Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

A Review on Modified Polyethersulfone-based Membranes Prepared by Blending Method for Water Treatment

Ahmed Abdel-Karim [1,2], Amer S. El-Kallinyn [1], Sebastian Leaper [2], Patricia Gorgojo [2], Mohamed I Badawy [1], Tarek A. Gad-Allah [1]

[1] *Water* Pollution *Research Department, National Research Centre, Giza 12622, Egypt*

[2] *Department of Chemical* Engineering *and Analytical Science, School of Engineering, The University of Manchester, Manchester, M13 9PL, UK*

Abstract

Blending as a modification method of membranes has gained much attention recently in the membrane industry, membrane material, and process development. The major preferred criterion in any membrane process/materials is to possess high performance in terms of flux and selectivity, as well as reduced fouling parameters. Polyethersulfone (PES) membranes have been widely used for separation and purification purposes due to their chemical stability, thermal stability, and outstanding oxidative property. However, the PES membrane itself is susceptible to fouling (which causes a catastrophic loss in flux) via adsorbing the pollutants either on the membrane external surface or within the membrane pores due to the intrinsic hydrophobic features of PES. Hence, blending PES membranes with different hydrophilizing agents has been demonstrated. Given the importance of the modifying material for PES membranes and their operation, we decided to dedicate this review solely to up-to-date used additives blended with PES. In the first section, a general introduction related to membrane technology-water, problem nexus has been mentioned. While in the second section, a wide range of hydrophilizing agents (e.g. amphiphilic polymers, graphene oxide (GO)-based nanofillers, and GO-based nanofillers combined with pore-forming agents) added to PES membranes were reviewed. The key factor of additives addition is to overcome flux-rejection trade-off. From this review, we can say that these additives did improve the permeance of water with a minimal loss of solute rejection. Findings from various individual studies were analyzed and discussed to provide a critical review of this subject.

Keywords: PES; Membrane filtration; Blending; Hydrophilizing agents; Fouling; Water treatment.

1. Introduction

This review article is organized into five subsections, the most comprehensive one will be concerned with the polymeric additives used for improving the performance of PES-based membranes that are used for water filtration applications. An attempt had been made to cover the most important and up-to-date additives (at least by mentioning them in the respective context).

In general, the membranes may be made up of either polymeric or inorganic based materials. Polymeric membranes are much favoured than inorganic membranes from a practical point of view, due to ease in processing and appropriate robustness [1]. Some of these membranes are already applied at an industrial scale such as desalination by reverse osmosis (RO), wastewater treatment, lithium-ion batteries, and membrane-based fuel cells [2]. Even though, they still need to be improved in terms of cost and affordability, energy consumption, and expertise. To bridge the gap between the advantages and drawbacks of membrane technology, advances in membrane materials specifically are urgently required.

Various membrane materials, such as cellulose

*Corresponding author e-mail: ahmedabdelkarimnrc@hotmail.com ahmed.ahmedabdelkarim@manchester.ac.uk.
Receive Date: 29 March 2022, **Revise Date:** 09 May 2022, **Accept Date:** 11 May 2022, **First Publish Date:** 11 May 2022
DOI: 10.21608/EJCHEM.2022.130336.5744

acetate (CA) [1, 3, 4], polysulfone (PSU) [5-8] polyethersulfone (PES) [9-14], polyacrylonitrile (PAN) [13], and polyvinylidene fluoride (PVDF) [15-17] have been used extensively for membrane-based water treatment (see

Table 1 for chemical structure and summarized comparison among the four polymers).

For the membranes to be utilized in various applications, polymeric membrane materials should possess desired properties such as excellent mechanical strength, good anti-fouling resistance, high selectivity, high permeability, and good control of the pore size distribution over the entire membrane surface area [18]. This eventuates in a reduction in the production and maintenance costs over the long term [18] and guarantees sustainability. Technically, membranes made from purely hydrophilic materials are suffered from water swelling problem and so damage their integrity and rejections performance [8]. Consequently, as we devote this review to membrane-based water treatment topic, a survey has been done of peer-reviewed publications related to "water treatment" and "type of membrane" of the last 16 years, which is shown in Figure 1. Although few numbers of publications on polymeric membranes for water treatment were observed compared to the rest of water treatment technologies, PES and PSU-based membranes (Figure 1a) have gained much attention compared with other polymeric membranes, probably due to the fact that they show outstanding oxidative, thermal, and hydrolytic stability as well as good mechanical property [7, 19-22]. The percentages of published review articles for PSU, PVP, PP, CA-based membranes within the last 16 years ranged between 14.8% to 19.6%, while for PES-based membranes the percentage is 11.2% (Figure b). To the best of authors' knowledge, there are rare literature review has been made regarding blending PES with different kinds of additives. Usually, the review articles concerning PES membrane are deal with the modification generally through different methods such as bulk modification, blending, surface coating, grafting [18], and functionalization [23]. This review will shed the light on the preparation method, phase inversion, and the modification of the PES membrane by blending with different additives.

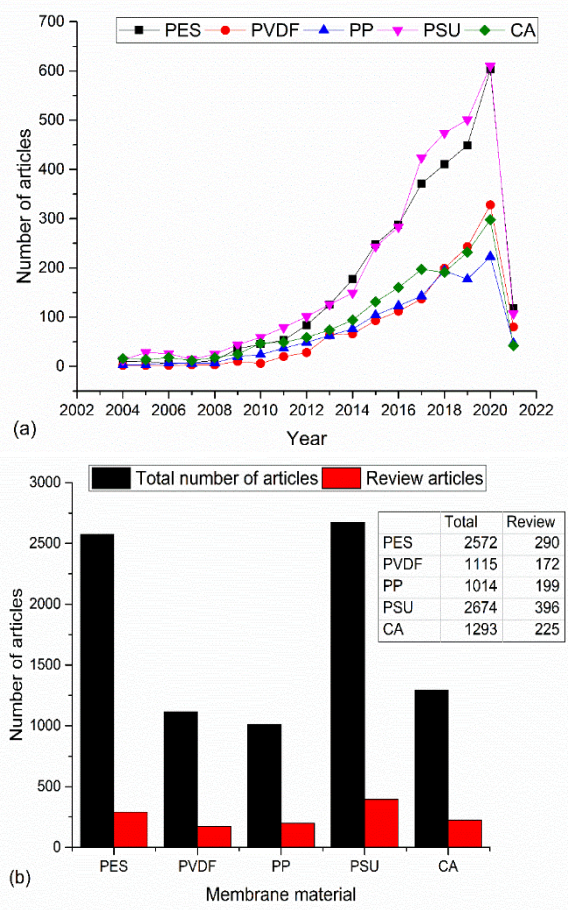
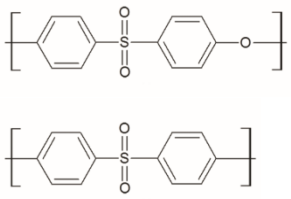
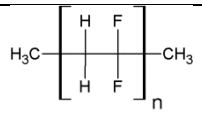
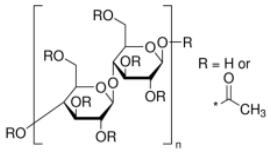


Figure 1 (a) Number of peer-reviewed publications relevant to polymeric membranes for water treatment since 2004. (Data analysis of publications has been done using the Scopus scholar search system with the term "Water treatment" and "X membranes", as of January 2021, where X is polyethersulfone (PES) or polyvinylidene fluoride (PVDF) or polypropylene (PP) or polysulfone (PSU) or Cellulose acetate (CA). (b) Comparison of the number of peer-reviewed publications from 2004 until 2021 as well as review articles on different membrane materials.

Table 1 Main polymers used in membrane formation via the non-solvent induced phase separation (NIPS) method [5, 15, 19, 24].

Polymer	Chemical structure	Advantages	Disadvantages
PES and PSU		▪ High thermal resistance. ▪ High chemical resistance (pH 1-13).Good chlorine resistance. Flexibility in fabrication (different modules). ▪ High mechanical stability.	▪ Low operating pressure limits ▪ Hydrophobicity
PVDF		▪ High thermal resistance. ▪ High chemical resistance (pH 1-13).	▪ Hydrophobicity
CA		▪ Hydrophilicity ▪ Low cost ▪ Flexibility in fabrication	▪ Low thermal resistance (< 30 ^{0}C. ▪ Low chemical resistance (pH 4-6). ▪ Easily attacked by microorganism

2. Phase inversion methods

Phase inversion is a widely accepted method to fabricate membranes with various porous structures to meet the various demands of different membrane technologies [25]. In this method, as displayed in Figure 2, a homogeneous polymer solution with a certain composition is prepared beforehand. After casting this solution over a glass or support (e.g. polypropylene support; non-woven supports) and let to be coagulated, the thermodynamic equilibrium of the prepared polymer solution is then varied through some physical ways, resulting in a transformation of the solution from a single-phase into two phases. The concept of phase inversion covers a range of different techniques such as non-solvent induced phase separation (NIPS), thermally-induced phase separation (TIPS), evaporation induced phase separation (SIPS), vapor-induced phase separation (VIPS), and immersion precipitation [26], based on different physical ways of changing the thermodynamic states of the solution. The differences among these phase separation processes are as follow:

- TIPS: A method for preparing a polymer membrane by mixing the polymer with a substance that acts as a solvent at a high temperature and casting the solution into a film. When the solution is cooled, solidification occurs [27].
- NIPS: the homogenous polymer solution is dropped in a non-solvent coagulation bath (in most cases water). The exchange of solvent and non-solvent is happened owing to the miscibility between the solvent and non-solvent results in demixing and precipitation behavior.
- VIPS: the polymer solution is exposed to an atmosphere containing a non-solvent (typically water); the non-solvent will then diffuses into the solution inducing phase separation [28].
- SIPS: Here, the used solvent and/or non-solvent are volatile where the volatility of solvent is higher than that of non-solvent, and the solvent is allowed to evaporate, leading to precipitation or demixing/precipitation. The porous morphology is thus formed by the thermal removal of non-solvent [26].

