Communication

Effect of Mixing Technique on Physico-Chemical Characteristics of Blended Membranes for Gas Separation

Danial Qadir *, **Humbul Suleman** and **Faizan Ahmad**

School of Computing, Engineering and Digital Technologies, Teesside University, Middlesbrough TS1 3BX, UK; f.ahmad@tees.ac.uk (F.A.)

* Correspondence: d.qadir@tees.ac.uk; Tel.: +44-01642342489

Abstract: Polymer blending has attracted considerable attention because of its ability to overcome the permeability–selectivity trade-off in gas separation applications. In this study, polysulfone (PSU)-modified cellulose acetate (CA) membranes were prepared using *N*-methyl-2-pyrrolidone (NMP) and tetrahydrofuran (THF) using a dry–wet phase inversion technique. The membranes were characterized using scanning electron microscopy (SEM) for morphological analysis, thermogravimetric analysis (TGA) for thermal stability, and Fourier transform infrared spectroscopy (FTIR) to identify the chemical changes on the surface of the membranes. Our analyses confirmed that the mixing method (the route chosen for preparing the casting solution for the blended membranes) significantly influences the morphological and thermal properties of the resultant membranes. The blended membranes exhibited a transition from a finger-like pore structure to a dense substructure in the presence of macrovoids. Similarly, thermal analysis confirmed the improved residual weight (up to 7%) and higher onset degradation temperature (up to 10 °C) of the synthesized membranes. Finally, spectral analysis confirmed that the blending of both polymers was physical only.

Keywords: blended membranes; mixed solvents; cellulose acetate; polysulfone; gas separation

1. Introduction

Membrane processes are currently regarded as a promising technology for gas separation because of their simplicity, which eliminates the need for additional steps required for other conventional processes such as absorbent regeneration or chemical waste [1,2]. Gas separation membranes have found their application in various industrial processes, for instance hydrogen separation from refinery streams, nitrogen separation from air and CO_2 separation from natural gas and oxygen enrichment. Among these, CO_2 removal using polymeric membranes is particularly appealing because of their high energy efficiency, operational flexibility and environmental sustainability [1,3].

Cellulose acetate (CA) has been employed as a synthesis material for a variety of membrane applications since the inception of membrane technology. For CO_2 removal from natural gas and hydrogen purification, CA membranes have always been a preferable choice for their superior features. The success of CAs is due to their characteristics, such as accessibility, affordability, and stability (mechanical and chemical stability) [4]. Similarly, Polysulfone (PSU) has also been extensively studied for gas (particularly CO_2 removal) and liquid separation owing to its structural rigidity and excellent selectivity. Additionally, PSU exhibits economic viability, excellent compact durability, tensile stability, outstanding chemical stability, and barrier properties, all of which are crucial for the resilience of membranes in use [5]. Cellulose acetate (CA) and polyimides (PI) are commonly utilized in addition to polysulfone (PSU) for gas separation, as they tend to demonstrate higher selectivity for the gas pair CO_2/CH_4, as well as for their greater CO_2 permeabilities when compared to PSU. However, PSU has a higher plasticization pressure for CO_2, which refers to the pressure at which a specific gas induces significant swelling of the membrane.

It is believed that swelling results in substantially increased permeabilities for all the gases in the mixture, leading to decreased selectivity. Researchers have found that CA has a plasticization pressure, of 10 bar, while for PI it is 12 bar. In contrast, PSU has a higher plasticization pressure of 34 bar under identical conditions. Hence, for practical gas separation applications, a higher plasticization pressure of PSU is especially advantageous, making it a reasonable candidate as an additive [6,7]. Moreover, for all practical purposes, cellulose acetate, which is a thermally and chemically sensitive material, should be modified through any modification technique (such as blending, grafting, crosslinking, etc.) prior to its intended use in any gas separation configuration [2]. Hence, blending cellulose acetate and polysulfone could be advantageous for gas separation membranes, particularly CO_2/CH_4 separation membranes.

