Materials Technology Reports 2023; 1(1): 103.
Review Article

A brief review on systematic approach to polymer selection for development of capillary/hollow-fibre membrane for practical applications

Vijay Suresh Mamtani[1,2], **Asim Kumar Ghosh**[1,2,*], **Asis Kumar Adak**[2]

[1] *Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India*

[2] *Desalination & Membrane Technology Division, Bhabha Atomic Research Centre, Mumbai 400085, India*

*** Corresponding author:** Asim Kumar Ghosh, akghosh@barc.gov.in

ARTICLE INFO

Received: 29 June 2023
Accepted: 25 July 2023
Available online: 20 October 2023

doi: 10.59400/mtr.v1i1.103

ABSTRACT: Polymeric membranes are widely used for treatment of lean stream in chemical process industries. These membranes are used in different configurations such as tubular, plate & frame, disc-tube, spiral and capillary/hollow-fibre. Membrane modules with capillary/hollow-fibre configuration appears promising in ultrafiltration applications due to its relatively higher packing density, ease of backwashing, ease of cleaning and lower pressure drops since it can be operated at laminar flow regime with high cross-flow velocity. Hence, efforts are being made by researchers to make capillary/hollow-fibre membrane modules from various polymers, ranging from most hydrophilic polyacrylonitrile (PAN) to super-hydrophobic polypropylene (PP) and polytetrafluorethylene (PTFE). Here, we discuss the qualifying properties of the polymeric materials suitable to spin into capillary/hollow-fibre ultrafiltration membranes. Selection of polymers for making fibres requires in-depth knowledge of properties of base polymer and its processability/fabricability. The important properties to be considered for making capillary/hollow-fibre membrane are intrinsic structural properties of the base polymer like degree of crystallinity, tensile strength, tensile modulus, etc. The functional properties such as permeability, hydrophilicity/hydrophobicity etc. also plays role in selecting polymer for a given application. The polymer should also have appreciable dissolution in available solvents or should have degradation temperature higher than melting point so that it can be processed through appropriate membrane preparation process.

KEYWORDS: polymers; membranes; capillary; hollow-fibre; ultrafiltration

1. Introduction

A membrane is a physical barrier that allows preferential transport of one or more specie over other, thus causing separation. The main advantages of membrane separation systems are its compact size, no additives requirement, ambient temperature operation, low specific power consumption, etc. In addition, owing to its modular nature, it can be easily scaled up and scaled down, as well as it can be easily integrated with other separation or reaction processes[1]. The polymeric membranes are widely deployed in industrial applications such as water treatment, gas separation, pretreatment of seawater, desalination using reverse osmosis membrane, fruit juice concentration using forward osmosis membrane and in separations process of the dairy, paper, textile industries, etc.[2]. It can be used in different module configurations such as tubular, plate and frame, disc tube, spiral and capillary/hollow-fibre. The capillary/hollow-fibre module configuration has the highest packing density and thus offer more contact area per unit volume for the separation. Other advantages of capillary module are ease of backwashing and cleaning, operation in laminar flow regime to give lower pressure drop with high cross-sectional velocity.

The capillary/hollow-fibre membranes are cylindrical supportless membrane with diameter in the range of 0.5 mm to 5 mm[3]. As these are supportless membrane, it requires good mechanical strength so as to deploy in the pressurised environment when compared to the supported membranes used in other membrane module configurations. The mechanical properties of the capillary/hollow-fibre membrane depend on the mechanical properties of the polymer from which it is prepared. Polymer selection is therefore one of the important criteria for preparation of the membrane. Intrinsic structural properties of base polymer help in imparting mechanical strength to the final capillary membrane. These properties are degree of crystallinity, tensile strength, tensile modulus, etc. Polymer should also be processable i.e., it should be easily soluble in common solvents or melt before degradation. It should be chemically stable with the process fluids, that is, it should withstand operating pH condition and should not undergo degradation or oxidation. It should be thermally stable and work without degrading at required temperature condition. In addition, hydrophilicity, adsorption characteristics to avoid fouling, biocompatibility plays crucial role depending on the field of application. Systematic approach to polymer selection for development of capillary/hollow-fibre membrane for practical applications is not available in the literature.