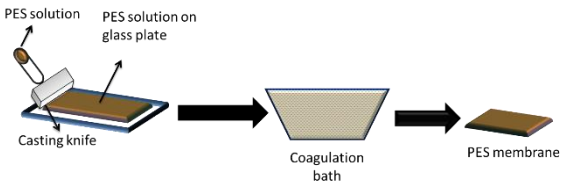


Figure 2 Representation of NIPS of PES membrane

3. Modification of PES-based membranes

Membrane modification is a classic solution for fouling issues raised by using PES-based membranes. it can be achieved by using different approaches such as (1) bulk modification of PES material, then to prepare PES membrane; (2) surface modification of

the already fabricated PES membrane; and (3) blending of PES polymer before casting [18, 20, 21]. Sulfonation and carboxylation methods of PES materials were mostly reported for bulk modification [18]. Surface modification of PES membranes is another approach in mitigation PES fouling (see **Error! Reference source not found.** as an example) [29]. Recently, ***Kochkodan et al.,*** [29] have published a review about surface modification of polymeric membranes for minimizing (bio)colloidal fouling. In this review, more specifically, PES membranes have been grafted, treated with plasma, and coated. Apart from membrane modification, in blending modification; modifying the entire membrane can be done at the dope solution level.

The blending technique is characterized by its simplicity and effectiveness; so, it is used extensively to fabricate high-performance membranes. Also, blending these polymers with other materials can combine the advantages of the individual materials to enhance the characteristics of the final product such as the reported results [5, 9, 11]. In this context, many additives have been blended to PES to improve membrane performance such as polyethylene glycol (PEG)[5, 30], polyvinylpyrrolidone (PVP)[14, 31-34], and alcohols [35].

What we know about blending PES with additives is largely based upon empirical studies that investigate how these additives altered the properties of PES membranes [36]. In this regard, blending is a highly demanded method as stated previously. Hence, the miscibility of each polymer (i.e. PES and the additive) in the used solvent is a critical factor.

4. Additives used for improving PES membrane performance

In 2018, Otitoju et al., [37] have published a review discussing recent advances in hydrophilic modification and the performance of the PES membrane via additives blending approach. This review offers some important insights into the tailored criteria of PES-based membranes in terms of membrane characters and performance. However, this review gave low attention to polymeric additives. This point is critical as vast of available-commercial membranes are composed of base polymers (e.g., PES) and polymeric additives. Besides, the review published by Al-anzi et al [23] in which the blending technique has not been covered very well instead, different surface modification techniques were given attention. Surface modification of PES-based polymers is still not scalable modification way unlike the blending one. So, in this review, we have covered these issues.

1.1. Hydrophilic additives

There is a consensus among membrane scientists that decreasing the membrane surface contact angle values is an effective approach to diminish membrane fouling [7, 11, 20, 38, 39]. Enormous numbers of hydrophilic additives are being used for this purpose including but not limited to PVP [9, 30, 32], PEG [38, 40], and poly(1-vinylpyrrolidone-costyrene) [40].

1.1.1. PVP

PVP is used extensively with PES membranes due to not only its ability to reduce the hydrophobicity of PES, but also, for pore formation [9, 33, 41]. They found that the addition of small quantities of PVP of different molecular weights to a phase inversion ultrafiltration membrane resulted in an increase in permeability without significant changes in the selectivity [42]. A considerable amount of literature has been published on blending PVP with PES membranes.

Table ***2*** depicts some of these publications.

Table 2 PVP additive blended with PES membrane

PES Type	M. Wt.	PES (%)	PVP % (MW)	Solvent	PWP $L.m^{-2}.h^{-1}.bar^{-1}$	Rejection % (solute)	Ref
Ultrason E6020P	58000	16	25,000	DMAc	77	99 (protein)	[42]
Ultrason E6020P	58000	20	25,000	DMF	1.1	75 (3,5 Dinitrosalicylic acid)	[43]
Solvay Company	62000 – 64000 Da	15	158,000	NMP	377	-	[39]
Solvay Company	62,000 – 64,000 Da	20	188,000	NMP	110	-	[39]
Solvay company 3100P		16	10 (40,000)	NMP	418	50 (bovine serum albumin (BSA))	[32]

3100P Solvay company		18	10 (40,000)	NMP	108	90 (BSA)	[32]
		15Ultrason E 6020 P	1,010,000	NMP	≈110	71 (BSA)	[9]
		20Ultrason E 6020 P	3 (40,000)	DMF	≈44	65(BSA)	[7]
		20Radel A-200	1,010,000	NMP	13	98±2	[44]
		25Veradel P 3100, 35,000 Da	16 (40,000)	NMP	135	95 (PEG,35000 Da)	[31]
		18Ultrason E6020P with MW= 58,000 g/mol)	1 (25,000)	DMAc	1.3	20 (Na_2SO_4)	[45]
		21 Ultrason E6020P with MW= 58,000 g/mol)	1 29,000	DMAc	≈5	89 (Reactive Green 19 dye)	[21]
		18 Ultrason E6020P with MW= 58,000 g/mol)	1 25,000	DMAc	≈ 67	98 (BSA)	[22]
		17 Ultrason E6020P with MW= 58,000 g/mol)	1 25,000	DMAc	≈ 13	No rejection data	[46]
		16Ultrason E6020P with MW= 58,000 g/mol	225,000	DMAc	≈17	≈ 62 (HA)	[47]
		20Ultrason E6020P with MW= 58,000 g/mol	130,000	DMAc	2.1	≈ 90 (Direct Red 16)	[48]
		22SOLVAY (MW not defined)	4PVP (MW not defined)	NMP	1.5	17 ($MgSO_4$)	[49]
		18Ultrason E6020P with MW= 58,000 g/mol	229,000	DMAc	≈167	No rejection data	[50]

MW of PVP has a dramatic effect on PES membrane characteristics as detailed by Astakhov *et al.*, (2013) [51]. In their work, PVP K30 and PVP K90 brands were used as hydrophilizing additives for the PES membrane. PVP addition has resulted in formation of membranes with higher porosity compared to neat PES which confirms that PVP changed the thermodynamic characteristics of the system during NIPS. Additionally, it is worth noting that PVP with higher MW leads to the formation of more pronounced "nodular" structures (see Figure 3).

1.1.1. PEG

Much of the current literature on PEG blended PES membranes pays particular attention to the effects of MW and concentration of the used PEG on the membrane properties (see

Table 3). In terms of PEG's MW and concentration, Idris *et al.* (2007) and Liu *et al.* (2003) [38, 52], observed that using higher MW of PEG from 200 Da to 600 Da increased both membrane porosity and PWP, however, molecular weight cutoff (MWCO) of the fabricated membranes had been increased from 26 KDa to 45 KDa (i.e. low rejection efficacy).

Table 3 PEG additive blended with PES polymer from different companies

PES type and %	PEG%, MW	Solvent	PWP L/ m^2 .h^1.bar^1	Rejection	modulation	Ref
BASF PES 20 %	-15 -600	DMF	≈76.5	MWCO (45KDa)	HF	[52]
PES 25%	-6 -600	NMP	56	98±1 (BSA)	HF, spinning	[53]
PES Ultrason E6010P 20	-37.5 -400	NMP	940	100 (BSA)	HF, spinning	[38]
PES Ultrason E6010P 20	-3-9 -MW is not defined	DMF	1-14	5-10 (Cu II)	FS	[54]

HF: Hollow fibre, FS: flat sheet

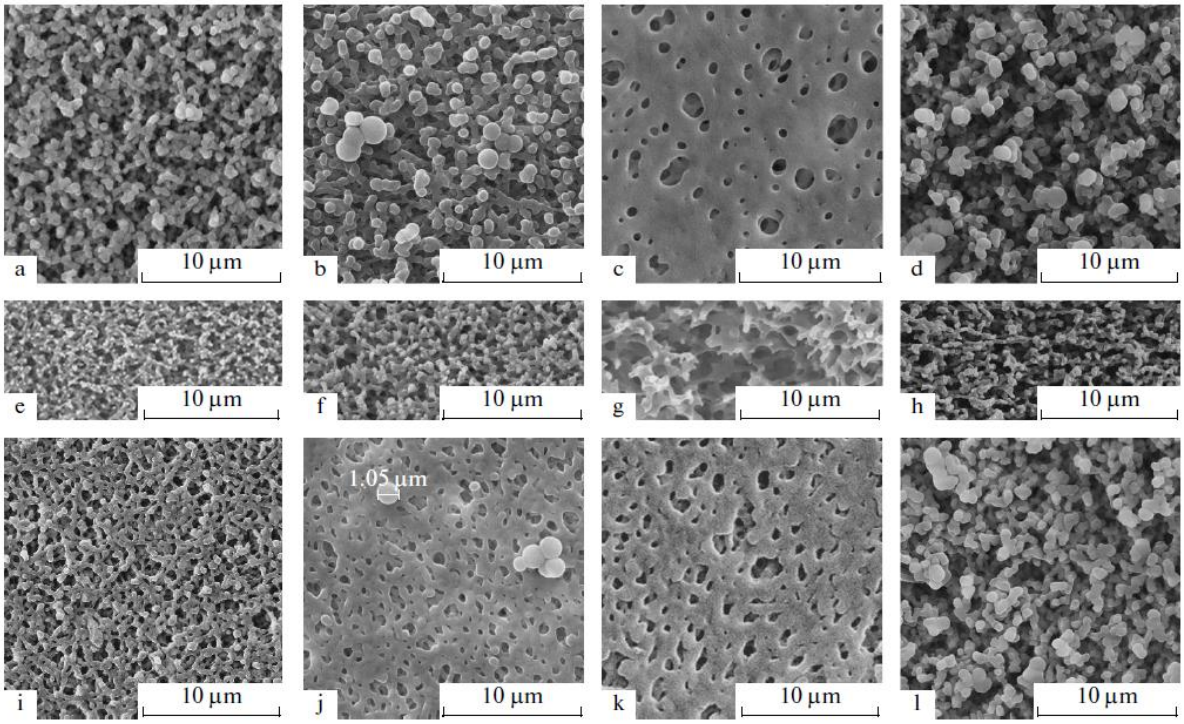


Figure 3 Electron microscopic images of the top surface, the centre of the cleaved surface, and the substrate side of membranes prepared from solutions with admixed PVP of various molecular weights: (a,e,i) 0 % PVP, (b,f,j) 2.5% PVP with Mw=1.3×106, (c,g,k) 5% PVP with Mw=1.3×106, (d,h,I) 5% PVP with Mw=58×106 [51].

