPa}^{1/2})$, indicating better solubility of PVP in DMF. Moreover, the solubility parameter difference for solvent and non-solvent (DMFwater) was $31.14 \text{ MPa}^{1/2}$. The interaction between the components of the membrane casting solutions in pairs was evaluated by χ value. At 60°C, the temperature at which the membrane casting solution was mixed, the χ values for PVDF-DMF and PVP-DMF were 0.080 and 1.64, respectively. At the temperature of the solution poured onto the glass plate (25 °C), the X values for PVDF-DMF and PVP-DMF were 0.090 and 1.842, respectively. The χ values showed that the miscibility between polymers and solvent increased with increasing temperature. The interaction between PVDF-DMF was stronger than the PVDF-PVP interaction at 25 °C and 60 °C.

3.2. Surface morphology of nanocellulose particles

SEM images of CNC and CNF powders are shown in Fig. 2. The CNC powder exhibited a shrunken, wrinkled, and rough structure (Fig. 2(a) and Fig. 2(b)). The CNC powder in this study displayed a similar appearance to the CNC agglomerates observed in a previous SEM analysis by Abdallah and Kamal (2018). In contrast, the CNF powder appeared more densely packed, with a relatively flatter and smoother surface compared to the CNC powder (Fig. 2(c) and Fig. 2(d)).

3.3. Viscosity of membrane casting solutions

The viscosity of the membrane casting solution significantly affects the membrane morphology during phase inversion. As the viscosity increases, the rate of solvent and non-solvent exchange during phase inversion decreases. [47] Conversely, as the viscosity decreases, the rate of liquid-liquid exchange increases. Previous studies have reported that the rate of liquid-liquid exchange during phase inversion, as a function of casting solution viscosity, affects the porosity and average pore size of the final membrane. Fig. 3 shows the viscosities of the casting solutions



Fig. 3. Viscosity values of membrane casting solutions.

measured at 22°C. The viscosity of the PVDF membrane casting solution was 4.27 Pa.s. The viscosity increased with the addition of CNC and CNF to the casting solution. The viscosity of membrane casting solutions doped with CNF was higher than those doped with the same amount of CNC. The elongated structure of CNF likely contributed to a more entangled network, causing a greater increase in viscosity [48]. The viscosity of the casting solution with 0.25 wt% CNC and 0.25 wt% CNF (total 0.5 wt% nanocellulose) was 4.68 Pa.s. The viscosities of the casting solutions with 0.5 wt% CNC and 0.5 wt% CNF were 4.62 and 4.73 Pa.s, respectively. Although the PVDF/CNC-CNF casting solution contained a lower amount of CNC than the PVDF/CNC/0.5 casting solution, it had a higher viscosity, indicating that CNF was more effective in increasing the viscosity of the membrane casting solution.

3.4. Surface morphology of membranes

The surface morphologies of the membranes were examined by SEM analysis at 20000x magnification (Fig. 4). All membranes produced by the non-solvent-induced phase inversion method were porous and exhibited cambered circle-like structures on their surfaces, resulting in a rough surface texture. The pore size distribution of the membranes ranged from 1 to 100 nm, categorising them as ultrafiltration (UF)



Fig. 2. SEM images of CNC powder at 500x (a) and 2000x magnification (b), and SEM images of CNF powder at 500x (c) and 2000x magnification (d).



Fig. 4. SEM surface views of the membranes at 20000x magnification: (a) PVDF, (b) PVDF/CNC/0.5, (c) PVDF/CNC/1, (d) PVDF/CNF/0.5, (e) PVDF/CNF/1 and (f) PVDF/CNC-CNF.

membranes [49]. UF membranes are widely used for the removal of suspended solids, organic matter, bacteria, and viruses from water. Therefore, the membranes produced in this study can be employed in water disinfection (pathogen removal), turbidity removal, and organic matter removal processes. The addition of 0.5 wt% CNC or 0.5 wt% CNF to the PVDF membrane significantly decreased the membrane's porosity (Fig. 4 (a), (b), and (d)). However, when the addition of CNC or CNF increased from 0.5 wt% to 1 wt%, the porosity of the PVDF membrane increased (Fig. 4 (c) and (e)).

As mentioned earlier, the incorporation of nanocellulose into the PVDF membrane increased the viscosity of the membrane casting solution. The higher solution viscosity reduced the rate of liquid-liquid exchange during phase inversion, leading to a decrease in membrane porosity. Conversely, hydrophilic nanomaterials incorporated into the membrane have a high affinity for water, which has been reported in previous studies to increase the liquid-liquid exchange rate and subsequently increase porosity. Therefore, in this study, the decrease in porosity of the PVDF membrane at lower nanocellulose addition (0.5 wt %) can be explained by the increase in solution viscosity. The increase in porosity at higher nanocellulose addition (1 wt%) can be attributed to the abundant hydrophilic nanocellulose particles in the membrane matrix, which significantly accelerate the liquid-liquid exchange. Additionally, hydrophilic nanomaterials such as CNC and CNF tend to migrate toward the membrane surface during phase inversion [50], potentially leading to the formation of more pores on the membrane surface.

3.5. Surface roughness of membranes

AFM analysis was performed to examine the surface morphology of the membranes and compare their surface roughness. Fig. 5 shows the 2D and 3D surface views of the membranes obtained from AFM analysis, while Table 4 presents the roughness parameters of the membranes. In the AFM views, the light-bright areas and dark areas represent the peaks and valleys on the membrane surface, respectively. Consistent with the SEM surface view, the 2D AFM view also showed that the PVDF membrane had the highest surface roughness. The PVDF membrane exhibited the highest R_a value (8.30 nm), and the R_a value decreased as the amount of CNC or CNF in the membrane matrix increased. Among all membranes produced, PVDF/CNF/1 had the lowest Ra (5.52 nm), Rrms (7.37 nm), and R_z (28.96 nm) values. Similarly, in a study, it was reported that compared to pristine PVDF (14 wt% PVDF) membrane, the nodules and valleys of PVDF/CNC membrane (12.5 wt% PVDF and 1.4 wt% CNC) were reduced and CNC reinforced membrane had a smoother surface [51].