Several polymers namely, polysulfone (PSf)[4,5], polyethersulfone (PES)[6,7], polyethylene (PE)[8,9], polyvinylchloride (PVC)[10,11], polyvinylidene difluoride (PVDF)[12,13], polypropylene (PP)[14,15], and polyacrylonitrile (PAN)[16] are presently used for making capillary/hollow-fibre membranes. Different processes viz. Non-Solvent Induced Phase Separation (NIPS), Vapour Induced Phase Separation (NIPS), Thermal Induced Phase Separation (TIPS), etc. are used for making capillary/hollow-fibre membranes.

2. Prerequisites of polymer to form a capillary/hollow-fibre membrane

Selection of the proper polymer is the first step of development of any useful membrane. A polymer should have membrane forming properties and fibre forming properties so that it can be used to make capillary/hollow-fibre membrane. In addition, also it is important to understand the polymer properties that can affect the membrane characteristics and performances. **Figure 1** gives the summary of the criteria for polymer selection to prepare capillary/hollow-fibre membranes.

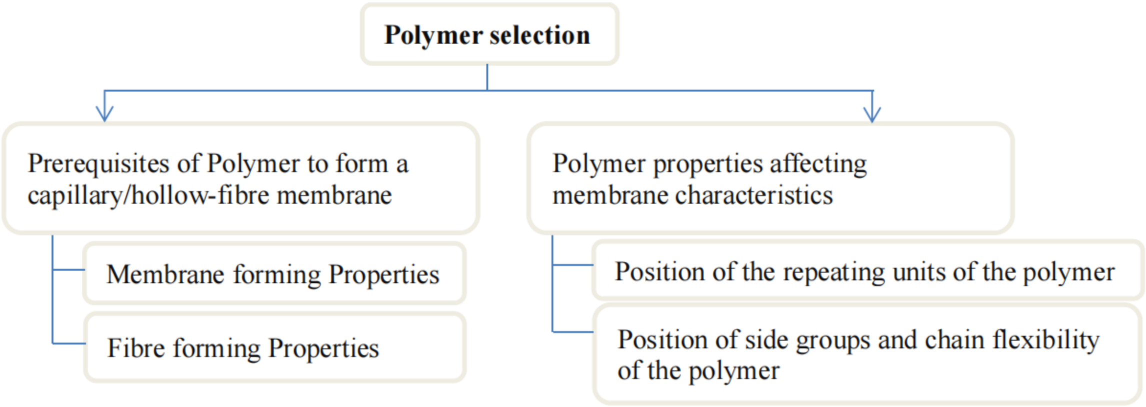


Figure 1. Criteria for polymer selection to prepare capillary/hollow-fibre membranes.

2.1. Membrane forming properties

Polymer forms a membrane film and one of the physical properties of the film formed is its mechanical strength to withstand the operating pressure. This is especially required for support-less capillary/hollow-fibre membranes. Also, the polymer chosen must be compatible and have desired properties required for the application where membrane, prepared from such polymer, is deployed. This restricts the selection of the polymer for preparing a membrane. The capillary/hollow-fibre membrane can be open porous membrane, primarily used in Ultrafiltration (UF) and Microfiltration (MF) or non-porous membranes which find application in pervaporation and gas separation[3]. For the porous membrane, the pore size of the membrane determines membrane performance. The polymer material is selected based on membrane manufacturing requirement, its mechanical strength, fouling tendency, chemical inertness, and thermal stability required in the final membrane. The selection of polymer material is not determined by separation characteristics of the membrane as the separation characteristics are tuned by the process parameters by which membranes are prepared. For example, porous membranes that are prepared by non-solvent induced phase separation (NIPS) method whose separation property is determined by the choice of solvent/nonsolvent, the rate of phase separation, presence of additives, etc.[3].