1.1.2. Other hydrophilic additives

For instance, aaddition of cellulose-based derivatives such as cellulose acetate and cellulose acetate phthalate (CAP) proved enhancements in PES membrane properties [55, 56]. Sun and Chen (2016) [56] blended CA with PES to form UF membranes of improved hydrophilicity and antifouling properties. Maleic acid and piperazine were blended with PES polymer as reported by ***Chaturvedi et al.,*** (2001) [57] to examine the effects of acidic or basic nature (of the additive) on the PES-membrane performance. It has been found that Maleic acid addition almost tripled the water flux of neat PES membrane, while piperazine retarded the resultant flux to its half. Such behaviour may be attributed to the viscosity effect. Mehrparvar et al., (2014) [47] modified PES membranes using 3,5-diaminobenzoic acid (DBA) and gallic acid (GA) utilizing the NIPS method. Experimental results showed that the different component ratios of each monomer affected the structural property of blended membranes and surface roughness. Phosphotungstic acid (PWA, $12WO_3.H_3PO_4.xH_2O$) has been added to polymer matrix by both Ghaemi and Nasirmanesh (2018) [58] in this TFC membranes for herbicide removal. The study carried out by Kumar and Arthanareeswaran [59] explored novel additives to PES such as nanocurcumin. They found that the addition of extracted nanocurcumin material to PES has improved the biofouling resistance ability of the PES membrane against *Escherichia coli* and *Pseudomonas aeruginosa* combined with improved water permeance.

Rahimpour et al. (2010) [60], utilized hydrophilic monomers with small MW such as acrylic

acid (AA) and 2-hydroxyethyl methacrylate (HEMA) as additives for PES polymer. Both monomers bear hydroxyl and carbonyl functionalities leading to better surface hydrophilicity and porosity of the blended PES membrane. Besides, atomic force microscopy (AFM) and scanning electron microscopy (SEM) images (Figure 4) showed that a smooth and nano-porous membrane with a smaller pore size is obtained. As a result, the pure water fluxes of the membranes were decreased while protein rejections and antifouling properties of the membranes were improved. In separate work, Propionic acid (PA) has been studied as an additive [25]; where Laninovic (2005) [61] showed that the addition of propionic acid in a polymer solution inhibited the growth of macro voids, which resulted in improved mechanical characteristics of the formed membranes as well as decreased water flux. Besides, Fang ***et al.*** (2015) [62], proved that the introduction of Polyethyleneimine (PEI) to PES increased both the pore density and thickness of the skin layer. In addition to, the water contact angle, protein adsorption and platelet adhesion were obviously decreased after grafting BSA onto the membrane surface, meanwhile the water flux of the membrane was significantly increased.

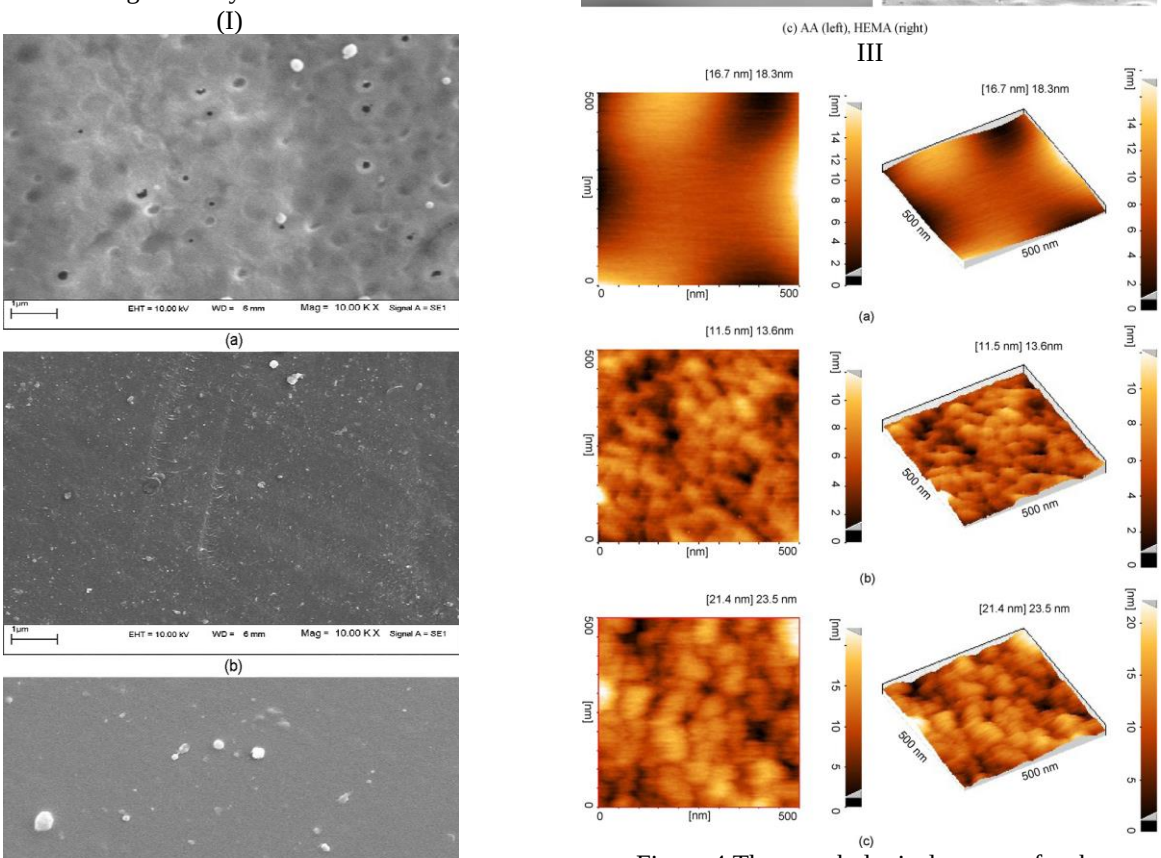


Figure 4 The morphological patterns for the fabricated membranes (I) surface SEM images (II) Cross-sectional SEM images, and (III) AFM images of membranes prepared: (a) without hydrophilic monomers (b) with 5wt.% AA and HEMA (c) with 15wt.% AA and HEMA [60].

1.2. Amphiphilic Co-additives

One general issue of using pure hydrophilic additives is the elution of this additive from the PES matrix; so that, more recent attention has focused on the provision of amphiphilic block copolymers as additives in membrane preparation processes [63]. Soybean phosphatidylcholine (SPC) has been used to modify PES to increase the membrane resistance to protein adsorption [64]. Similarly, Zhu et al. (2007) [65], increased the fouling resistance of the fabricated membranes by adding styrene-maleic anhydride (SMA) to the PES membrane. Also, Fang ***et al.*** [66] blended PES with SMA alternating copolymer and it was found that the surface hydrophilicity and protein-adsorption resistance were improved. The amphiphilic sulfobetaine copolymer (DMMSA–BMA) was added to PES and hydrophilicity was increased noticeably [64] but the modified membranes showed a slight improvement in pure water flux. In the same track, a pH-sensitive hollow fiber membrane was prepared using a synthesized terpolymer of poly (methylmethacrylate–acrylic acid–vinyl pyrrolidone) P(MMA-AA-VP) [63].

Pluronics copolymer composed of a central hydrophobic poly (propylene oxide) (PPO) edged by two hydrophilic poly(ethylene oxide) (PEO) (e.g. Pluronic F127) [67]. This sequence is reversed when PEO units are in the centre (e.g. P31R1) [7]. There are limited studies regarding blending Pluronic polymers with PES. The first systematic study of blending Pluronic polymers with PES was reported by Wang ***et al.*** [67] in 2005. They alleviated the protein adsorption on PES membranes by blending Pluronic F127. Following this study, Wang ***et al.,*** (2006) [68] studied the effect of Pluronic polymer content, kind, and PEO chain length on UF performance and fouling-resistant ability of blend membranes. In another work, Wang et al.,(2006) [69] studied the effect of Pluronic F127 content on UF performance and sieving properties under different operating pressures from 0.5 bar to 3.0 bar. It has been found that the operating pressure had a more favourable effect on the flux of blend membranes than that of the PES-control membrane.

Susanto and Ulbricht [70] compared the effect of three different macromolecular additives PVP, PEG, and Pluronic F127 on the PES membrane structure and their stability in the polymer membrane

Table 4.