Jami'an et al. reported the synthesis of a cellulose-acetate-based gas separation membrane for CO_2/CH_4 separation using NMP as a solvent. Their study revealed that by manipulating the evaporation time, selectivity and permeability could be controlled as they showed that the change in evaporation time from 10 s to 30 s doubled the selectivity for the respective gas pair [8]. Moghadassi et al. synthesized cellulose-acetate-based blended membranes using THF as a solvent and employed multiwalled carbon nanotubes for gas separation applications. They reported that using carboxylic modified MWCNTs in conjunction with polyethylene glycol resulted in increased membrane performance for CO_2/CH_4 separation. They claimed that at a lower pressure of 2 bar, the resultant membranes achieved a selectivity of 53.98 along with improved mechanical properties [9]. A similar trend of improved membrane performance has been reported in the literature by many researchers [10–13], where polymer blending was used as a successful modification technique to enhance the overall performance of cellulose-acetate-based gas separation membranes.

A look Into the literature reveals that for phase inversion membranes, the choice of an appropriate solvent is an important step in achieving the complete dissolution of the polymer which controls the features of these membranes [14]. The introduction of an additional solvent can alter the polymer's solubility and the casting solution's viscosity, irrespective of other parameters such as the polymer concentration constant. The inclusion of another solvent can either inhibit or facilitate the emergence of voids in the membrane's support structure, owing to dissimilar rates of solvent exchange during precipitation or diverse viscosities of the casting solution. Therefore, the solvent ratio employed in the casting solution plays a crucial role in determining the membrane morphology [15]. NMP as a solvent has been reported by many researchers to possess the ability to alter the polymer structure by enhancing its free fractional volume, resulting in improved permeabilities. In addition, NMP has been found to influence the selectivity of gas separation membranes by reducing the nonselective voids through increased hydrogen bonding [16]. On the other hand, tetrahydrofuran (THF) is a hazardous solvent; however, it offers delayed mixing of the polymer/THF/water system, resulting in a denser membrane structure which is contrary to the NMP/water-based system [17]. Therefore, in this study, a mixed solvent of NMP and THF was chosen at a fixed composition to synthesize the membrane and study the effect of the mixing method on the membranes' resultant features.

Many authors have reported the use of mixed solvents to tune the features of the membranes. However, no studies have addressed the key idea of mixing polymers into solvents under various mixing sequences and their effects on the physico-chemical characteristics of membranes. Therefore, this study aimed to investigate the effects of the mixing sequence of polymers on the said features of cellulose acetate/polysulfone blended membranes, which could open a new avenue for researchers to explore the possibility of tuning blended membranes through mixing.

2. Materials and Methods

2.1. Materials

Cellulose acetate with an average weight of 30,000 g/mol (Sigma Aldrich, Dorset, England) was used as the base polymer for the preparation of the blended membranes. Polysulfone (pellets, M.W. 60 k) was purchased from Sigma Aldrich and used as an additive for the synthesis of blended membranes. For this study, solvents such as *N*-methyl-2-pyrrolidone (NMP) and tetrahydrofuran (99% stabilized with 250–350 ppm BHT) were purchased from Fisher Scientific (Loughborough, England), and they were of analytical grade purity. Deionized water was used as the non-solvent during the synthesis process.

2.2. Methods

2.2.1. Synthesis of Membranes

Flat sheet CA/PSU blended membranes were synthesized using a dry–wet phase inversion technique. The polymers were dried at 80 °C for 12 h to remove moisture prior to any further use. For the synthesis of blended membranes, three different types of solutions were prepared based on their mixing sequence, as shown in Table 1. All the prepared membranes had a fixed composition of base polymer, i.e., CA (10%), blending polymer, that is, PSU (10% of base polymer) and NMP/THF (50/50%). Doping solutions for each membrane type were prepared by stirring the solution at 200 rpm for 12 h, and then, for the removal of gas bubbles, dope solutions were left overnight before casting. Casting of the blended membranes was carried out using an automatic casting machine on an immaculate glass plate at 200 μm casting thickness. This plate was then left at room temperature (15 °C) for 12 h for solvent evaporation. Finally, the glass plates were dipped in a non-solvent bath (water) overnight to completely remove the solvent. The membranes were then rinsed and dried at room temperature for further analysis.

Table 1. Mixing sequence of CA/PSU-based blended membranes.

Membrane Code	Polymer	Solvent	Mixing Method
M1	CA (2.25 g)	NMP (11.25 mL)	MIX
	PSU (0.25 g)	THF (11.25 mL)	MIX
	CA + PSU blend solutions together		
M2	CA (2.25 g)	THF (11.25 mL)	MIX
	PSU (0.25 g)	NMP (11.25 mL)	MIX
	CA + PSU blend solutions together		
M3	By adding CA (2.25 g) + PSU (0.25 g) in a mixed solvent of NMP (11.25 mL) + THF (11.25 mL)		

2.2.2. Characterization of Membranes

Scanning Electron Microscopy

Morphological analysis of all the synthesized membranes was completed using HITACHI Model S-3400N (HITACHI, Maidenhead, UK). Membrane samples were snapped in liquid nitrogen and then gold sputtered before cross-sectional and top surface analysis at various magnifications.