2.2. Fibre forming properties

Capillary/hollow-fibre membranes can be made from polymers having the fibre forming properties. Fibres are built up by crystallites and less ordered or amorphous regions of the polymer. The crystallites are oriented in such a manner that the molecules from which they are built are parallel with the fibre axis[17]. This orientation can also be imparted during and after the spinning of the capillary/hollow-fibre membrane. The crystallites can be regarded as the high softening reinforcing filler for the disordered regions of the drawn fibres[18]. The entropy factor presents in the macromolecules of the polymer favours return to maximum randomness, however, in the case of fibres, the forces opposing retraction are greater which causes the macromolecules to remain in the extended form which otherwise would have retracted, as in case for rubbers[18].

The polymer crystallinity determines the physical and mechanical characteristics of a fibre which is turn depends on the chemical structure of the polymer and on the manner in which the fibre is built up from the polymer[17]. The chemical structure greatly influences the intermolecular forces. Hydrogen bonding systems, strong polar groups, readily ionisable segments are responsible for inter chain attraction to further increase the crystallinity[18]. Branched-chain in the polymer may result in reducing the packing efficiency, thus reducing crystallinity and departing from fibre properties. Molecular weight also influences the properties of the final fibre formed. The molecular weight of the polymer is usually characterised in terms of intrinsic viscosity (η). Value of η should be 0.5 for most of condensation polymers for achieving fibre forming properties[17]. It should be even higher for better physical properties. Crystalline melting point is another important factor in the fibre forming properties and can be considered as a measure of the stability. Higher crystalline polymer shows higher crystalline melting point[17]. However, it may be noted that higher crystallinity of polymer will lead to difficulties in converting the polymer satisfactorily into the fibre as it may not be easily soluble in solvents for wet spinning and will require higher temperature for melt spinning. Hence, an optimum crystallinity is required for preparation of membranes with desired separation characteristics.

3. Polymer properties affecting membrane characteristics

A brief review of polymer properties affecting the characteristics of the membrane is mentioned in this section.

3.1. Position of the repeating units of the polymer

A polymer with the same repeating units is said to be a homopolymer, whereas a polymer with different repeating unit is said to be a copolymer. However, a copolymer is considered random if it has sequence of the irregular structural units. Due to the fact that many synthetic rubbers are random copolymers, they cannot be used to prepare capillary or hollow fibres. In a block copolymer, each monomer blocks are linked together to form the chain. The free volume and thus the permeability of produced membranes will increase if the main chain is rigid and the side chains are bulky. Crosslinking of chains of polymers causes reduced solubility of the polymer. Additionally, melt casting will be challenging since it will be more difficult to slide one chain over another, resulting in mobility reduction during membrane preparation as compared to linear chain polymers. Increase in free volume brought on by chain length result in increased permeability. Linearity tends to increase close packing in the polymer material and hence tend to increase the crystallinity. The increase in close packing increases the density. Thus, higher chain length suggests higher density of the polymer and higher crystallinity[19]. The polymer's molecular weight may be used to express the chain length pretty well. Because polymers contain several chains of various lengths, their molecular weight is not uniform. The molecular weight of the polymer is expressed using the number average molecular weight (Mn) and the weight average molecular weight (Mw). The polymer's molecular weight distribution is given by its polydispersity index (PDI), which is Mw/Mn[3]. The optimum molecular weight with narrow molecular weight distribution is desired for preparation of capillary/hollow-fibre membranes with desired properties.

3.2. Position of side groups and chain flexibility of the polymer

The polymers viz. PVDF, PP, PVC, PE, PAN are basically vinyl polymers having chemical formula [$–CH_2–CRR'–$] repeat units with side group −R and −R' being different for different polymers as shown in **Table 1**. The position of the side group R and R' plays an important role in polymer properties. Based on the arrangement on the side group, the polymer can be classified as isotactic, atactic, syndiotactic[3]. Isotactic arrangement in a polymer is a configuration in which the main chain and the side groups are in the same side, which leads to the formation of crystalline polymers. Isotactic arrangement in a polymer is desired for making capillary fibre. In atactic arrangement in a polymer, random arrangements of side groups are present along the main chain and thus it is non-crystalline in nature. In case of syndiotactic polymer, the configuration is such that main chain and side groups are on the alternate side[3]. This kind of arrangement also gives rise to crystallinity in the polymer, making it suitable to be used in capillary fibre making. However, it must be noted that higher crystallinity reduces permeability in the membrane[20].