Tetronic acids (TA) are used as amphiphilic additives with PES-based membranes in very few research publications. To the best of the authors' knowledge, the first paper that utilized TAs as additives was published in 2008 by Arahman et al., [73]. In this work, Tetronic 1307 was used as an additive to form PES hollow fiber membrane and the prepared membranes were treated with hypochlorite to test their stability. Recently, Abdel-Karim *et al*. (2017) [7], used Tetronic 904 as a subclass from TAs. In their work, it was found that the addition of 5 wt% of T904 improved the flux of PES membranes from 2 LMH/bar to ≈64 LMH/bar without retarding BSA rejection. Abdelsamad *et al.* (2017) [74], prepared electrospun PES/T901 nanofibrous for water treatment purposes.

matrix of the PES membrane. In another study, Pluronic F127 is used by Arahman et al., [71] to compare with other additives such as Tetronic 1307 and PVP. All of these pluronic polymers having normal sequence (PPO-PEO-PPO) while in the work done by Abdel-Karim *et al.* (2017) [7], the used Pluronic was in reverse sequence (i.e. PEO-PPO-PEO) (e.g. P31R1). Recently, Pluronic F127 at different ratios was blended with PES to separate xylitol from sugars solutions, and also the fouling mitigation effect under the presence of Pluronic in the membrane was observed and reflected in production of higher water flux [72]. Different types of Pluronic utilized with the PES matrix are tabulated in Tetronic acids (TA) are used as amphiphilic additives with PES-based membranes in very few research publications. To the best of the authors' knowledge, the first paper that utilized TAs as additives was published in 2008 by Arahman et al., [73]. In this work, Tetronic 1307 was used as an additive to form PES hollow fiber membrane and the prepared membranes were treated with hypochlorite to test their stability. Recently, Abdel-Karim *et al.* (2017) [7], used Tetronic 904 as a subclass from TAs. In their work, it was found that the addition of 5 wt% of T904 improved the flux of PES membranes from 2 LMH/bar to ≈64 LMH/bar without retarding BSA rejection. Abdelsamad *et al.* (2017) [74], prepared electrospun PES/T901 nanofibrous for water treatment purposes.

Apart from amphiphilic polymers, various surfactants, which is amphiphilic in nature, have been used to improve the properties of PES. In a study carried out by Rahimpour ***et al.,*** (2007) [75], the effects of three different kinds of surfactants namely sodium dodecyl sulfate (SDS) as an anionic surfactant, cetyl three methyl ammonium bromide (CTAB) as a cationic surfactant, and Triton X-100 as non-ionic surfactant on the structure and ultrafilter behavior of PES were investigated. The experimental data showed that the small wt.% of surfactants in the dope solution increases the porosity of the membrane support layer, improves permeation and separation characters. To be more precise, pure water flux without addition surfactants was 170 kg/m2.h and the addition of SDS, CTAB, and Triton-X 100 caused about 3-4 fold increase in water flux with a minimal reduction in protein rejection.

[7], used Tetronic 904 as a subclass from TAs. In their work, it was found that the addition of 5 wt% of T904 improved the flux of PES membranes from 2 LMH/bar to ≈64 LMH/bar without retarding BSA rejection. Abdelsamad *et al.* (2017) [74], prepared electrospun PES/T901 nanofibrous for water treatment purposes.

Apart from amphiphilic polymers, various surfactants, which is amphiphilic in nature, have been used to improve the properties of PES. In a study carried out by Rahimpour ***et al.,*** (2007) [75], the effects of three different kinds of surfactants namely

sodium dodecyl sulfate (SDS) as an anionic surfactant, cetyl three methyl ammonium bromide (CTAB) as a cationic surfactant, and Triton X-100 as non-ionic surfactant on the structure and ultrafilter behavior of PES were investigated. The experimental data showed that the small wt.% of surfactants in the dope solution increases the porosity of the membrane support layer, improves permeation and separation characters. To be more precise, pure water flux without addition surfactants was 170 kg/m2.h and the addition of SDS, CTAB, and Triton-X 100 caused about 3-4 fold increase in water flux with a minimal reduction in protein rejection.

Table 4 Various Pluronic polymers with PES membrane

Pluronic	Total MW	PEO content (wt. %)	MW of PPO (Da)	MW of PEO (Da)	HLB* (-)	Ref
L44	2200	40	1160	1040	12-18	[68]
P123	5800	30	3920	1880	7-12	[68]
F68	8400	80	1680	6320	>24	[68]
F127	12600	70	3780	8820	18-23	[67-71]
F108	14600	80	2920	11680	>24	[68]
P31R1	3250	10	2925	325	1-7	[7]

* Hydrophilic / lipophilic balance.

1.3. Nanoparticles as additives for enhanced PES membrane performance

More recent attention has focused on the incorporation of inorganic materials in the membrane matrix (i.e. mixed matrix membranes MMMs) [11, 24] . The main purposes of using NPs are tuning the membranes with a required structure besides their ability to alter membrane fouling resistance through the hydrophilic functional groups on NPs surface [11, 21, 76].

For example, Khosravi et al (2022) [https://doi.org/10.1016/j.chemosphere.2021.133335] has blended PES polymer with Mil-125(Ti)/Chitosan nanocomposite to form PES-Mil-125 (Ti)/Chitosan MMMs. Morphological changes as proved by SEM analysis showed uniform size and more compatible structure for synthesized nanocomposite. High surface wettability and flux observed for the PES-Mil-125(Ti)/Cs membranes (from 12.8 L/m^{2}h for bare PES to 131.6 L/m^{2}h for the best performing one). Arefi-Oskoui et al (2022) [https://doi.org/10.1016/j.seppur.2021.119822] has prepared a nanocomposite of MoS2 nanosheets and oxidized multi-walled carbon nanotubes (O-MWCNTs) using the hydrothermal method and then used as a nanoadditive for the improvement of PES polymeric membrane. Well defined asymmetric structure as well as improved performance (in terms of permeability of 64.1 L/m2 h bar, and high pollutants removal of 93.5% for reactive blue 19, 97.5% for rifampicin, 98.4% for reactive red 195, and 99% for bovine serum albumin) has been obtained. Besides, Ni@UiO-66) [https://doi.org/10.1016/j.jcis.2022.03.106] and Fe_3O_4 decorated halloysite nanoclay [https://doi.org/10.1016/j.envres.2021.112113] were used to improve PES performance. it had been reported that GO nanoparticles have been proved to enhance the mechanical stability of PES-based membranes [11]. In the aforementioned example, how hydrophilic functional groups such as carboxyl, epoxy, and hydroxyl functional groups on edges and planes of graphene oxide (GO) would provide the membrane surface with a large negative charge which prevents the accumulation of foulants (e.g. Bovine serum albumin; BSA) on the membrane surface as a result of electrostatic repulsion between the surface and BSA.

1.3.1. Ag NPs

Biofouling is a detrimental phenomenon to membrane-based water treatment, as a result, many efforts have been done to overcome this obstacle. Basri et al., have used Ag NPs to inhibit bacterial growth on the membrane surface [77]. Besides, it has been found that Ag NPs can hinder the intra-pore biofouling and inhibit the biofilm growth at the membrane surface [78, 79]. It has been reported that the loss of Ag NPs may result from a weak adhesion of the Ag NPs with the PES matrix [77]. In another work, the addition of 2,4,6-triaminopyrimidine (TAP) and PVP had been proved to be effective additives in diminishing the leaching of Ag NPs as well as to produce membranes with an improved distribution in the membrane matrix [80]. Zhang and co-workers [81] used an alternative form of Ag called biogenetic Ag NPs (bio-Ag) as an additive to the PES during the membrane fabrication. PWP and antibacterial activity of modified PES membranes have been improved significantly (i.e. duplicate in PWP). Recently, combining Ag with other metal NPs has to form bimetallic NPs has been reported such as the study reported by Masheane et al., (2017) [82].

Ghalamchi et al., [83] prepared and characterized a new PES MF membrane containing g-C_3N_4 nanosheets/Ag_3PO_4 nanoparticles. High hydrophilicity and the antibacterial properties of Ag_3PO_4-NH_2 NPs made them a superior choice to be combined with carbon nitride (g-C_3N_4) nanosheets to

modify the PES membrane characteristics as a nanofiller additive.

1.3.2. TiO_2

Utilizing TiO_2 NPs in membrane technology has attracted considerable attention due to their superior surface, catalytic and antifouling characters [84, 85]. Vatanpour ***et al.,*** [86] used three types of TiO_2 NPs (P25, PC105, and PC500) with various sizes that were applied for the preparation of mixed matrix PES-based membranes. The flux recovery percentage of the nascent PES membrane was increased from 56% to 91% by blending 4 wt.% P25 NPs. Interestingly, at a low concentration of TiO_2, the nanoparticles with small size caused more biofouling reduction because the aggregation of the NPs was not prominent at a low amount. In another work, coupling TiO_2 NPs with UV irradiation for modification of PES-based membranes [87]. Sotto ***et al.,***[88] utilized lab prepared TiO_2 (anatase) in order to study the effect of NPs aggregation at low concentrations of TiO_2 on the hydrophilicity, morphology, and fouling resistance of PES–TiO_2 membranes. Antibacterial activity is also a characteristic property of TiO_2 NPs [89]. Consequently, toxic TiO_2 NPs had been transformed into benign TiO_2 via sulfonation ($STiO_2$) step [90]. this study may suggest that the PES-TiO_2 and PES-$STiO_2$ nanocomposite membrane is more sustainable than the PES membrane. Ayyaru and Ahn [91] have found that PES/sulfonated TiO_2 ($STiO_2$) NPs UF blended membranes possessed an enhanced properties (e.g. surface roughness, porosity, and pore size when compared to the PES membrane). More literature regarding NPs is tabulated in

Table 5.