Thermal Analysis

Thermal degradation analysis of the prepared membranes was performed using a STA-1600 PerkinElmer analyser (PerkinElmer, Buckinghamshire, UK). Membrane samples (20 g) were loaded into a pan and preheated above 120 °C to remove the moisture. After cooling, the samples were reheated at 10 °C/min from 25 °C to 500 °C in a nitrogenous environment.
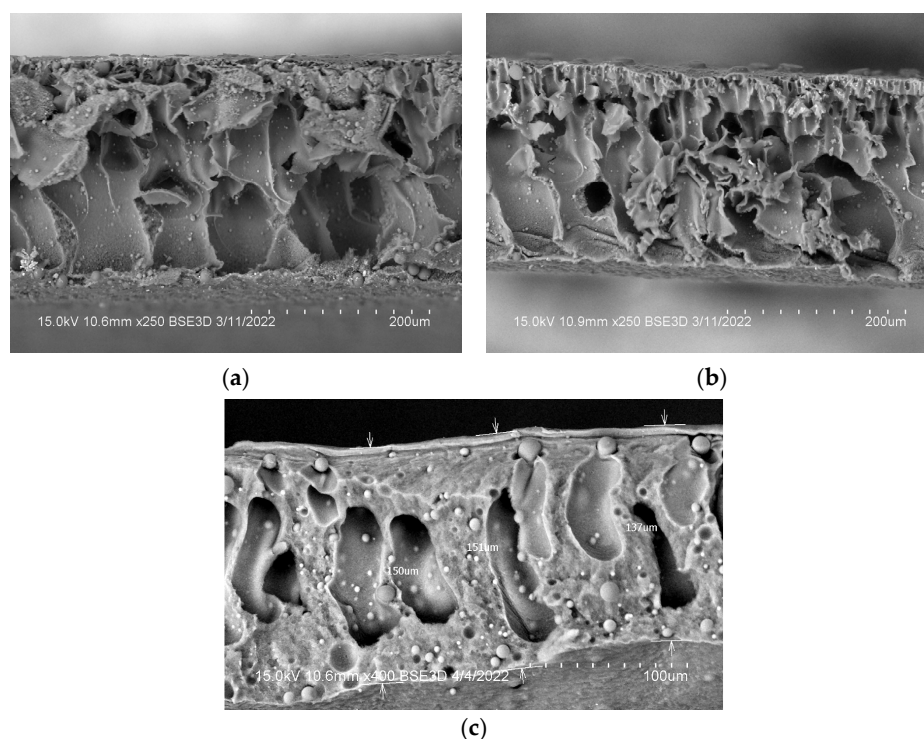
FTIR Analysis

A PerkinElmer spectrometer (Spectrum 100) was used in transmission mode for the analysis of blended membranes by scanning the samples for wavenumbers ranging from

400 cm^{-1} to 4000 cm^{-1}. Spectral analysis was employed to identify the changes in chemical bonds and functional groups in all synthesized membranes.

3. Results and Discussion

3.1. Morphological Analysis of Blended Membranes

Figure 1 illustrates the cross-sectional images of the blended membranes prepared using different mixing methods. From Figure 1, it can be clearly seen that all prepared membranes had distinct cross-sectional features. It can be clearly observed that during the air drying of the membranes, THF played its role and evaporated, resulting in a dense-like structure, and the subsequent exchange of NMP with non-solvent (water) controlled the voids and finger-like pores. Figure 1a shows that a dense but collapsed finger-like structure was prominent across the M1 membrane's cross-sectional area. However, it can be deduced that the morphology of the membrane was mainly controlled by THF evaporation during the drying phase of phase inversion, which was later overcome by the solvent–nonsolvent exchange mechanism in the coagulation bath. A similar structure can also be observed for the M2 membrane in Figure 1b; however, a clear dense and finger-like structure can be observed, probably due to the dissolution of the base polymer (i.e., CA) into THF first, which resulted in the development of a denser structure during the drying phase. Finally, a more compact and discrete structure was observed for the M3 membrane (Figure 1c), for which the dope solution was prepared by dissolving the polymers in a mixed solvent. Here, M3 showed a significantly dense top layer and notable macrovoids in its cross-section, which could be the result of delayed de-mixing during the solvent–nonsolvent exchange in a coagulation bath, as reported by [7,18]. This formation of macrovoids under dense skin could be attributed to the intrusion of non-solvent into the initial dense film because THF has a slower exchange rate with non-solvent than NMP [18]. The presence of these macrovoids in the substructure of the M3-type membrane reveals that the viscosity of the casting solution plays an important role during the phase inversion process. It could be speculated that the improved chain entanglement of polymers in mixed solvents resulted in a higher viscosity and promoted the formation of macrovoids in the substructure of the M3 membrane, as reported by many researchers [15,18,19].