Table 1. Vinyl polymers with different side groups.

Polymer	**–R**	**–R'**
PE	–H	–H
PVC	–Cl	–H
PVDF	–F	–F
PP	$–CH_3$	–H
PAN	–CN	–H

The chain flexibility is one of the important characteristics of polymer which affects the membrane mechanical property. Character of main chain and the side chain, if present, decides chain flexibility and thus the membrane mechanical property. Flexibility in the polymer is attained because of oscillation of atoms about its equilibrium position and because of rotation of certain parts of molecules with respect to each other. The rotation is possible in single covalent bond[21] present in the polymer. Additionally, side groups affect whether rotation around the main chain is easily achievable or difficult due to steric hindrance. Presence of aromatic or heterocyclic groups in the main chain reduces the flexibility but increase chemical and thermal stability[3] as in case of polysulfone and polyethersulfone. Higher flexibility in polymer will impart higher impact strength of the membrane but tensile strength will be lower as compared to the membrane obtained from rigid polymer[19]. The chain interaction and flexibility in the polymer determines its glass transition temperature (Tg). It is the temperature at which the polymer changes its state of amorphous polymer changes glassy to rubbery state. In glassy state, the polymer has high tensile modulus (E) whereas in the rubbery state the polymer has three to four order lower tensile modulus[3]. The polymer chain has restricted motion in glassy state and increase in temperature cause increase in motion and hardly any change in the specific volume of polymer. However, after Tg, the polymer gets converted into rubbery state in which the segments of polymer chain can rotate freely and there is increase in free and specific volume of the polymer, increasing the polymer permeability. Glassy polymers are preferred for capillary/hollow-fibre membrane preparation and most of the time the polymer casting solutions are prepared at higher temperature.

4. Common polymers used for capillary/hollow-fibre membrane preparation: Properties, preparation methods & applications

A list of polymers with their properties/characteristics used for development of useful membranes are given in **Tables 2** and **3** based on several literature search. A summary of the solvents used for dissolution of selected polymer to cast membranes and the methods used for their preparation are given in **Figures 2** and **3** respectively. Schematics of common fibre preparation techniques like nonsolvent-induced phase separation (NIPS) and melt spinning-cold stretching method (MSCS) are given in **Figure 4**.