The findings of the efficient absorbing ability of magnetite (Fe_3O_4) NPs towards As(V) [92] should make an important contribution to the field of membrane. However, to obtain desirable performance of Fe_3O_4, surface modification of Fe_3O_4 NPs, using a silane agent (APTES), is a novel method utilized to reduce their agglomeration before impregnation into PES membranes [93]. The findings from [94] may make an important contribution to the field of membrane technology. In this report, and for the first time according to authors, in situ-generated homogenous yttrium (Y)-based NP/polyethersulfone (PES) composite adsorptive membranes were developed.

Currently, few studies considered incorporating activated carbon nanoparticles (ACNPs) into mixed matrix PES-based membranes. In a study conducted by Hosseini ***et al.,*** [95], ACNPs embedded mixed matrix asymmetric PES based NF membranes were prepared by solution casting to increase the removal efficiency of sulfate and copper ions from water. Another study [50] provided an important opportunity to advance the understanding of adding two different NPs with different loading to the PES matrix. In this study, novel PES UF membranes blended with different contents of the CuO/ZnO (CZN) nanocomposite were prepared by NIPS. The authors claimed the usage of ZnO NPs with CuO caused a higher hydrophilic behaviour for the fabricated membranes than usage ZnO alone in improving the membrane properties. Mohammadnezhad ***et al.,*** [96] have developed a new PES NF membrane modified with nanocrystalline Ce(III) metal-organic framework (MOF), prepared via the NIPS method and characterized using SEM, AFM, water contact angle, and porosity measurements.

In a separate piece of work, Gumbi ***et al.,*** [97] succeeded in preparing macro void-free PES/SPSf/O-MWCNT ultrafiltration membranes with improved mechanical strength, antifouling, and antibacterial properties. Such spongy morphology provided excellent mechanical strength as well as BSA separation properties. Salim ***et al.,*** [98] studied the effects of hydrophilic surface macromolecule modifier loading on PES/O-g-C_3N_4 (LSMM) hybrid photocatalytic membrane for phenol removal. The results show that the LSMM addition increased the membrane hydrophilicity which may consequently prevent the membrane from comprehensive fouling.

Table 5 Performance comparison of some mixed matrix membranes (MMMs).

PES (wt.%)	NPs (wt.%)	Co-additive (wt. %)	Permeability ($L.m^{-2}.h^{-1}.bar^{-1}$)	Rejection % (pollutant)	Ref
20	MWCNTs (0.5)	No additive	≈26	30 (NOM)	[99]
16	CNT (1)	PVP (4)	≈60	86 (BSA)	[76]
15	TiO_2 (0.5)	PVP (5)	≈596	No rejection data	[100]
18	Al_2O_3 (0.05)	No additive	≈1268	No rejection data	[101]
15	$AgNO_3$ (0.5)	PVP (0.5)	≈32	No rejection data	[77]
18	Biogenic-Ag^0 (1)	No additive	≈120	No rejection data	[79]
27	ZnO (0.125)	No additive	≈50	≈40 (Methylene blue)	[102]
15	HMO;hydrous manganes oxide (23.08)	PVP (1.15)	≈ 28.5	≈ 97.2 (Oil)	[103]
18	Nano Cu (0.002)	No additive	≈ 249 ±(21.4)	≈ 51 (BSA)	[104]

18	Nano Se (0.002)	No additive	≈ 121 ±(17.1)	≈ 55 (BSA)	[104]
15	Cellulose nanocrystal (1)	PVP (2)	≈ 195	≈ 96 (BSA)	[105]
19	Sodium lignofulfonate-CNTs (2)	PVP (1)	≈ 600	≈ 95 (BSA)	[106]
NA wt.%	indium tin oxide ITO (NA)	Surfactant BYK-106 (NA)	≈ 70	42 (TOC)	[107]
15	ZrO_2 (85)	No additive	467	90 (Dextran 40,000 Da)	[108]
17	Sulfonated hyperbranched polyethersulfone (SHBPES)-modified halloysite nanotubes (HNTs) (8)	PVP (4)	351.6	98 (BSA)	[109]

1.3.3. Graphene-based nanofillers

Over the past decade, most research in the material field has emphasized the use of GO due to its high hydrophilic nature as well as possessing attractive properties such as high mechanical strength, low thickness, high flexibility, and a negatively charged surface, offering water dispersibility and good miscibility with polymers [11, 110]. Besides, GO can significantly improve the physical properties of the host polymers at very low dope concentration [11, 21] due to its high specific surface area.

Table 6, the membranes that contain GO-based nanofillers have PWP up to 13 $L.m^{-2}.h^{-1}.bar^{-1}$ [11]. This improvement may confirm the pore-forming ability of GO-based nanofillers. However, these values may be not sufficient for real applications; so that, pore-forming agents have been added with GO. PVP is the most common pore-forming agent used [11, 49, 111] and the wt.% of PVP ranges generally from 1.0% – 8.0%. In some papers, the performance of the fabricated membranes without PVP has not been studied [20, 22, 112] so the improvement of membranes may be attributed to PVP, not GO-based nanofillers. It was found that GO addition has significantly improved the water flux of PES MMMs. GO also reduced the fouling property of PES membranes as proved by contact angle data and this ensures that membrane surface hydrophilicity was improved considerably due to the existence of functional groups of both GO and PAA. Moreover, GO+PAA and GO+LiCl enhanced the membrane performance in terms of flux, rejection and antifouling properties. This may suggest synergistic effects between GO and PAA and LiCl.

Alternative forms of GO have been used recently in membrane fabrication and proved

Table 6 that there is a growing attention in using GO with PES polymer.

Table 6 demonstrates performance data (PWP and rejection) of some recently published papers. As a general remark deduced from enhancements in different aspects. It is worth mentioning the work done by Vatanpour et al. [22] who achieved a pure water flux of 429.8 $L.m^{-2}.h^{-1}$ with MMMs composed of PES and rGO/Ag. Also, as-prepared GO was modified by hyperbranched polyethylenimine (HPEI) and then blended into PES casting solution to prepare PES UF membrane via phase inversion method [113]. Decorated TiO_2 NPs onto reduced graphene oxide (rGO) sheets (rGO/TiO_2) nanocomposite was used as an additive with PES membranes [21]. From this work, it was found that the addition of TiO_2 to rGO has minimized the agglomeration of rGO as well as showed a better distribution in the PES matrix. rGO/TiO_2 not just improved the hydrophilicity of PES membranes but also the antifouling properties of the PES nanofiltration membranes. In another work, PES/GO-ZnO/PVP has been prepared via a unique membrane synthesis approach called double-casting phase inversion (DCPI). In this technique, the casting solutions are cast twice before coagulation [49]. Recently, Abdi ***et al.,*** [114] utilized magnetic graphene oxide/metformin hybrid as a novel nanofiller additive to improve the morphological and performance criteria of PES-based membranes. It can be depicted from

Table 6 Summary of PES/Graphene-based filtration membranes.

PES (%)	Solvent type	GO-based filler type	Additive Type and concentration	Membrane performance in term of rejection % (solute)	Ref.
18	DMAc	HPEI-GO 0 to 5 wt%	PVP 8wt%+0.8 wt.% acetone	60-85 % (PEG, 20,000 Da)	[113]
20	DMAc	0 to 1 wt%	PVP 1 wt%	5.1 90-99 % (direct red 16 dye 637.5 Da)	[112]
18	DMAc	rGO/Ag 0.05 to 0.5wt%	PVP 1wt%	66.7 No rejection data	[22]
13-17	DMAc	GO 0.5 and 1 wt%	PVP 1wt%	91.4 (COD removal)	[46]
21	DMAc	0.05 to 0.2 wt.% of rGO/TiO_2	PVP 1 wt%	9 60-95 % (Three organic dyes, C. I. Reactive Green 19 (1418.9 g mol-1), C. I. Direct Yellow 12 (680.7 g mol-1) and C. I. Reactive Blue 21 (377.4 g mol-1))	[21]
20	DMF	0.3 % GO	5% T904	245 74.3 % (BSA) 62.3 % (SY dye)35.4 % (AO dye)	[11]
20	DMF	0.1 % GO	5% P31R1	91 96% (BSA) 84.9 % (SY dye) 38% (AO dye)	[11]
20	DMF	0.1 % GO	3% PVP	68.5 90.1 % (BSA)94.5 % (SY dye)43.7 % (AO dye)	[11]
20	DMF	0.1 to 1.0% GO	No additives	2-13 90-96 (BSA)80-84 % (SY dye)	[11]
17.5	DMAc	0-1 wt.% GO	No additives	≈1.9-3.1≈45-59% (synthetic melanoidin)≈40-54 % (spent wash)	[115]
17.5	DMAc	1.0 wt.% GO	1 wt.% LiCl	≈3.5 ≈54% (synthetic melanoidin)≈50 % (spent wash)	[115]
17.5	DMAc	1.0 wt.% GO	1 wt.% PAA	≈4.4 ≈56% (synthetic melanoidin)≈49 % (spent wash)	[115]
16	NMP	0.5 % GO	2% PVP	≈41.5 ≈26% (MB dye) ≈50% (MO dye) ≈85% (CR dye)	[116]
22	NMP	0-0.2 % GO-ZnO	4% PVP	1.5-13.5 17-28 % (MgSO4)	[49]
20	DMAc	0-0.25 % PANI ©GO	1% PVP	1.5-2.180-98 % (Pb)	[117]
18	DMAc	0-3 % UiO66 and UiO-66@GO	8 % PVP	1.3-5 88-98 % (DR dye)80-88% (MO dye)	[111]
18	DMAc	0-1 % GO and chitosan-GO	1 % PVP	4.4-9.1 67-90 % (Na_2SO_4)	[118]