(a)   (b)

(c)

Figure 1. Micrographs (cross-section) of blended membranes: (**a**) M1, (**b**) M2 and (**c**) M3.

3.2. FTIR Analysis of Blended Membranes

Figure 2 represents a spectral analysis of the synthesized blending membranes. Common CA peaks have been reported at 3500–3100, 2944, 2889, 1744, 1433, 1375–1288, 1044, 1161 and 902 cm^{-1}, which represent –OH, –CH, C=O stretching, CH deformation, –C–O stretching mode, C–O–C backbone and –CH stretching mode [20–22]. Similarly, for pure PSU, peaks have been identified at 688, 715, 832, 852 and 871 cm^{-1} for aromatic C–H vibrations, 1101 and 1148 cm^{-1} for O=S=O stretching, 1292 and 1321 cm^{-1} for asymmetric O=S=O stretching, 1011 and 1235 cm^{-1} for asymmetric C–O–C stretching vibrations, 1484 and 1582 cm^{-1} for C=C stretching and 1385 and 1504 cm^{-1} for CH_3–C–CH_3 stretching, and 1168 cm^{-1} showed etheric stretching vibration from the aromatic rings and oxygen atoms [5,23,24]. The analysis showed characteristics peaks at 904 cm^{-1}, 1036 cm^{-1}, 1227 cm^{-1}, 1369 cm^{-1}, 1644 cm^{-1}, 1734 cm^{-1}, 2935 cm^{-1} and 3400 cm^{-1}. These peaks were consistent across all three types of membranes prepared using the different mixing sequences. However, a significant change was noted, particularly at 3400 cm^{-1}. From this spectral analysis, it can be concluded that the peak at 904 cm^{-1} was due to the β link. Meanwhile, the peaks at 1036 cm^{-1}, 1227 cm^{-1} and 1369 cm^{-1}, 1644 cm^{-1}, 1734 cm^{-1} and 2935 cm^{-1} corresponded to the skeletal movement of the C–O bond, C–C–O bonds, C=O stretching, CH_3 symmetric vibration and the presence of–OH bonds in the blended membranes, respectively. Interestingly, the disappearance of hydroxyl ions (–OH) was prominent for M3-blended membranes which were synthesized by mixing the polymers into a mixed solvent. Nevertheless, in the M1-blended membrane where NMP and cellulose acetate polymer were mixed first, the presence of higher –OH ions was distinct because NMP as a solvent tends to promote hydrogen bonding between the –OH groups of the polymers [15]. Interestingly, the spectra of all the blended membranes confirmed the fact that interaction between these two polymers was of a physical nature only, and no apparent chemical interaction was found, which affirms the influence of the solvent's role on the chemical nature of the prepared membranes. Similar results have been reported by I. Douna et al. for CA/PSU blended membranes, where it was concluded that the nature of blended polymers was purely physical [7].
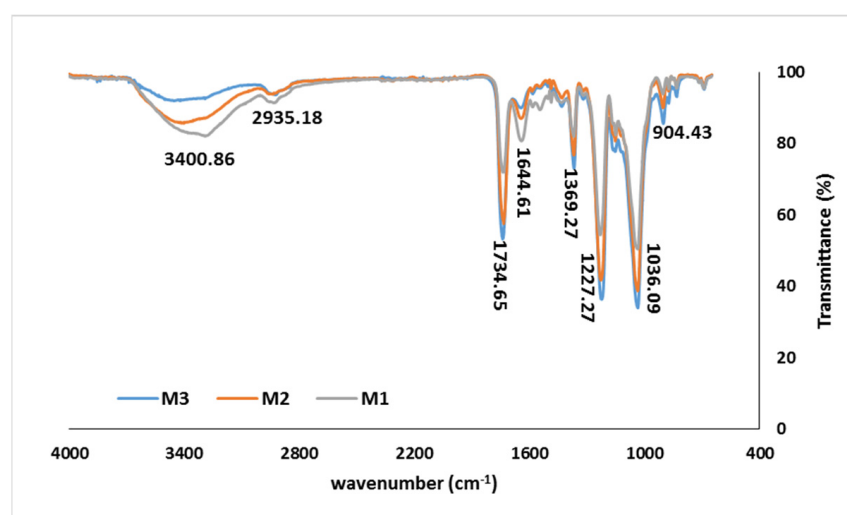
Figure 2. FTIR spectra of blended membranes.