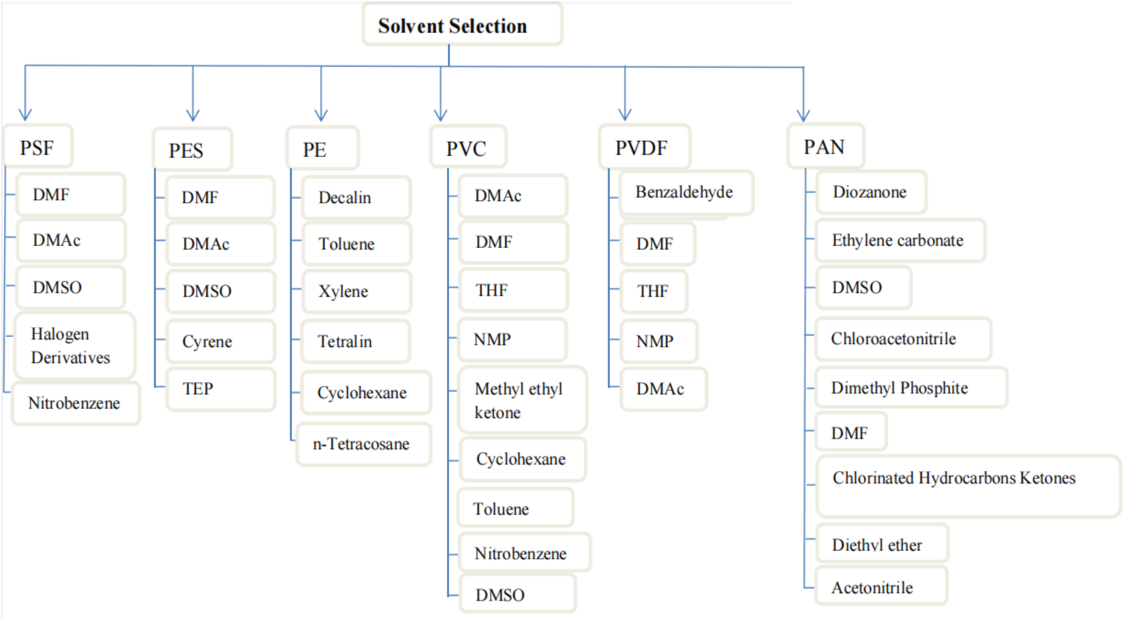


Figure 2. Solvents used for dissolution of selected polymer to prepare casting solution.

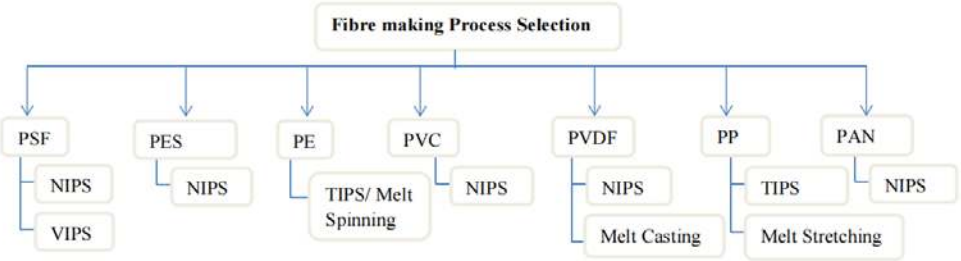
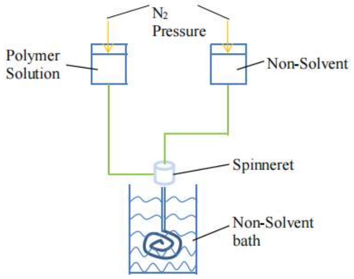
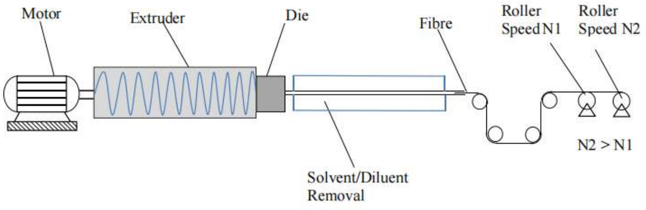


Figure 3. Summary of the methods used for preparation of membranes from selected polymers.



(a) Nonsolvent-induced phase separation (NIPS)



(b) Melt spinning-cold stretching method (MSCS)

Figure 4. Schematic of **(a)** nonsolvent-induced phase separation (NIPS) and **(b)** melt spinning-cold stretching (MSCS) techniques for fibre preparation.

Table 2. Properties/characteristics of PSf, PES, PVC, PVDF & PAN polymers used to make porous membranes.

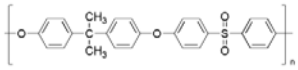
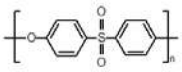
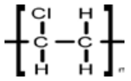
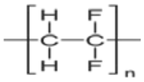
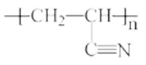
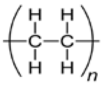
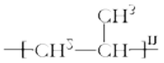
Polymer property	**PSf**	**PES**	**PVC**	**PVDF**	**PAN**
Structure					 $-\!\!\!+\!CH_2-\underset{\underset{C\equiv N}{\vert}}{CH}\!+\!\!\!-_n$
Molecular weight	17,600–58,000	26,000–49,000	43,000–126,000	300,000–700,000	70,000–400,000
Density, g/cm^3	1.24	1.37	1.388	1.675	1.184
Solubility parameter, (MPa)$^{1/2}$	23.7	23.12	19.6	19.2	26.2
Water absorption, (24 h), %	0.2–0.8	0.1–1.7	0.2–1	0.03–0.05	0.3
Tensile strength, MPa	69	82.8	55.5	43	35
Tensile modulus, MPa	2600	2777	276–75,884	1194	350
Thermal expansion coefficient, 10^{-5} K^{-1}	21	5.5	47–62	7–15	6–7
Glass transition temperature Tg, K	459	498	344	239	382
Melting point Tm, K	458–468	493–503	473–573	443–473	593

Table 3. Properties/characteristics of PE & PP polymers used to make porous membranes.