**role of GO in these publications is mainly pore forming agent and enhances solute rejection*

2. Conclusions

The relevance of added additives to PES polymer is supported by the current findings in this review. Hydrophilic additives such as PVP or PEG, they are playing a critical role in the structural and performance characteristics of the fabricated PES membranes. However, these polymers were found to be unstable in the formed membrane due to their solubility in water. Apart from using PVP and PEG polymers, other hydrophilic additives were reported to influence the characteristics of the membrane. Using amphiphilic additives reduced the protein adsorption resistance as well as increased the flux recovery ratio. In terms of stability of amphiphilic polymers on the membrane surface, the surface hydrophilicity was decreased due to the detachment of the hydrophilic group from the membrane surface as reported in used some Pluronic polymers. However, the copolymers of Pluronic showed better stability during the filtration experiment. The NPs that have been reported assists in our understanding of their ability to improve the characteristics of the PES membranes. NPs assist in the formation of a membrane with superior thermal and mechanical properties. The findings of the mentioned reports in this review suggest that the dispersion of NPs is a critical issue so optimizing the loading of NPs has been studied extensively. An increase in their concentration leads to aggregation in

the membrane structure. Ag and TiO_2 NPs were found to be used to diminish the biofouling of polymeric membranes. Recently, graphene-based nanofillers such as GO and functionalized GO have drawn marvellous attention in membrane technology due to their exceptional mechanical and thermal properties.

3. References

1. Fu, X., et al., *Effect of surface morphology on membrane fouling by humic acid with the use of cellulose acetate butyrate hollow fiber membranes.* Journal of Membrane Science, 2008. **320**(1-2): p. 483-491.
2. Le, N.L. and S.P. Nunes, *Materials and membrane technologies for water and energy sustainability.* Sustainable Materials and Technologies, 2016. **7**: p. 1-28.
3. Abdel-Karim, A., et al., *High-performance mixed-matrix membranes enabled by organically/inorganic modified montmorillonite for the treatment of hazardous textile wastewater.* Chemical Engineering Journal, 2021. **405**: p. 126964.
4. Mohammadi, T. and E. Saljoughi, *Effect of production conditions on morphology and permeability of asymmetric cellulose acetate membranes.* Desalination, 2009. **243**(1-3): p. 1-7.
5. Khalid, A., et al., *PEG-CNTs nanocomposite PSU membranes for wastewater treatment by membrane bioreactor.* Separation and Purification Technology, 2018. **190**: p. 165-176.
6. Khalid, A., et al., *Preparation and properties of nanocomposite polysulfone/multi-walled carbon nanotubes membranes for desalination.* Desalination, 2015. **367**: p. 134-144.
7. Abdel-Karim, A., et al., *Fabrication of modified polyethersulfone membranes for wastewater treatment by submerged membrane bioreactor.* Separation and Purification Technology, 2017. **175**: p. 36-46.
8. ElSherbiny, I.M.A., et al., *Isotropic macroporous polyethersulfone membranes as competitive supports for high performance polyamide desalination membranes.* Journal of Membrane Science, 2015. **493**: p. 782-793.
9. Susanto, H., N. Stahra, and M. Ulbricht, *High performance polyethersulfone microfiltration membranes having high flux and stable hydrophilic property.* Journal of Membrane Science, 2009. **342**(1-2): p. 153-164.
10. Susanto, H. and M. Ulbricht, *Performance of surface modified polyethersulfone membranes for ultrafiltration of aquatic humic substances.* Desalination, 2006. **199**(1-3): p. 384-386.
11. Abdel-Karim, A., et al., *High flux and fouling resistant flat sheet polyethersulfone membranes incorporated with graphene oxide for ultrafiltration applications.* Chemical Engineering Journal, 2018. **334**: p. 789-799.
12. Konieczny, K., *Disinfection of surface and ground waters with polymeric ultrafiltration membranes.* Desalination, 1998. **119**(1-3): p. 251-258.
13. Lohokare, H.R., et al., *Effective arsenic removal using polyacrylonitrile-based ultrafiltration (UF) membrane.* Journal of Membrane Science, 2008. **320**(1-2): p. 159-166.
14. Abdel-Karim, A., et al., *Probing protein rejection behavior of blended PES-based flat-sheet ultrafiltration membranes: A density functional theory (DFT) study.* Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2020. **238**: p. 118399.
15. Kang, G.-d. and Y.-m. Cao, *Application and modification of poly(vinylidene fluoride) (PVDF) membranes – A review.* Journal of Membrane Science, 2014. **463**: p. 145-165.
16. Song, H., et al., *Natural organic matter removal and flux decline with PEG–TiO2-doped PVDF membranes by integration of ultrafiltration with photocatalysis.* Journal of Membrane Science, 2012. **405-406**: p. 48-56.
17. Leaper, S., et al., *Flux-enhanced PVDF mixed matrix membranes incorporating APTS-functionalized graphene oxide for membrane distillation.* Journal of Membrane Science, 2018. **554**: p. 309-323.
18. Zhao, C., et al., *Modification of polyethersulfone membranes – A review of methods.* Progress in Materials Science, 2013. **58**(1): p. 76-150.
19. Ulbricht, M., *Advanced functional polymer membranes.* Polymer, 2006. **47**(7): p. 2217-2262.
20. Kumar, M., et al., *Preparation and characterization of low fouling novel hybrid ultrafiltration membranes based on the blends of GO−TiO2 nanocomposite and polysulfone for humic acid removal.* Journal of Membrane Science, 2016. **506**: p. 38-49.
21. Safarpour, M., V. Vatanpour, and A. Khataee, *Preparation and characterization of graphene oxide/TiO2 blended PES nanofiltration membrane with improved antifouling and separation performance.* Desalination, 2016. **393**: p. 65-78.
22. Vatanpour, V., et al., *Fabrication and characterization of anti-fouling and anti-bacterial Ag-loaded graphene oxide/polyethersulfone mixed matrix membrane.* Journal of Industrial and Engineering Chemistry, 2015. **30**: p. 342-352.
23. Alenazi, N.A., et al., *Modified polyether-sulfone membrane: a mini review.* Designed Monomers and Polymers, 2017. **20**(1): p. 532-546.
24. Ahmad, A.L., et al., *Recent development in additives modifications of polyethersulfone*

membrane for flux enhancement. Chemical Engineering Journal, 2013. **223**: p. 246-267.
25. Guillen, G.R., et al., *Preparation and Characterization of Membranes Formed by Nonsolvent Induced Phase Separation: A Review.* Industrial & Engineering Chemistry Research, 2011. **50**(7): p. 3798-3817.
26. Lu, W., et al., *Porous membranes in secondary battery technologies.* Chem Soc Rev, 2017. **46**(8): p. 2199-2236.
27. Lloyd, D.R., K.E. Kinzer, and H.S. Tseng, *Microporous membrane formation via thermally induced phase separation. I. Solid-liquid phase separation.* Journal of Membrane Science, 1990. **52**(3): p. 239-261.
28. Irfan, M. and A. Idris, *Overview of PES biocompatible/hemodialysis membranes: PES-blood interactions and modification techniques.* Mater Sci Eng C Mater Biol Appl, 2015. **56**: p. 574-92.
29. Kochkodan, V., D.J. Johnson, and N. Hilal, *Polymeric membranes: surface modification for minimizing (bio)colloidal fouling.* Advances in colloid and interface science, 2014. **206**: p. 116-40.
30. Li, J.-F., et al., *Hydrophilic microporous PES membranes prepared by PES/PEG/DMAc casting solutions.* Journal of Applied Polymer Science, 2008. **107**(6): p. 4100-4108.
31. Kourde-Hanafi, Y., et al., *Influence of PVP content on degradation of PES/PVP membranes: Insights from characterization of membranes with controlled composition.* Journal of Membrane Science, 2017. **533**: p. 261-269.
32. Vatsha, B., J.C. Ngila, and R.M. Moutloali, *Preparation of antifouling polyvinylpyrrolidone (PVP 40K) modified polyethersulfone (PES) ultrafiltration (UF) membrane for water purification.* Physics and Chemistry of the Earth, Parts A/B/C, 2014. **67-69**: p. 125-131.
33. Ochoa, N.A., et al., *Pore size distributions based on AFM imaging and retention of multidisperse polymer solutes.* Journal of Membrane Science, 2001. **187**(1-2): p. 227-237.
34. Kim, J.H., et al., *Phase behavior and morphological studies of polyimide/PVP/solvent/water systems by phase inversion.* Journal of Applied Polymer Science, 2001. **81**(14): p. 3481-3488.
35. Xu, Z.-L. and F. Alsalhy Qusay, *Polyethersulfone (PES) hollow fiber ultrafiltration membranes prepared by PES/non-solvent/NMP solution.* Journal of Membrane Science, 2004. **233**(1-2): p. 101-111.
36. Forrest, J.A., et al., *Effect of Free Surfaces on the Glass Transition Temperature of Thin Polymer Films.* Phys Rev Lett, 1996. **77**(10): p. 2002-2005.
37. Otitoju, T.A., A.L. Ahmad, and B.S. Ooi, *Recent advances in hydrophilic modification and performance of polyethersulfone (PES) membrane via additive blending.* RSC Advances, 2018. **8**(40): p. 22710-22728.
38. Liu, Y., G.H. Koops, and H. Strathmann, *Characterization of morphology controlled polyethersulfone hollow fiber membranes by the addition of polyethylene glycol to the dope and bore liquid solution.* Journal of Membrane Science, 2003. **223**(1-2): p. 187-199.
39. Al Malek, S.A., et al., *Formation and characterization of polyethersulfone membranes using different concentrations of polyvinylpyrrolidone.* Desalination, 2012. **288**: p. 31-39.
40. Kim, J.H. and C.K. Kim, *Ultrafiltration membranes prepared from blends of polyethersulfone and poly(1-vinylpyrrolidone-co-styrene) copolymers.* Journal of Membrane Science, 2005. **262**(1-2): p. 60-68.
41. Sanchez, B.T., R.I. Ortiz-Basurto and E.B. Fuente, *Effect of nonsolvents on properties of spinning solutions and polyethersulfone hollow fiber ultrafiltration membranes.* J. Membr. Sci., 1999. **152**: p. 19-28.
42. Rahimpour, A., S.S. Madaeni, and Y. Mansourpanah, *Fabrication of polyethersulfone (PES) membranes with nano-porous surface using potassium perchlorate (KClO4) as an additive in the casting solution.* Desalination, 2010. **258**(1-3): p. 79-86.
43. Ghaemi, N., et al., *Preparation, characterization and performance of polyethersulfone/organically modified montmorillonite nanocomposite membranes in removal of pesticides.* Journal of Membrane Science, 2011. **382**(1): p. 135-147.
44. Torrestiana-Sanchez, B., R.I. Ortiz-Basurto, and E. Brito-De La Fuente, *Effect of nonsolvents on properties of spinning solutions and polyethersulfone hollow fiber ultrafiltration membranes.* Journal of Membrane Science, 1999. **152**: p. 19-28.
45. Vatanpour, V., et al., *Fabrication and characterization of novel antifouling nanofiltration membrane prepared from oxidized multiwalled carbon nanotube/polyethersulfone nanocomposite.* Journal of Membrane Science, 2011. **375**(1-2): p. 284-294.
46. Zinadini, S., et al., *Preparation and characterization of antifouling graphene oxide/polyethersulfone ultrafiltration membrane: Application in MBR for dairy wastewater treatment.* Journal of Water Process Engineering, 2015. **7**: p. 280-294.
47. Mehrparvar, A., A. Rahimpour, and M. Jahanshahi, *Modified ultrafiltration membranes*