Membranes with high roughness are more prone to the accumulation of foulants in valleys during water and wastewater treatment [52]. In this study, nanocellulose-reinforced nanocomposite PVDF-based membranes had lower roughness than the PVDF membrane. Therefore, foulants are likely to accumulate less on the surface of nanocellulose-reinforced nanocomposite PVDF-based membranes, allowing these membranes to be used in filtration for a longer duration.



Fig. 5. (1) 2D and (2) 3D AFM views of PVDF-based membranes: (a) PVDF, (b) PVDF/ CNC/0.5, (c) PVDF/CNC/1, (d) PVDF/CNF/0.5 and (e) PVDF/CNF/1.

Table 4

Roughness parameters of membranes.

	R _a (nm)	R _{rms} (nm)	R _z (nm)
PVDF	8.30	10.21	39.21
PVDF/CNC/0.5	7.22	9.11	32.09
PVDF/CNC/1	6.92	9.34	41.91
PVDF/CNF/0.5	7.28	10.18	46.60
PVDF/CNF/1	5.52	7.37	28.96

3.6. XRD patterns of membranes

A significant proportion of polymers exhibit a combination of crystalline and amorphous regions, making many polymers semi-crystalline. PVDF is a semi-crystalline polymer. The regular arrangement of CH2 and CF2 groups along the polymer chains contributes to the crystalline structure of PVDF [53]. Sharp peaks in the XRD spectrum represent the crystalline structure of the sample, while broad peaks indicate the presence of amorphous regions and non-crystalline components.

Fig. 6 shows the XRD spectra of the membrane samples. The XRD spectra exhibited sharp peaks within the range of $2\theta = 9-32^{\circ}$. The sharp peak with the highest intensity in all spectra was at $2\theta = 16.8^{\circ}$. There was no significant difference in the intensities and areas of the peaks in the XRD spectrum of the membranes with CNC and CNF additions compared to the PVDF membrane. The peaks at $2\theta = 18^{\circ}$ (020), 19° (020) and 25° (021) were related to the crystalline peaks of PVDF α phase [54]. However, the XRD spectra of the membranes with 0.5 wt% CNC and 0.5 wt% CNF additions exhibited very low intensity peaks at 31.6° and 11.3°, respectively. These peaks indicate that the low amount of nanocellulose addition contributed to the crystalline structure of the PVDF membrane. On the other hand, the absence of significant changes in the peaks at high CNC or CNF reinforcement levels (1 wt%) may be due to the uneven dispersion of nanocellulose in the membrane matrix. A recent study by Du et al. showed that several peaks in the XRD spectrum of PVDF nanofiber membranes in the range of $2\theta = 35-45^{\circ}$ disappeared after the addition of PVP to the membrane [55]. However, to the best of the authors' knowledge, there is no study available for direct comparison regarding the changes in the XRD spectrum of PVDF-based flat sheet membranes caused by CNC or CNF additives.

3.7. Porosity, average pore size, water content of membranes

Fig. 7 (a) and Fig. 7 (b) show the porosity and average pore size values of the membranes, respectively. The porosity of the PVDF membrane was 40.83 %, while the porosity of nanocellulose-added nanocomposite membranes varied between 30.31 % and 39.67 %. The porosity of the membranes decreased with the addition of CNC, CNF, and CNC-CNF to the PVDF membrane. This can be explained by the fact that the porosity of nanocellulose-reinforced nanocomposite PVDFbased membranes is affected by the viscosity of the solution and the amount of hydrophilic nanocellulose in the casting solution. The hydrophilic properties of CNC and CNF increased the exchange rate between the solvent (DMF) and non-solvent (distilled water) during phase inversion, which simultaneously increased the viscosity of the casting solution, resulting in a decrease in the exchange rate between solvent and non-solvent. Therefore, the porosity of the nanocellulose-added membranes produced was lower than that of the PVDF membrane, indicating that solution viscosity plays a more dominant role in membrane formation during the liquid-liquid exchange in the production of nanocellulose-added membranes by phase inversion. In a previous study, it was reported that the porosity of the membrane decreased when 1 wt% CNF was added to the PES membrane [25].

It should be noted that since the average pore size of all membranes was in the range of 1–100 nm, the produced membranes were confirmed to be UF membranes by both the calculation method and SEM surface views. While the average pore size of the PVDF membrane was



Fig. 6. XRD patterns of membranes: (a) PVDF, (b) PVDF/CNC/0.5, (c) PVDF/CNC/1, (d) PVDF/CNF/0.5 and (e) PVDF/CNF/1.



Fig. 7. (a) Porosity, (b) average pore size and (c) water content of membranes.

56.09 nm, the average pore size of the membrane increased with the addition of CNF and CNC-CNF. On the other hand, the average pore size of the PVDF membrane was almost unaffected by 0.5 wt% (56.24 nm) and 1 wt% CNC reinforcement (56.06 nm). This may be due to the elongated structure of CNF, which stretches the polymeric matrix more during membrane formation, leading to the expansion of the pores.

Some studies have reported that the incorporation of hydrophilic nanomaterials into membranes increases the water content of the membrane [12,24]. However, in this study, the water content of the PVDF membrane (80.75 %) decreased with the addition of CNC, CNF, and CNC-CNF (Fig. 7 (c)). As the porosity of the membrane decreased with 0.5 wt% and 1 wt% nanocellulose addition to the PVDF membrane, the amount of water retained in the membrane structure also decreased. The decreased porosity may have increased the resistance of the membrane to water penetration, resulting in less water entering the membrane structure.

3.8. Zeta potential of membranes

The zeta potential of membranes is a parameter that affects membrane surface charge, separation efficiency and antifouling ability. When the charge of the foulants in the feed filtered through the membrane carries the same charge as the membrane surface, repulsion occurs between the membrane surface and the foulants. This interaction makes it difficult for the foulants to adhere to the membrane surface. Table 5 shows the zeta potential of membranes at pH 8. While the zeta potential of the PVDF membrane was -9.3 mV, the negativity of the surface charge of the membrane increased with 0.5 wt% and 1 wt% CNC reinforcement. The zeta potential of 0.5 wt% CNC and 1 wt% CNF reinforced membranes were -27.6 and -33.8 mV, respectively. The zeta potential of 0.5 wt% and 1 wt% CNF-reinforced PVDF-based membranes were -24.3 and -30.4, respectively. The surface charge of all

Table 5Zeta potential of membranes.