Polymer property	**PE**					**PP**			
	LHDE	LLDE	LDE	MLLDE	Elastomeric	Syndiotactic	Atactic	Elastomeric	Isotactic
Structure									
Molecular weight	1000–8,000,000	50,000–200,000	30,000–40,000	40,000–110,000	-	127,000–290,000	-	-	12,000–585,000
Density, g/cm^3	0.92–0.99	0.912–0.930	0910–0935	-	-	0.91–0.989	0.855	0.868–0.8787	0.85–0.946
Degree of Crystallinity, %	35–90	33–53	33–53	33–53	9–21	21–29	Some/none	9–27	50–70
Solubility parameter, (MPa)$^{1/2}$	16.7	16.7	16.7	16.7	16.7	16.2	16.2	16.2	16.2
Water absorption (24 h), %	0.005–0.01	0.005–0.01	0.005–0.01	0.005–0.01	0.005–0.01	0.01	0.01	0.01	0.01
Tensile strength, MPa	10–60	9–20	9–15	30–48	-	10.85	1–2	3.2–39	23–36
Tensile modulus, MPa	60–290	137–520	102–310	4–700	1.5–12.5	483	-	23–359	482.6
Glass transition Temp. Tg, K	140–155	~193	140–170	~193	221–244	~263	260	265	275.5–283.7
Melting temp. Tm, K	391–419	378–383 & 394–398	378–388	363–398	322–349	398–421	6.1×10^{-3}–9.3×10^{-3}	316.5–433	452

4.1. Polysulfone (PSf)

Polysulfone is a thermoplastic and slightly hydrophilic polymer [water absorption (24 h) <0.3%][22]. It has excellent properties such as good solubility in a wide range of aprotic polar solvents like dimethylformamide (DMF), dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), nitrobenzene etc. It has good mechanical stability of the films (tensile strength: 69 MPa, tensile modulus: 2482 MPa), good stability in oxidative environment (hydrogen peroxide 3%–5%, hypochlorite 5%–7%), good chemical stability, high thermal resistance property with glass transition temperature 'Tg' = 459 K[22] and moderate reactivity in aromatic electrophilic substitutions reactions (sulfonation, nitration, chloromethylation, acylation, etc.[23]. The aromatic ring in the chain of polysulfone gives rigidity to the polymer chain which is reflected in its higher tensile strength. PSf also has high impact strength (80.4 J/m)[22], indicating higher flexibility, and has high tensile modulus. The mechanical properties of PSf make it more resistant to fibre breakage/bursting. As a result, it can withstand higher operating pressure condition. The glass transition temperature 'Tg' is also high owing to presence of aromatic group. The operating temperature can be kept higher because of higher Tg value. However, the thermal expansion coefficient (2.1×10^{-4} K^{-1}[22]) of the PSf is relatively higher. This may decide the operating temperature while using the polymer in capillary/hollow-fibre membrane configuration. Polysulfone membrane can be prepared in fibre form both by non-solvent-induced phase separation (NIPS)[4] & vapor induced phase separation (VIPS)[5].

Common applications of PSf capillary/hollow-fibre ultrafiltration membranes are in pretreatment of seawater desalination, waste water recovery, food and beverage processing, support for thin-film composite membrane preparation etc.[24].