for humic acid removal. Journal of the Taiwan Institute of Chemical Engineers, 2014. **45**(1): p. 275-282.
48. Zinadini, S., et al., *Preparation of antibiofouling polyethersulfone mixed matrix NF membrane using photocatalytic activity of ZnO/MWCNTs nanocomposite.* Journal of Membrane Science, 2017. **529**: p. 133-141.
49. Mahlangu, O.T., et al., *Hydrophilic fouling-resistant GO-ZnO/PES membranes for wastewater reclamation.* Journal of Membrane Science, 2017. **524**: p. 43-55.
50. Nasrollahi, N., et al., *Preparation and characterization of a novel polyethersulfone (PES) ultrafiltration membrane modified with a CuO/ZnO nanocomposite to improve permeability and antifouling properties.* Separation and Purification Technology, 2018. **192**: p. 369-382.
51. Astakhov, E.Y., et al., *Influence of polyvinylpyrrolidone on morphology, hydrophilicity, and performance of polyethersulfone microfiltration membranes.* Petroleum Chemistry, 2013. **52**(8): p. 557-564.
52. Idris, A., N. Mat Zain, and M.Y. Noordin, *Synthesis, characterization and performance of asymmetric polyethersulfone (PES) ultrafiltration membranes with polyethylene glycol of different molecular weights as additives.* Desalination, 2007. **207**(1-3): p. 324-339.
53. Xu, Z.-L. and F.A. Qusay, *Effect of polyethylene glycol molecular weights and concentrations on polyethersulfone hollow fiber ultrafiltration membranes.* Journal of Applied Polymer Science, 2004. **91**(5): p. 3398-3407.
54. Chan, K.H., et al., *Enhanced Cu(II) rejection and fouling reduction through fabrication of PEG-PES nanocomposite ultrafiltration membrane with PEG-coated cobalt doped iron oxide nanoparticle.* Journal of the Taiwan Institute of Chemical Engineers, 2015. **47**: p. 50-58.
55. Rahimpour, A. and S.S. Madaeni, *Polyethersulfone (PES)/cellulose acetate phthalate (CAP) blend ultrafiltration membranes: Preparation, morphology, performance and antifouling properties.* Journal of Membrane Science, 2007. **305**(1-2): p. 299-312.
56. Sun, Z. and F. Chen, *Hydrophilicity and antifouling property of membrane materials from cellulose acetate/polyethersulfone in DMAc.* International Journal of Biological Macromolecules, 2016. **91**: p. 143-50.
57. Chaturvedi, B.K., et al., *Preparation, characterization and performance of polyethersulfone ultrafiltration membranes.* Desalination, 2001. **133**(1): p. 31-40.
58. Ghaemi, N. and F. Nasirmanesh, *Synthesis of a hybrid organic-inorganic polyethersulfone membrane incorporated with phosphotungstic acid: Controversial performance in removal of dinitroaniline herbicides from water.* Journal of Cleaner Production, 2018. **182**: p. 259-271.
59. Kumar, R.S. and G. Arthanareeswaran, *Nano-curcumin incorporated polyethersulfone membranes for enhanced anti-biofouling in treatment of sewage plant effluent.* Materials Science and Engineering: C, 2019. **94**: p. 258-269.
60. Rahimpour, A. and S.S. Madaeni, *Improvement of performance and surface properties of nano-porous polyethersulfone (PES) membrane using hydrophilic monomers as additives in the casting solution.* Journal of Membrane Science, 2010. **360**(1-2): p. 371-379.
61. Laninovic, V., *Structure of flat sheet membranes obtained from the system polyethersulfone-dimethylacetamide-nonsolvent additive-water.* Polymer science. Series A, 2005. **47**(7): p. 744-749.
62. Fang, X., et al., *Polyethyleneimine, an effective additive for polyethersulfone ultrafiltration membrane with enhanced permeability and selectivity.* Journal of Membrane Science, 2015. **476**: p. 216-223.
63. Zou, W., et al., *Poly (methyl methacrylate–acrylic acid–vinyl pyrrolidone) terpolymer modified polyethersulfone hollow fiber membrane with pH sensitivity and protein antifouling property.* Journal of Membrane Science, 2010. **358**(1-2): p. 76-84.
64. Wang, Y.-q., et al., *Protein-adsorption-resistance and permeation property of polyethersulfone and soybean phosphatidylcholine blend ultrafiltration membranes.* Journal of Membrane Science, 2006. **270**(1-2): p. 108-114.
65. Zhu, L.P., et al., *Improved protein-adsorption resistance of polyethersulfone membranes via surface segregation of ultrahigh molecular weight poly(styrene-alt-maleic anhydride).* Colloids and surfaces. B, Biointerfaces, 2007. **57**(2): p. 189-97.
66. Fang, B., et al., *Modification of polyethersulfone membrane by grafting bovine serum albumin on the surface of polyethersulfone/poly(acrylonitrile-co-acrylic acid) blended membrane.* Journal of Membrane Science, 2009. **329**(1-2): p. 46-55.
67. Wang, Y.-q., et al., *Remarkable Reduction of Irreversible Fouling and Improvement of the Permeation Properties of Poly(ethersulfone) Ultrafiltration Membranes by Blending with Pluronic F127.* Langmuir 2005. **21**(25): p. 11856-11862.