Membrane	Zeta potential (mV)
PVDF	-19.3
PVDF/CNC/0.5	-27.6
PVDF/CNC/1	-33.8
PVDF/CNF/0.5	-24.3
PVDF/CNF/1	-30.4
PVDF/CNC-CNF	-25.2

nanocellulose-reinforced PVDF-based membranes produced was more negative than that of pure PVDF membrane.

3.9. Water flux performance of membranes

The pure water flux (J_{w1}) and lake water flux (J_{lake}) of clean membranes were analysed at 3 bar in a dead-end filtration setup. Subsequently, the pure water fluxes (J_{w2}) of the fouled membranes were determined at 3 bar after filtering the lake water (Fig. 8). The J_{w1} value of the PVDF membrane (445 L/m².h) decreased to 396.24 L/m².h and 428 L/m².h with the addition of 0.5 wt% and 1 wt% CNC, respectively. The J_{w1} value of the membrane decreased with 0.5 wt% CNF addition to the PVDF membrane, while the J_{w1} value increased with 1 wt% CNF addition. The highest Jw1 value was 476.17 L/m².h for the PVDF/CNF/ 1 membrane.

The pure water flux performance of membranes significantly depends on the morphology of the membrane and the presence of hydrophilic groups in the membrane structure. As the average pore size of the membrane increases, the water flux also increases because water can more easily pass through larger pores. From SEM views and calculated porosity results, it was determined that the porosity of nanocelluloseadded nanocomposite membranes was lower than that of the PVDF





membrane. Despite the lower porosity of the PVDF/CNF/1 membrane, the high average pore size (67.28 nm) and the abundant hydrophilic CNFs in the membrane structure may have contributed to the easier penetration of pure water through the membrane.

Surface water (lake water) contains organic and inorganic foulants not present in pure water. These foulants accumulate on the membrane surface and within the pores during filtration, causing membrane fouling. The passage of water through fouled membranes with blocked pores becomes difficult, and the flux of the membrane decreases [3]. Therefore, the J_{lake} value of all membranes was lower than the J_{w1} value. The Jlake value of the PVDF membrane was 355.96 L/m².h, while the Jlake value of the nanocomposite membranes varied between 363.69 L/m².h and 403.87 L/m².h.

The increase in the Jlake value of the membrane with CNC, CNF, and CNC-CNF addition to the PVDF membrane was due to the nanocellulose addition reducing the fouling tendency of the polymeric membrane. The membrane with the highest J_{lake} value was PVDF/CNF/1 (403.87 L/m². h). The J_{w2} values of the membranes were lower than the J_{w1} values but higher than the Jlake values. This indicated that the membrane could not completely reach the flux performance of the new (clean) membrane after hydraulic cleaning for 15 minutes, but hydraulic cleaning was able to remove some of the foulants weakly attached to the membrane surface. The PVDF/CNF/1 membrane had the highest pure water flux (464.43 L/m².h) after hydraulic cleaning.

Nanocomposite membranes with higher amounts (1 wt%) of CNC or CNF had higher $J_{w1},\,J_{lake},\,$ and J_{w2} values than nanocomposite membranes with lower amounts (0.5 wt%) of CNC or CNF. The increase in membrane porosity and membrane hydrophilicity due to the effect of CNC and CNF facilitated the passage of water molecules through the membrane and increased the affinity of the membrane for water molecules. Moreover, CNC and CNF reinforcement increased the membrane hydrophilicity and prevented the attachment of foulants to the membrane surface.

In a study by Turossi et al. the flux for distilled water at 1 bar of a flat sheet membrane prepared by phase inversion method from 16 wt% PVDF and 84 wt% DMF solution was 5.21 L/m^2 .h. In the study, the flux performance of the membrane for distilled water increased to 15.99 L/m^2 .h with the addition of 0.5 wt% CNF to the PVDF membrane [56]. In another study, Tofighy et al. produced flat sheet membranes by phase inversion method from a solution prepared by mixing 20 % PVDF, 3 % PVP and 77 % DMF. In the study, the pure water flux of the PVDF/PVP-based membrane was approximately 280 L/m².h at 1 bar [57]. In polymeric solutions, the presence and proportion of additives in the solution [58–60], the molecular weight of the components [61], and the type and proportion of the solvent [58,62] affect the viscosity of the casting solution, leading to a change in the liquid-liquid exchange rate of the membrane during phase inversion. Depending on the viscosity of the polymeric solution, final membranes with different morphologies and

flux performance are formed during the phase inversion process. The properties and amount of PVDF, PVP, CNC and CNF used in membrane production, solvent type, production conditions and filtration conditions (temperature, pressure, filtration technique, etc.) cause the flux performance of the membranes to vary.

3.10. Antifouling ability of membranes

The antifouling ability of membranes is a critical factor in determining their efficiency and longevity in filtration applications. A high Flux Recovery Ratio (FRR) value indicates that the membrane is more resistant to fouling. Fig. 9 (a) shows the FRR values of the membranes. The FRR value of the PVDF membrane (89.49 %) increased with the addition of CNC, CNF, and CNC-CNF. The presence of CNC and CNF in the membrane enhances the surface hydrophilicity, which helps prevent the accumulation of hydrophobic organic and inorganic foulants on the membrane surface when filtering polluted water, such as lake water.

The PVDF/CNF/0.5 membrane exhibited the highest FRR value at 98.0 %, indicating the best fouling resistance among the tested membranes. This was followed closely by the PVDF/CNF/1 membrane, which had an FRR value of 97.53 %. These high FRR values suggest that the addition of CNF significantly improves the antifouling properties of the membranes.