3.3. Thermogravimetric Analysis of Blended Membranes

Figure 3 highlights the thermal degradation and stability of the three blended membranes prepared with varying mixing sequences. The absence of moisture content was confirmed because there was no weight loss at or around 100 °C among all membranes. Similarly, the presence of residual solvent was investigated by observing the weight loss around 66 °C (boiling point of THF) and 202 °C (boiling point of NMP) for THF and NMP,

respectively. These observations confirmed that no significant amounts of moisture or residual solvents were present in the synthesized membranes, except for the M1 membrane, for which a slight dip (up to 3%) in weight percentage around 200 °C could be attributed to the presence of the solvent (NMP). Moreover, it can be observed that the M3 membrane showed higher thermal stability than M1 and M2. It was found that for M3, M2 and M1 residual weights were 25%, 18% and 19%, respectively, proving that M3 was more thermally stable among all of them. This fact could also be confirmed by the analysis of the thermal degradation behaviour of these membranes, where M3 again showed an increased degradation temperature of up to 10 °C in comparison to M1 and M2. Finally, thermogravimetric analysis confirmed the complete removal of the solvent from these membranes, the presence of which could inflict adverse effects on the mechanical stability of the membranes. In addition, the presence of residual solvent in the membranes hampered their permeability by occupying or blocking the sorption sites and reducing the free volume of the respective polymers [25,26].
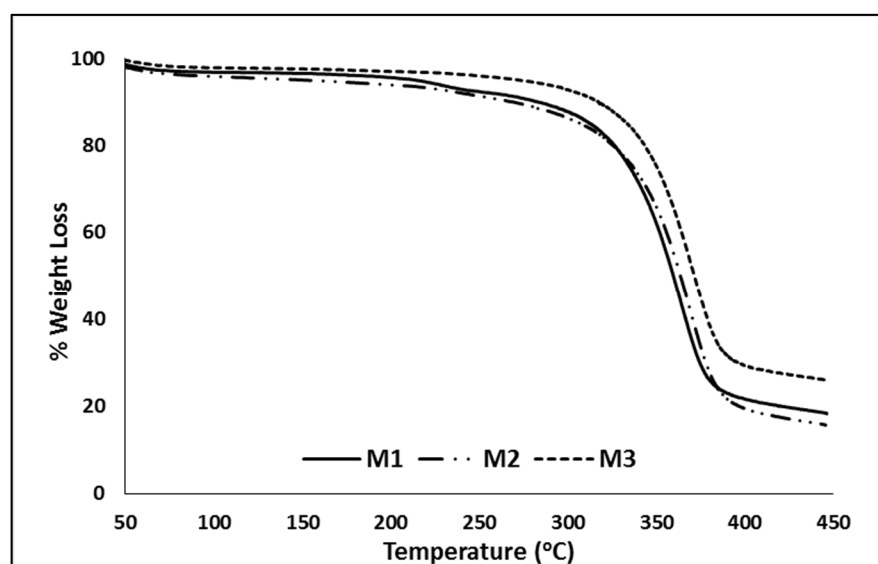

Figure 3. Thermogravimetric analysis of blended membranes.

4. Conclusions

Polysulfone-modified cellulose-acetate-blended membranes were prepared through a dry–wet phase inversion technique using varying mixing sequences to investigate the effect of the mixing sequence on the characteristics of the resultant membranes. The morphological analysis of these membranes confirmed that the mixing sequence/method used to prepare the casting solution eventually influenced the substructure of the membranes because the membrane structure transitioned from finger-like pores (for M1 and M2) to a dense substructure in the presence of macrovoids (M3). Similar observations were made upon thermal analysis of these membranes, which demonstrated that M3-type membranes showed not only a higher thermal stability, but also an onset degradation temperature 10 °C higher than that of their counterparts (M1 and M2). Finally, it can be concluded from the spectral analysis that the blending of cellulose acetate and polysulfone was physical in nature and the only noticeable difference was the presence of hydroxyl ions in the subsequent membranes. Hence, it can be asserted that the characteristics of the membranes can be tuned and manipulated to achieve certain desirable features by modifying the mixing/blending methods for the preparation of casting/doping solutions. The prospective application of this modification technique can certainly improve the performance of membranes for wider targeted applications.