68. Wang, Y.-Q., et al., *Pluronic polymers and polyethersulfone blend membranes with improved fouling-resistant ability and ultrafiltration performance.* Journal of Membrane Science, 2006. **283**(1-2): p. 440-447.
69. Wang, Y., et al., *Improved permeation performance of Pluronic F127–polyethersulfone blend ultrafiltration membranes.* Journal of Membrane Science, 2006. **282**(1-2): p. 44-51.
70. Susanto, H. and M. Ulbricht, *Characteristics, performance and stability of polyethersulfone ultrafiltration membranes prepared by phase separation method using different macromolecular additives.* Journal of Membrane Science, 2009. **327**: p. 125-135.
71. Arahman, N., et al., *Structure Change of Polyethersulfone Hollow Fiber Membrane Modified with Pluronic F127, Polyvinylpyrrolidone, and Tetronic 1307.* Materials Sciences and Applications, 2012. **03**(02): p. 72-77.
72. Faneer, K.A., R. Rohani, and A.W. Mohammad, *Influence of pluronic addition on polyethersulfone membrane for xylitol recovery from biomass fermentation solution.* Journal of Cleaner Production, 2018. **171**: p. 995-1005.
73. Arahman, N., et al., *Effect of hypochlorite treatment on performance of hollow fiber membrane prepared from polyethersulfone/N-methyl-2-pyrrolidone/tetronic 1307 solution.* Journal of Applied Polymer Science, 2008. **110**(2): p. 687-694.
74. Abdelsamad, A.M.A., et al., *Hydrophilic polyethersulfone-based microfiltration membranes by electrospinning of polymer blends.* Desalination and Water Treatment, 2017. **86**: p. 89-95.
75. Rahimpour, A., S. Madaeni, and Y. Mansourpanah, *The effect of anionic, non-ionic and cationic surfactants on morphology and performance of polyethersulfone ultrafiltration membranes for milk concentration.* Journal of Membrane Science, 2007. **296**(1-2): p. 110-121.
76. Rahimpour, A., et al., *Novel functionalized carbon nanotubes for improving the surface properties and performance of polyethersulfone (PES) membrane.* Desalination, 2012. **286**: p. 99-107.
77. Basri, H., A.F. Ismail, and M. Aziz, *Polyethersulfone (PES)–silver composite UF membrane: Effect of silver loading and PVP molecular weight on membrane morphology and antibacterial activity.* Desalination, 2011. **273**(1): p. 72-80.
78. Ng, L.Y., et al., *Polymeric membranes incorporated with metal/metal oxide nanoparticles: A comprehensive review.* Desalination, 2013. **308**: p. 15-33.
79. Zhang, M., et al., *Biogenic silver nanoparticles (bio-Ag 0) decrease biofouling of bio-Ag 0/PES nanocomposite membranes.* Water Res, 2012. **46**(7): p. 2077-87.
80. Basri, H., et al., *Silver-filled polyethersulfone membranes for antibacterial applications — Effect of PVP and TAP addition on silver dispersion.* Desalination, 2010. **261**(3): p. 264-271.
81. Zhang, M., et al., *Biogenic silver nanoparticles (bio-Ag 0) decrease biofouling of bio-Ag 0/PES nanocomposite membranes.* Water research, 2012. **46**(7): p. 2077-2087.
82. Masheane, M.L., et al., *Synthesis of Fe-Ag/f-MWCNT/PES nanostructured-hybrid membranes for removal of Cr(VI) from water.* Separation and Purification Technology, 2017. **184**: p. 79-87.
83. Ghalamchi, L., et al., *A novel antibacterial mixed matrixed PES membrane fabricated from embedding aminated Ag3PO4/g-C3N4 nanocomposite for use in the membrane bioreactor.* Journal of Industrial and Engineering Chemistry, 2019. **70**: p. 412-426.
84. Ghasemzadeh, G., et al., *Applications of nanomaterials in water treatment and environmental remediation.* Frontiers of Environmental Science & Engineering, 2014. **8**(4): p. 471-482.
85. Teow, Y.H., et al., *Studies on the surface properties of mixed-matrix membrane and its antifouling properties for humic acid removal.* Journal of Applied Polymer Science, 2013. **128**(5): p. 3184-3192.
86. Vatanpour, V., et al., *TiO2 embedded mixed matrix PES nanocomposite membranes: Influence of different sizes and types of nanoparticles on antifouling and performance.* Desalination, 2012. **292**: p. 19-29.
87. Rahimpour, A., et al., *Coupling TiO2 nanoparticles with UV irradiation for modification of polyethersulfone ultrafiltration membranes.* Journal of Membrane Science, 2008. **313**(1): p. 158-169.
88. Sotto, A., et al., *Effect of nanoparticle aggregation at low concentrations of TiO2 on the hydrophilicity, morphology, and fouling resistance of PES–TiO2 membranes.* Journal of Colloid and Interface Science, 2011. **363**(2): p. 540-550.
89. Rahimpour, A., et al., *TiO2 entrapped nano-composite PVDF/SPES membranes: Preparation, characterization, antifouling and antibacterial properties.* Desalination, 2011. **278**(1): p. 343-353.
90. Pandiyan, R., S. Ayyaru, and Y.-H. Ahn, *Non-toxic properties of TiO2 and STiO2 nanocomposite PES ultrafiltration membranes*

for application in membrane-based environmental biotechnology. Ecotoxicology and Environmental Safety, 2018. **158**: p. 248-255.
91. Ayyaru, S. and Y.-H. Ahn, *Fabrication and separation performance of polyethersulfone/sulfonated TiO2 (PES–STiO2) ultrafiltration membranes for fouling mitigation.* Journal of Industrial and Engineering Chemistry, 2018. **67**: p. 199-209.
92. Mohan, D. and C.U. Pittman, *Arsenic removal from water/wastewater using adsorbents—A critical review.* Journal of Hazardous Materials, 2007. **142**(1): p. 1-53.
93. Rowley, J. and N.H. Abu-Zahra, *Synthesis and characterization of polyethersulfone membranes impregnated with (3-aminopropyltriethoxysilane) APTES-Fe3O4 nanoparticles for As(V) removal from water.* Journal of Environmental Chemical Engineering, 2019. **7**(1): p. 102875.
94. He, J., et al., *In situ-generated yttrium-based nanoparticle/polyethersulfone composite adsorptive membranes: Development, characterization, and membrane formation mechanism.* Journal of Colloid and Interface Science, 2019. **536**: p. 710-721.
95. Hosseini, S.M., et al., *Activated carbon nanoparticles entrapped mixed matrix polyethersulfone based nanofiltration membrane for sulfate and copper removal from water.* Journal of the Taiwan Institute of Chemical Engineers, 2018. **82**: p. 169-178.
96. Mohammadnezhad, F., M. Feyzi, and S. Zinadini, *A novel Ce-MOF/PES mixed matrix membrane; synthesis, characterization and antifouling evaluation.* Journal of Industrial and Engineering Chemistry, 2019. **71**: p. 99-111.
97. Gumbi, N.N., et al., *Macrovoid-free PES/SPSf/O-MWCNT ultrafiltration membranes with improved mechanical strength, antifouling and antibacterial properties.* Journal of Membrane Science, 2018. **566**: p. 288-300.
98. Salim, N.E., et al., *Effects of hydrophilic surface macromolecule modifier loading on PES/O-g-C3N4 hybrid photocatalytic membrane for phenol removal.* Applied Surface Science, 2019. **465**: p. 180-191.
99. Celik, E., et al., *Carbon nanotube blended polyethersulfone membranes for fouling control in water treatment.* Water research, 2011. **45**(1): p. 274-82.
100. Wu, G., et al., *Preparation and characterization of PES/TiO2 composite membranes.* Applied Surface Science, 2008. **254**(21): p. 7080-7086.
101. Maximous, N., et al., *Preparation, characterization and performance of Al2O3/PES membrane for wastewater filtration.* Journal of Membrane Science, 2009. **341**(1-2): p. 67-75.
102. Balta, S., et al., *A new outlook on membrane enhancement with nanoparticles: The alternative of ZnO.* Journal of Membrane Science, 2012. **389**: p. 155-161.
103. Lai, G.S., et al., *Novel mixed matrix membranes incorporated with dual-nanofillers for enhanced oil-water separation.* Separation and Purification Technology, 2017. **178**: p. 113-121.
104. Akar, N., et al., *Investigation of characterization and biofouling properties of PES membrane containing selenium and copper nanoparticles.* Journal of Membrane Science, 2013. **437**: p. 216-226.
105. Zhang, D., et al., *Fabrication of antifouling and antibacterial polyethersulfone (PES)/cellulose nanocrystals (CNC) nanocomposite membranes.* Journal of Membrane Science, 2018. **549**: p. 350-356.
106. Wang, W., et al., *Preparation and characterization of SLS-CNT/PES ultrafiltration membrane with antifouling and antibacterial properties.* Journal of Membrane Science, 2018. **548**: p. 459-469.
107. Khorshidi, B., et al., *Thermally resistant and electrically conductive PES/ITO nanocomposite membrane.* Journal of Membrane Science, 2016. **500**: p. 151-160.
108. De Sitter, K., et al., *The use of nanoparticles as alternative pore former for the production of more sustainable polyethersulfone ultrafiltration membranes.* Journal of Membrane Science, 2014. **471**: p. 168-178.
109. Liu, Z., et al., *The influence of sulfonated hyperbranched polyethersulfone-modified halloysite nanotubes on the compatibility and water separation performance of polyethersulfone hybrid ultrafiltration membranes.* Journal of Membrane Science, 2018. **557**: p. 13-23.
110. Zhu, Y., et al., *Graphene and graphene oxide: synthesis, properties, and applications.* Adv Mater, 2010. **22**(35): p. 3906-24.
111. Ma, J., et al., *Composite ultrafiltration membrane tailored by MOF@GO with highly improved water purification performance.* Chemical Engineering Journal, 2017. **313**: p. 890-898.
112. Zinadini, S., et al., *Preparation of a novel antifouling mixed matrix PES membrane by embedding graphene oxide nanoplates.* Journal of Membrane Science, 2014. **453**: p. 292-301.
113. Yu, L., et al., *Preparation and characterization of HPEI-GO/PES ultrafiltration membrane with antifouling and antibacterial properties.* Journal of Membrane Science, 2013. **447**: p. 452-462.

114. Abdi, G., et al., *Removal of dye and heavy metal ion using a novel synthetic polyethersulfone nanofiltration membrane modified by magnetic graphene oxide/metformin hybrid.* Journal of Membrane Science, 2018. **552**: p. 326-335.
115. Aditya Kiran, S., et al., *Impact of graphene oxide embedded polyethersulfone membranes for the effective treatment of distillery effluent.* Chemical Engineering Journal, 2016. **286**: p. 528-537.
116. Makhetha, T.A. and R.M. Moutloali, *Antifouling properties of Cu(tpa)@GO/PES composite membranes and selective dye rejection.* Journal of Membrane Science, 2018. **554**: p. 195-210.
117. Ghaemi, N., S. Zereshki, and S. Heidari, *Removal of lead ions from water using PES-based nanocomposite membrane incorporated with polyaniline modified GO nanoparticles: Performance optimization by central composite design.* Process Safety and Environmental Protection, 2017. **111**: p. 475-490.
118. Bagheripour, E., et al., *Novel composite graphene oxide/chitosan nanoplates incorporated into PES based nanofiltration membrane: Chromium removal and antifouling enhancement.* Journal of Industrial and Engineering Chemistry, 2018. **62**: p. 311-320.