To further investigate the membranes' resistance to fouling during filtration, the Total Fouling Ratio (R_t) , Reversible Fouling Ratio (R_r) , and Irreversible Fouling Ratio (R_{ir}) were calculated (Fig. 9 (b)). In water filtration applications, membranes with lower Rt values are preferred as they indicate higher fouling resistance. The PVDF membrane had the highest Rt value at 20.17 %. The addition of CNC, CNF, and CNC-CNF to the PVDF membrane resulted in a decrease in the Rt value. Notably, membranes with 0.5 wt% CNC or 0.5 wt% CNF had lower Rt values than membranes with 1 wt% CNC or 1 wt% CNF. Among all membranes, the PVDF/CNF/0.5 membrane had the lowest Rt value at 4.62 %, highlighting its superior resistance to fouling. It is important to note that the Rr value accounted for the majority of the Rt value in the PVDF/CNF/1 membrane. Specifically, the Rr value was 12.71 % out of the total Rt value of 15.18 %. This indicates that most of the fouling in the PVDF/ CNF/1 membrane was reversible and could be easily removed by physical cleaning. This characteristic is highly desirable as it means that the membrane can maintain its performance over multiple filtration cycles with minimal permanent fouling.

Synthetic solutions are frequently used to evaluate the fouling resistance of PVDF-based membranes. Among these solutions, bovine serum albumin (BSA) [58,63–65] was used for protein-based fouling, humic acid [65] for natural organic matter-based fouling, and oil-water solution [66] for oil-based fouling. In a study by Enayatzadeh and Mohammadi, 1 g/L BSA solution was filtered at 100 kPa through flat sheet membranes prepared by phase inversion method after dissolving





Fig. 9. (a) FRR values of membranes and (b) fouling ratio of membranes.

10 wt%, 13 wt% and 15 wt% PVDF in DMF. The results of the study showed that the FRR of BSA filtered 10 wt%, 13 wt% and 15 wt% PVDF-based membranes were 42.31 %, 40 % and 39.65 %, respectively. In the same study, the FRR values of flat sheet membranes prepared by phase inversion method after dissolving 10 %, 13 % and 15 % PVDF in dimethyl sulfoxide (DMSO) and filtered with BSA solution were found to be 53.13 %, 70.08 %, and 75.56 %, respectively [58]. In the study in which 1 g/L BSA was filtered at 0.1 MPa from a flat sheet membrane produced by phase inversion method using a solution consisting of 15 % PVDF, 1 % PVP and 84 % dimethyl acetamide mixture, the FRR value of the membrane was 43.3 % [63]. Rt and FRR values of 1 g/L vacuum pump oil solution filtered through flat sheet membrane based on 15 wt% PVDF and 5 wt% polyethylene glycol at 0.1 MPa were 75.3 % and ~40 %, respectively [66]. The FRR values of PVDF, TiO₂-coated PVDF and TiO₂/carbon nanotube-coated PVDF membranes filtering oily wastewater were 35 %, 64 % and 77 %, respectively [67]. The differences in the antifouling ability performance of PVDF-based membranes in this and other studies can be explained by the variations in the membrane composition and membrane properties (hydrophilicity, surface roughness, porosity, pore size, etc.); the composition of the feed solution, the concentration of foulants in the feed solution, filtration conditions and membrane cleaning procedures (type of cleaning, cleaning time, etc.).

3.11. Surface views of fouled-cleaned membranes

The SEM surface views at 5000x (low) and 20000x (high)

magnifications of the "fouled-cleaned" membranes filtered with pure water, filtered with lake water, physically cleaned with distilled water for 15 minutes, and filtered with pure water, respectively, are shown in Fig. 10. It was found that foulants accumulated on the surface of the PVDF membrane, and the foulants were not completely removed from the membrane surface by physical cleaning. This phenomenon can be attributed to the fact that the PVDF membrane exhibits a higher roughness value than the nanocomposite membranes. This can be explained by the accumulation of foulants in the lake water in the valleys on the membrane surface, which provide favorable conditions for foulants accumulation. Furthermore, the foulants may not be removed effectively from these valleys by physical cleaning.

The SEM surface views of the produced membranes were compared with the SEM surface views of fouled-cleaned membranes that were subjected to several filtration processes and cleaned for 15 minutes, and it was found that a significant increase in the surface porosity and pore size of the nanocomposite membranes occurred.

The pores on the surface of the membranes, which were subjected to filtration three times at 3 bar and immersed in distilled water for 15 minutes, were enlarged due to factors such as pressure applied during the filtration process, hydraulic impact, and cleaning. Large pores can accelerate the passage of more water through the membrane in a short time, i.e. large pores can increase the water flux of the membrane. However, it is worth noting that large membrane pores can also cause foulants in the feed solution to pass through the membrane more easily, and large pores can reduce the separation performance of the membrane.



Fig. 10. SEM surface views of membranes at (1) low (5000x) and (2) high (20000x) magnification after filtering pure water through fouled-cleaned membranes: (a) PVDF, (b) PVDF/CNC/0.5, (c) PVDF/CNC/1, (d) PVDF/CNF/0.5, (e) PVDF/CNF/1 and (f) PVDF/CNC-CNF.

3.12. Mechanical properties of membranes

To determine the mechanical properties of polymers, polymeric blends and polymeric membranes, the stress-strain curve, modulus of elasticity, tensile strength and elongation at break of such materials have been widely studied [68-71]. The stress-strain curves for various PVDF-based membranes reinforced with different types and amounts of nanocellulose are shown in Fig. 11 (a). The curves indicate that the addition of nanocellulose, whether CNC or CNF, affects the mechanical performance of the membranes. Specifically, membranes reinforced with CNF demonstrated higher stress at given strain values compared to those reinforced with CNC. This suggests that CNF, due to its elongated fibrous structure, provides more effective reinforcement, thereby enhancing the stiffness and load-bearing capacity of the membranes. In detail, the pure PVDF membrane exhibited a typical stress-strain behaviour for semi-crystalline polymers, showing a relatively low stress response. As nanocellulose was introduced into the membrane matrix, the stress-strain curves shifted upward, indicating improved mechanical properties. For membranes containing 0.5 wt% CNC, the initial slope of the curve, which represents the stiffness, was slightly higher than that of the pure PVDF membrane. When the CNC content was increased to 1 wt%, a more pronounced increase in stiffness was observed, as reflected by a steeper initial slope and higher stress values at given strains. Similarly, the introduction of CNF into the PVDF/PVP matrix also resulted in an upward shift of the stress-strain curves. Membranes with 0.5 wt% CNF showed a significant increase in stiffness compared to the pure PVDF membrane and those reinforced with CNC at the same concentration. When the CNF content was increased to 1 wt%, the stiffness and strength of the membrane further improved, surpassing all other compositions tested. The membrane reinforced with a combination of CNC and CNF (PVDF/CNC-CNF) displayed a stress-strain behaviour that combined the attributes of both types of nanocellulose reinforcements. This hybrid reinforcement approach provided a balance between stiffness and strength, benefiting from the unique properties of both CNC and CNF. The stress-strain curve for this hybrid membrane was superior to the pure PVDF membrane and comparable to the