References

1. Kadirkhan, F.; Goh, P.S.; Ismail, A.F.; Wan Mustapa, W.N.F.; Halim, M.H.M.; Soh, W.K.; Yeo, S.Y. Recent advances of polymeric membranes in tackling plasticization and aging for practical industrial CO_2/CH_4 applications—A review. *Membranes* **2022**, *12*, 71. [CrossRef] [PubMed]

2. Vatanpour, V.; Pasaoglu, M.E.; Barzegar, H.; Teber, O.O.; Kaya, R.; Bastug, M.; Khataee, A.; Koyuncu, I. Cellulose acetate in fabrication of polymeric membranes: A review. *Chemosphere* **2022**, *295*, 133914. [CrossRef] [PubMed]

3. Mubashir, M.; Yeong, Y.F.; Lau, K.K.; Chew, T.L.; Norwahyu, J. Efficient CO_2/N_2 and CO_2/CH_4 separation using NH_2-MIL-53 (Al)/cellulose acetate (CA) mixed matrix membranes. *Sep. Purif. Technol.* **2018**, *199*, 140–151. [CrossRef]

4. Raza, A.; Farrukh, S.; Hussain, A.; Khan, I.; Othman, M.H.D.; Ahsan, M. Performance Analysis of Blended Membranes of Cellulose Acetate with Variable Degree of Acetylation for CO_2/CH_4 Separation. *Membranes* **2021**, *11*, 245. [CrossRef] [PubMed]

5. Singh, S.; Varghese, A.M.; Reddy, K.S.K.; Romanos, G.E.; Karanikolos, G.N. Polysulfone Mixed-Matrix Membranes Comprising Poly(ethylene glycol)-Grafted Carbon Nanotubes: Mechanical Properties and CO_2 Separation Performance. *Ind. Eng. Chem. Res.* **2021**, *60*, 11289–11308. [CrossRef]

6. Karimi, S.; Firouzfar, E.; Khoshchehreh, M.R. Assessment of gas separation properties and CO_2 plasticization of polysulfone/polyethylene glycol membranes. *J. Pet. Sci. Eng.* **2019**, *173*, 13–19. [CrossRef]

7. Douna, I.; Farrukh, S.; Hussain, A.; Salahuddin, Z.; Noor, T.; Pervaiz, E.; Younas, M.; Fan, X.F. Experimental investigation of polysulfone modified cellulose acetate membrane for CO_2/H_2 gas separation. *Korean J. Chem. Eng.* **2022**, *39*, 189–197. [CrossRef]

8. Jami'an, W.N.R.; Hasbullah, H.; Mohamed, F.; Yusof, N.; Ibrahim, N.; Ali, R.R. Effect of evaporation time on cellulose acetate membrane for gas separation. *IOP Conf. Ser. Earth Environ. Sci.* **2016**, *36*, 012008. [CrossRef]

9. Moghadassi, A.R.; Rajabi, Z.; Hosseini, S.M.; Mohammadi, M. Fabrication and modification of cellulose acetate based mixed matrix membrane: Gas separation and physical properties. *J. Ind. Eng. Chem.* **2014**, *20*, 1050–1060. [CrossRef]

10. Kim, W.-g.; Lee, J.S.; Bucknall, D.G.; Koros, W.J.; Nair, S. Nanoporous layered silicate AMH-3/cellulose acetate nanocomposite membranes for gas separations. *J. Membr. Sci.* **2013**, *441*, 129–136. [CrossRef]

11. Ali, M.; Zafar, M.; Jamil, T.; Butt, M.T.Z. Influence of glycol additives on the structure and performance of cellulose acetate/zinc oxide blend membranes. *Desalination* **2011**, *270*, 98–104. [CrossRef]