membranes reinforced with higher concentrations of individual nanocellulose types. The overall trend observed from the stress-strain curves suggests that the stiffness of the membranes increased as more cellulose nano reinforcements were added. This enhancement in mechanical performance can be attributed to the effective load transfer between the polymer matrix and the well-dispersed nanocellulose particles. The reinforcing effect of CNC and CNF is due to their high aspect ratio and mechanical properties, which provide significant resistance to deformation under applied stress. Moreover, the interaction between the polymer matrix and the nanocellulose particles plays a crucial role in determining the mechanical properties. The strong interfacial adhesion between PVDF/PVP and nanocellulose ensures efficient stress transfer, resulting in improved mechanical performance. The better performance of CNF-reinforced membranes compared to CNC-reinforced ones can be explained by the higher aspect ratio and better network formation of CNF, which contribute to a more pronounced reinforcing effect.

The elasticity modulus, also known as Young's modulus, is a measure of the stiffness of a material. It quantifies the material's ability to resist deformation under stress. Fig. 11 (b) illustrates the elasticity modulus values for various PVDF-based membranes reinforced with different types and amounts of nanocellulose. The pure PVDF membrane exhibited an elasticity modulus of 10.74 MPa, which serves as the baseline for comparison. The incorporation of nanocellulose into the membrane matrix significantly influenced the elasticity modulus, reflecting enhanced stiffness and rigidity. The addition of CNC to the PVDF membrane resulted in a notable increase in the elasticity modulus. For the membrane with 0.5 wt% CNC, the elasticity modulus increased to 11.54 MPa. This modest improvement suggests that CNC, even at a low concentration, contributes to the reinforcement of the polymer matrix. When the CNC content was increased to 1 wt%, the elasticity modulus further rose to 19.34 MPa, indicating a substantial enhancement in stiffness. This significant increase can be attributed to the high aspect ratio and excellent mechanical properties of CNC, which facilitate effective stress transfer from the polymer matrix to the reinforcing nanocellulose particles. The influence of CNF on the elasticity modulus was even more pronounced. For the membrane with 0.5 wt% CNF, the



Fig. 11. Mechanical properties of membranes (a) stress-strain curves, (b) elasticity modulus, (c) tensile strength and (d) elongation at break values of membranes.

elasticity modulus increased to 12.69 MPa, showing a greater improvement compared to the membrane with the same amount of CNC. This difference can be explained by the elongated fibrous structure of CNF, which provides a more effective reinforcement network within the polymer matrix. At a higher concentration of 1 wt% CNF, the elasticity modulus reached 20.81 MPa, the highest among all tested membranes. The superior reinforcing capability of CNF is due to its higher aspect ratio and better dispersion within the matrix, leading to enhanced loadbearing capacity and stiffness. The membrane reinforced with a combination of CNC and CNF (PVDF/CNC-CNF) exhibited an elasticity modulus of 12.93 MPa. This value reflects a synergistic effect, where the combined use of CNC and CNF offers a balance between the reinforcing mechanisms of both types of nanocellulose. While not as high as the membrane with 1 wt% CNF, the hybrid membrane still demonstrated significant improvement over the pure PVDF membrane and those reinforced with lower concentrations of individual nanocellulose types.

The results indicate that the incorporation of nanocellulose, particularly CNF, significantly enhances the stiffness of the PVDF membrane. The observed increase in elasticity modulus can be attributed to several factors:

- High aspect ratio: Both CNC and CNF have high aspect ratios, which enhance their ability to reinforce the polymer matrix by providing greater surface area for stress transfer.
- Mechanical properties of nanocellulose: CNC and CNF possess high intrinsic mechanical properties, contributing to the overall stiffness of the composite membrane.
- Interfacial adhesion: Strong interfacial adhesion between the nanocellulose and the PVDF/PVP matrix ensures efficient stress transfer, resulting in improved mechanical performance.
- Dispersion and network formation: The fibrous structure of CNF allows it to form an interconnected network within the matrix, which further enhances the stiffness and load-bearing capacity of the membrane.

The comparison between CNC and CNF reveals that CNF is more effective in enhancing the elasticity modulus of PVDF membranes. This can be attributed to the better network formation and higher aspect ratio of CNF, which provide more effective reinforcement compared to the rod-like structure of CNC.

Tensile strength is a critical mechanical property that measures the maximum stress a material can withstand while being stretched or pulled before breaking. It is a key indicator of the durability and robustness of the membranes. Fig. 11 (c) presents the tensile strength values for various PVDF-based membranes reinforced with different types and amounts of nanocellulose. The pure PVDF membrane exhibited a tensile strength of 1.52 MPa. This value serves as a baseline for evaluating the reinforcing effects of CNC and CNF on the membrane's mechanical properties. The incorporation of CNC into the PVDF membrane resulted in an increase in tensile strength. The addition of 0.5 wt% CNC increased the tensile strength to 1.65 MPa, demonstrating a modest improvement over the pure PVDF membrane. This enhancement can be attributed to the reinforcing effect of CNC, which helps distribute the applied stress more effectively within the polymer matrix. When the CNC content was increased to 1 wt%, the tensile strength further increased to 1.81 MPa. This significant improvement indicates that higher concentrations of CNC provide better reinforcement, enhancing the membrane's ability to resist tensile stress. The rod-like structure of CNC, along with its high aspect ratio and excellent mechanical properties, contributes to this enhanced tensile strength by improving the stress transfer from the polymer matrix to the nanocellulose particles. The addition of CNF had an even more pronounced effect on the tensile strength of the PVDF membrane. For the membrane with 0.5 wt% CNF, the tensile strength increased to 1.47 MPa, which is slightly lower than the 0.5 wt% CNC-reinforced membrane. However, when the CNF content was increased to 1 wt%, the tensile strength

significantly rose to 2.26 MPa, the highest value among all tested membranes. This substantial increase can be attributed to the unique fibrous structure of CNF, which forms an interconnected network within the polymer matrix. This network enhances the load-bearing capacity and resistance to tensile stress, providing superior reinforcement compared to CNC. The higher aspect ratio and better dispersion of CNF within the matrix contribute to the improved tensile strength. The membrane reinforced with a combination of CNC and CNF (PVDF/CNC-CNF) exhibited a tensile strength of 2.13 MPa. This value reflects a synergistic effect, where the combined use of CNC and CNF offers a balance between the reinforcing mechanisms of both types of nanocellulose. While slightly lower than the tensile strength of the membrane with 1 wt% CNF, the hybrid membrane still demonstrated a significant improvement over the pure PVDF membrane and those reinforced with lower concentrations of individual nanocellulose types.

The results indicate that the incorporation of nanocellulose, particularly CNF, significantly enhances the tensile strength of PVDF membrane. The observed increase in tensile strength can be attributed to several factors:

- Reinforcing effect of nanocellulose: Both CNC and CNF provide reinforcement by distributing the applied stress more effectively within the polymer matrix. This distribution helps prevent localised stress concentrations that can lead to premature failure.
- Interfacial adhesion: Strong interfacial adhesion between the nanocellulose and the PVDF/PVP matrix ensures efficient stress transfer, resulting in improved tensile strength.
- Network formation: The fibrous structure of CNF allows it to form an interconnected network within the matrix, which enhances the loadbearing capacity and resistance to tensile stress. This network formation is more pronounced in CNF-reinforced membranes compared to CNC-reinforced ones.
- Aspect ratio and dispersion: The higher aspect ratio and better dispersion of CNF within the matrix contribute to the improved tensile strength. The elongated fibers of CNF provide a greater surface area for stress transfer and improve the mechanical interlocking within the matrix.

The comparison between CNC and CNF reveals that CNF is more effective in enhancing the tensile strength of PVDF membrane. This can be explained by the better network formation and higher aspect ratio of CNF, which provide more effective reinforcement compared to the rodlike structure of CNC.

Elongation at break is a measure of a material's ability to undergo deformation before rupture, indicating its ductility and flexibility. Fig. 11 (d) illustrates the elongation at break values for various PVDFbased membranes reinforced with different types and amounts of nanocellulose. The pure PVDF membrane exhibited an elongation at break of 0.25, which serves as a baseline for evaluating the effects of CNC and CNF additions on the flexibility and ductility of the membranes. The addition of CNC to the PVDF membrane resulted in a decrease in elongation at break. The incorporation of 0.5 wt% CNC reduced the elongation at break to 0.23. This slight reduction suggests that even a small amount of CNC can restrict the membrane's ability to stretch under tensile stress. The rigid rod-like structure of CNC particles likely impedes the polymer chains' mobility, thereby reducing the overall ductility of the membrane. When the CNC content was increased to 1 wt%, the elongation at break further decreased to 0.13. This significant reduction indicates that higher concentrations of CNC have a more pronounced stiffening effect on the membrane, limiting its ability to undergo deformation. The high aspect ratio and rigidity of CNC particles create a more constrained polymer network, reducing the flexibility of the membrane. The addition of CNF also led to a decrease in elongation at break, although the effect was somewhat different compared to CNC. For the membrane with 0.5 wt% CNF, the elongation at break decreased to 0.16, which is lower than the corresponding CNC-

reinforced membrane. This reduction can be attributed to the fibrous and elongated structure of CNF, which forms a more interconnected and rigid network within the polymer matrix, thereby restricting its ductility. At a higher concentration of 1 wt% CNF, the elongation at break decreased to 0.17. Interestingly, the decrease in elongation at break for the membrane with 1 wt% CNF is less pronounced compared to the membrane with 1 wt% CNC. This could be due to the more uniform dispersion and better stress distribution offered by CNF's fibrous network, which, while still reducing ductility, provides a slightly better balance between strength and flexibility compared to CNC. The membrane reinforced with a combination of CNC and CNF (PVDF/CNC-CNF) exhibited an elongation at break of 0.10. This value reflects the combined effect of both types of nanocellulose, resulting in a significant reduction in ductility. The hybrid reinforcement likely creates a highly constrained polymer network, combining the stiffening effects of both CNC and CNF. The resultant membrane, while having superior mechanical strength, exhibits limited flexibility.

The results indicate that the incorporation of nanocellulose, whether CNC or CNF, generally reduces the elongation at break of PVDF membranes, indicating a trade-off between mechanical strength and ductility. Several factors contribute to this observed reduction in flexibility:

- Rigid reinforcement: Both CNC and CNF particles introduce rigidity into the polymer matrix, restricting the movement of polymer chains and reducing the overall ductility of the membrane.
- Network formation: The fibrous structure of CNF forms a more interconnected network compared to CNC, which provides superior mechanical reinforcement but also limits the material's ability to undergo deformation.
- Interfacial adhesion: Strong interfacial adhesion between nanocellulose particles and the polymer matrix enhances stress transfer but also contributes to a stiffer composite, reducing the elongation at break.
- Aspect ratio and dispersion: The high aspect ratio of both CNC and CNF creates a more constrained polymer network, with CNF's fibrous nature providing a slightly better balance between strength and flexibility compared to CNC.

The comparison between CNC and CNF reveals that CNF, despite reducing the elongation at break, offers a slightly better compromise between mechanical strength and flexibility compared to CNC. The hybrid reinforcement approach (CNC-CNF) results in a significant reduction in ductility, highlighting the importance of optimising the type and concentration of nanocellulose based on specific application requirements.