12. Ahmad, A.L.; Jawad, Z.A.; Low, S.C.; Zein, S.H.S. A cellulose acetate/multi-walled carbon nanotube mixed matrix membrane for CO_2/N_2 separation. *J. Membr. Sci.* **2014**, *451*, 55–66. [CrossRef]

13. Lam, B.; Wei, M.; Zhu, L.; Luo, S.; Guo, R.; Morisato, A.; Alexandridis, P.; Lin, H. Cellulose triacetate doped with ionic liquids for membrane gas separation. *Polymer* **2016**, *89*, 1–11. [CrossRef]

14. Miller-Chou, B.A.; Koenig, J.L. A review of polymer dissolution. *Prog. Polym. Sci.* **2003**, *28*, 1223–1270. [CrossRef]

15. Kluge, S.; Kose, T.; Tutuş, M. Tuning the Morphology and Gas Separation Properties of Polysulfone Membranes. *Membranes* **2022**, *12*, 654. [CrossRef]

16. Mubashir, M.; Fong, Y.; Leng, C.; Keong, L. Enhanced gases separation of cellulose acetate membrane using N-methyl-1-2 pyrrolidone as fabrication solvent. *Int. J. Automot. Mech. Eng.* **2018**, *15*, 4978–4986. [CrossRef]

17. Li, Z.; Ren, J.; Fane, A.G.; Li, D.F.; Wong, F.-S. Influence of solvent on the structure and performance of cellulose acetate membranes. *J. Membr. Sci.* **2006**, *279*, 601–607. [CrossRef]

18. Shieh, J.-J.; Chung, T.S. Effect of liquid-liquid demixing on the membrane morphology, gas permeation, thermal and mechanical properties of cellulose acetate hollow fibers. *J. Membr. Sci.* **1998**, *140*, 67–79. [CrossRef]

19. Shiva Prasad, N.; Babarao, R.; Madapusi, S.; Sridhar, S.; Choudhury, N.R.; Bhargava, S.K. Residual solvent induced physical morphology and gas permeation in polyamide-imide membrane: Experimental investigation and molecular simulations. *Eur. Polym. J.* **2022**, *165*, 111012. [CrossRef]

20. Ioniță, M.; Cricǎ, L.E.; Voicu, S.I.; Dinescu, S.; Miculescu, F.; Costache, M.; Iovu, H. Synergistic effect of carbon nanotubes and graphene for high performance cellulose acetate membranes in biomedical applications. *Carbohydr. Polym.* **2018**, *183*, 50–61. [CrossRef]

21. Dumitriu, C.; Voicu, S.I.; Muhulet, A.; Nechifor, G.; Popescu, S.; Ungureanu, C.; Carja, A.; Miculescu, F.; Trusca, R.; Pirvu, C. Production and characterization of cellulose acetate—Titanium dioxide nanotubes membrane fraxiparinized through polydopamine for clinical applications. *Carbohydr. Polym.* **2018**, *181*, 215–223. [CrossRef] [PubMed]

22. Corobea, M.C.; Muhulet, O.; Miculescu, F.; Antoniac, I.V.; Vuluga, Z.; Florea, D.; Vuluga, D.M.; Butnaru, M.; Ivanov, D.; Voicu, S.I. Novel nanocomposite membranes from cellulose acetate and clay-silica nanowires. *Polym. Adv. Technol.* **2016**, *27*, 1586–1595. [CrossRef]

23. Badrinezhad, L.; Ghasemi, S.; Azizian-Kalandaragh, Y.; Nematollahzadeh, A. Preparation and characterization of polysulfone/graphene oxide nanocomposite membranes for the separation of methylene blue from water. *Polym. Bull.* **2018**, *75*, 469–484. [CrossRef]

24. Saxena, M.; Sharma, S.; Bhattacharya, A. Recycling of polysulfone: Study properties of membranes. *Int. J. Membr. Sci. Technol.* **2015**, *2*, 39–46.

25. Lee, T.H.; Lee, B.K.; Park, J.S.; Park, J.; Kang, J.H.; Yoo, S.Y.; Park, I.; Kim, Y.-H.; Park, H.B. Surface Modification of Matrimid®; 5218 Polyimide Membrane with Fluorine-Containing Diamines for Efficient Gas Separation. *Membranes* **2022**, *12*, 256. [CrossRef] [PubMed]

26. Idris, A.; Man, Z.; Maulud, A.S.; Khan, M.S. Effects of phase separation behavior on morphology and performance of polycarbonate membranes. *Membranes* **2017**, *7*, 21. [CrossRef]