The mechanical strength of membranes is directly related to membrane morphology. The load applied to the membrane is carried by the non-porous parts of the membrane. Since high porosity and large pore sizes in membranes reduce the structural integrity of the membrane, the mechanical properties of the membrane may weaken. The pores of membranes operated under pressure may become larger over time due to the pressure applied during the filtration process and a decrease in the mechanical strength of the membrane may occur. As expected, the PVDF membrane with the highest porosity among the membranes produced had lower rigidity than the nanocellulose-reinforced membranes. As for nanocellulose-reinforced membranes, the porosity and pore size of the membrane and the ratio and properties of the nanocellulose reinforcements affect the mechanical strength of the membrane. In this study, membranes with higher CNC and CNF reinforcement had higher porosity and slightly larger pore sizes than membranes with lower CNC and CNF reinforcement. However, the elasticity modulus and tensile strength of membranes with higher nanocellulose reinforcement were higher than those of membranes with lower nanocellulose reinforcement. This showed that a high proportion of high-rigidity CNC and CNF nano reinforcements in the polymeric membrane matrix increased the

load-carrying capacity of the membrane despite its higher porosity and larger pore sizes. Lai et al. reported that the modulus of elasticity, tensile strength and elongation at max load of flat sheet membrane produced from polymer solution prepared by mixing 15 wt% PVDF and 85 wt% NMP were 10 ± 2 MPa, 4.9 ± 0.1 MPa and 144 ± 16 %, respectively [72]. In another study, Boruah et al. reported that the modulus of elasticity and tensile strength of flat sheet membrane produced by phase inversion method from polymeric solution consisting of 15 wt% PVDF, 83 wt% DMF and 2 wt% polyethylene glycol (PEG) were 0.95 ± 0.06 MPa, ~ 3.7 MPa and ~ 68 % [73]. Boruah et al. showed that membranes with lower PVDF content (12 wt%-14.5 wt%) and 0.5–3 wt% CNC reinforcement had higher modulus of elasticity and tensile strength but lower elongation than the 15 wt% PVDF-based membrane under conditions where DMF and PEG content were kept constant at 83 % and 3 % [73].

3.13. Membrane modelling results

In this study, the moduli of elasticity of nanocellulose-reinforced membranes were calculated using different numerical modelling methods. Table 6 shows the moduli of elasticity obtained from various modelling methods and the experimental (real) moduli of elasticity of the membranes. The findings indicate that the finite element and Mori-Tanaka mean-field homogenisation approaches provided results closer to the actual modulus of elasticity values of the membranes, both for single-type and dual-type nanocellulose reinforcement.

Finite Element and Mori-Tanaka Methods:

- The finite element method and the Mori-Tanaka mean-field homogenisation method yielded moduli of elasticity that closely matched the experimental values. These methods were found to have lower error margins in predicting the modulus of elasticity of the membranes.
- The finite element method, although time-consuming (approximately 8 hours per membrane analysis), provided the closest numerical results to the actual experimental values. This method involves creating detailed geometric models and performing complex calculations to simulate the mechanical behaviour of the membranes.
- The Mori-Tanaka mean-field homogenisation method, on the other hand, was significantly faster, taking about 10 minutes per membrane analysis. This method is advantageous for its efficiency and ease of use, making it a practical choice for rapid assessments. Despite its speed, it still offered reasonably accurate predictions, making it a valuable tool for initial evaluations.

Comparison of Modelling Methods:

- Mori-Tanaka Method: This method showed a good balance between accuracy and computational efficiency. For example, the PVDF/CNF/1 membrane had an experimental modulus of elasticity of 20.81 MPa, and the Mori-Tanaka method predicted it to be 19.75 MPa.
- Finite Element Method: This method provided the most accurate predictions, with the modulus of elasticity for the PVDF/CNF/1 membrane being predicted at 21.75 MPa, closely matching the experimental value of 20.81 MPa.
- Voigt and Reuss Models: These models provided upper and lower bounds for the modulus of elasticity. However, they showed less accuracy compared to the finite element and Mori-Tanaka methods. For instance, the PVDF/CNF/1 membrane had a Voigt modulus of 14.01 MPa and a Reuss modulus of 10.81 MPa.
- Self-Consistent Scheme: This method offered a middle ground but was less accurate than the finite element and Mori-Tanaka methods. For the PVDF/CNF/1 membrane, the modulus was predicted at 16.13 MPa.

Table 6

Numerical modelling	results of elasticity	/ modulus of PVDF-based	nanocellulose	reinforced	nanocomposite membran	es.
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	Experimental	Mori-Tanaka	Finite Element	Evoigt	E _{Reuss}	Self-Consistent Scheme	Halpin Tsai (E _{long})	Halpin Tsai (E _{trans})
PVDF	10.74	-	-	-	-	-	-	-
PVDF/CNC/0.5	11.54	13.10	12.02	12.04	10.77	13.54	12.28	11.48
PVDF/CNF/0.5	12.69	15.23	13.23	12.37	10.70	14.07	13.58	12.70
PVDF/CNC/1	19.34	15.48	18.48	13.34	10.81	15.36	14.06	12.28
PVDF/CNF/1	20.81	19.75	21.75	14.01	10.81	16.13	17.31	15.06
PVDF/CNC-CNF	12.93	14.17	13.17	12.24	10.74	13.81	12.88	12.06

• Halpin-Tsai Model: This model provided longitudinal and transverse moduli. For example, the PVDF/CNF/1 membrane had longitudinal and transverse moduli of 17.31 MPa and 15.06 MPa, respectively. These values were useful in understanding the directional dependencies of the membrane's mechanical properties.

The finite element method provided the closest predictions to experimental values but required significantly more computational time. The Mori-Tanaka method, while slightly less accurate, was far more efficient and still provided reasonably accurate predictions. For rapid assessments and practical applications where time is a constraint, the Mori-Tanaka mean-field homogenisation method is highly advantageous. For more detailed and precise modelling, the finite element method is preferred despite its longer computation time. The Voigt and Reuss models, along with the self-consistent scheme and Halpin-Tsai models, provided additional insights into the mechanical behaviour of the membranes but were generally less accurate than the finite element and Mori-Tanaka methods. The incorporation of nanocellulose, particularly CNF, significantly enhances the mechanical properties of PVDF membranes. The choice of modelling method can be tailored based on the specific requirements of accuracy and computational efficiency.

3.14. Organic matter removal efficiency of membranes from surface water

The presence of organic matter in water affects its taste and odor as well as its color and turbidity. The presence of organic matter in water leads to the loss of residues of disinfectants used to prevent microbial contamination in drinking water treatment [74]. In addition, the reaction of disinfectants and natural and anthropogenic organic matter in water leads to the formation of disinfection by-products [75]. Disinfection by-products are potential carcinogens and mutagens and therefore they pose a great risk to human health. This study investigated TOC removal efficiency. Table 7 shows the TOC removal efficiency of membranes from surface water. The TOC concentration was 3.8 \pm 0.3 mg/L in the feed. The concentration of organic matter in water depends on pH, temperature, salinity, microbial activity and vegetation surrounding the water body [76]. Even in the same water body, the concentration of organic matter can vary significantly depending on natural phenomena such as rainfall, floods, and droughts [77]. PVDF membrane had the lowest TOC removal efficiency from surface water (25.33±1.34 %) among all membranes. CNC, CNF and CNC-CNF reinforcement of PVDF membrane increased the TOC removal efficiency of the membrane from surface water. Membranes with 0.5 wt% CNC or 0.5 wt% CNF-reinforced membranes with lower porosity exhibited better TOC

Table 7

TOC removal	efficiency	of	membranes	from	surface	water

Membrane	TOC Removal Efficiency (%)
PVDF	25.33±1.34
PVDF/CNC/0.5	34.24±1.70
PVDF/CNC/1	$29.86{\pm}1.18$
PVDF/CNF/0.5	$39.98{\pm}1.88$
PVDF/CNF/1	$35.24{\pm}1.12$
PVDF/CNC-CNF	$31.82{\pm}1.09$

removal efficiency than those with 1 wt% reinforcement. PVDF/CNF/0.5 membrane with the lowest porosity had the highest TOC removal efficiency with 39.98±1.88 %. In this study, the separation of organic matter from water in the membrane filtration process was particularly related to the porosity of the membrane. In another study, Abbasi-Garravand et al. investigated TOC removal from river water with TOC concentration ranging from 4.77 to 10.44 mg/L by UF membrane in hollow fiber configuration [78]. The study found that at TOC concentrations of 4.77 mg/L and 10.44 mg/L, UF membrane removed approximately 35 % and 50 % of the TOC, respectively [78]. Factors affecting TOC removal by UF membranes include membrane properties, TOC concentration in the feed [78], feed flow rate [79], pressure [79] and filtration time [66]. It is also worth noting that the structure of TOC, the degree of solubility of organic compounds, and the size of organic particles in surface water may change over time depending on environmental factors. Therefore, it is likely that membranes exhibit different TOC removal efficiencies even when water samples collected from surface water at different times are filtered through the same membrane. The main mechanisms of membranes operated under low pressure such as UF to remove organic matter from water are size exclusion and sieve retention [80]. Organic compounds with a size smaller than the pore size of the membrane and a molecular weight lower than the molecular weight cutoff of the membrane can easily pass through the membrane [81]. In this study, UF membranes could not remove more than half of the TOC in surface water due to the limited removal of low molecular weight organic compounds and dissolved organic matter from water. On the other hand, suspended solids, colloids and large molecular organic compounds with sizes larger than the pore size of UF membranes (average pore sizes roughly 55-70 nm) were rejected by the membranes and the TOC concentration of the surface water decreased by 25.33±1.34 %-39.98±1.88 %.

4. Conclusion

In this study, the properties, flux performance, antifouling ability, and TOC removal efficiency of nanocellulose (CNC, CNF, and CNC-CNF) reinforced PVDF-based membranes produced by the phase inversion method were investigated. The findings demonstrate significant changes in the porosity and average pore size of the membranes with the incorporation of CNC, CNF, and CNC-CNF into the PVDF/PVP matrix. The mechanical analysis revealed that nanocellulose-reinforced PVDFbased membranes exhibited a higher modulus of elasticity compared to the pure PVDF membrane. Flux performance tests indicated that all types of nanocellulose reinforcements enhanced the FRR and decreased the Rt of the PVDF membrane. TOC removal efficiency of PVDF membrane from surface water (25.33±1.34 %) was improved with CNC, CNF and CNC-CNF reinforcement. In addition, the mechanical properties of PVDF membrane obtained from tensile test and the properties of nanocellulose were modeled by five different methods to predict the mechanical properties of nanocellulose-reinforced nanocomposite PVDF-based membranes. The predicted results were compared with the experimental mechanical properties of the nanocomposite membranes. The results obtained from the modeling of mechanical properties using five different numerical approaches showed that the finite element method and the Mori-Tanaka mean-field homogenization method were

more successful methods in predicting the mechanical properties of the membrane. This indicated that these methods are reliable in predicting the mechanical properties of nanocellulose-reinforced membranes.

Overall, the study underlines the benefits of incorporating nanocellulose into PVDF membranes. The reinforced membranes exhibit superior mechanical properties, enhanced flux performance, and improved antifouling characteristics. These improvements make nanocellulose-reinforced PVDF-based membranes highly suitable for advanced water filtration applications. However, it is important to note that CNC and CNFs are biodegradable materials. Therefore, CNCs and CNFs reinforced in polymer-based membranes may degrade over time depending on the membrane's continuity of contact with water and environmental conditions. This may lead to loss of function over time in CNC/CNF-reinforced nanocomposite membranes, which have improved properties and high performance due to the superior properties of CNC and CNF. In conclusion, there is a need to further investigate the persistence of CNC and CNF in polymer-based nanocomposite membranes produced by blending CNC or CNF into PVDF and other polymerbased membranes and the long-term performance of CNC/CNFreinforced polymer-based membranes.

CRediT authorship contribution statement

Neşe Tüfekci: Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization. Seren Acarer-Arat: Writing – review & editing, Writing – original draft, Visualization, Validation, Resources, Methodology, Investigation, Formal analysis, Data curation. Mertol Tüfekci: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. İnci Pir: Writing – original draft, Visualization, Validation, Software, Resources, Investigation, Formal analysis, Data curation.

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.

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Data Availability

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

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