4.2. Polyethersulfone (PES)

Polyethersulfone is a thermoplastic polymer and is relatively more hydrophilic as compared to PSf polymer [water absorption (24 h): 0.43%[22]]. It is widely used as a membrane material for liquid and gas[6] separation processes. The polymer has aromatic ring in its chain giving rigidity to the polymer chain and it is reflected in its mechanical properties. PES polymer is soluble in N, N-dimethylformamide (DMF), N, N-dimethyl acetamide (DMAc), 1-methyl-2-pyrrolidinone (NMP), and dimethyl sulfoxide (DMSO) and also in some of the "green solvents" like Dihydrolevoglucosenone (Cyrene), triethyl phosphate etc. The mechanical properties of PES are better than PSf polymer. It has high very high tensile strength (82.8 MPa), higher tensile modulus (2482 MPa)[22], higher impact strength (85.7 J/m[22]) which will increase its ability to withstand higher operating pressure condition. The glass transition temperature (498 K) is also high due to the presence of aromatic group. It also has lower linear thermal expansion coefficient (5.5×10^{-5} K^{-1}[22]). Thus, operating at higher temperature is possible with PES capillary membrane as compared to PSf membrane. The solubility parameter of PES is 23.12 $(MPa)^{1/2}$[22] and hence it can be processed with more ease than PSf.

Polyethersulfone membrane are being prepared in fibre form by non-solvent-induced phase separation (NIPS)[6,7]. Common applications of PES capillary/hollow-fibre ultrafiltration membranes are in pretreatment of seawater desalination, hemodialysis, biomedical applications, food and beverage processing, support for thin-film composite membrane preparation etc.

4.3. Polyethylene (PE)

Polyethylene is a hydrophobic polymer (water absorption (24 h) <0.02%) and has an advantage of being cost effective polymer, flexible and tough. It offers high impact strength and chemical resistance to acids and aqueous solvents[22]. Polyethylene can be classified based on density and branching as elastomeric/linear high-density (LHD)/linear low-density (LLD)/low-density (LD)/metallocene linear low-density (MLLD). Elastomeric PE is highly branched[22]. It has low packing density and poor tensile modulus (1.5–12.5 MPa). The degree of crystallinity (9%–21%) is also low for elastomeric PE. It has low melting point (322–349 K) and thus cannot be operated at higher temperatures. Hence, it should not be preferred for making capillary/ hollow-fibre membrane. LHD PE has large range of molecular weight (1×10^3–8×10^6 g/mol) and large range of PDI (1.07– > 10^7). It has density of 0.92–0.99 g/cm^3 and has lower melting temperature (391–419 K) restricting its operational temperature range. The degree of crystallinity (35%–90%) is very high indicating very good fibre forming properties. However, the processing of the polymer is difficult. It is soluble only above 353 K in hydrocarbons such as, aromatics, ketones, halogenated hydrocarbons, higher aliphatic esters, di-n-amyl ether, etc. It shows moderate mechanical properties with average tensile modulus (60–290 MPa), average tensile strength (10–60 MPa) and excellent impact strength (30–200 J/m). LLD PE has molecular weight range of 5×10^4–20×10^4 g/mol and narrow range of PDI (4–35). It has density of 0.912–0.930 g/cm^3. It has lower melting temperature (378–398 K) restricting temperature range of operation. The degree of crystallinity (33%–

53%) is very good for forming fibre. The processing of the polymer is difficult. It is soluble in decalin, toluene at 368 K, xylene at 369 K, tetralin at 371 K, cyclohexene at 341 K, n-tetracosane at 374 K. It shows moderate mechanical properties with good tensile modulus (137–520 MPa), average tensile strength (9–20 MPa) and very good impact strength (53.0 J/m)[22].

Low density PE has molecular weight range of 3 × 10^4–40 × 10^4 g/mol and narrow range of PDI (4–30). It has density of 0.910–0.935 g/cm^3 and lower melting temperature (378–388 K) and thus restricting temperature range of operation. The degree of crystallinity (33%–53%) is very good for forming fibre. The processing of the polymer is difficult. It is soluble in decalin, toluene at 368 K, xylene at 369 K, tetralin at 371 K, cyclohexene at 341 K, n-tetracosane at 374 K[22]. It shows moderate mechanical properties with average tensile modulus (102–310 MPa) and average tensile strength (9–20 MPa). MLD PE has molecular weight range of 4 × 10^4–11× 10^4 g/mol and narrow range of PDI (2–2.5). It has density of 0.910–0.935 g/cm^3 and has lower melting temperature (363–398 K), thus restricting temperature range of operation. The degree of crystallinity (33%–53%) is very good for forming fibre. It shows moderate mechanical properties with average tensile modulus (4–700 MPa), average tensile strength (30–48 MPa) and excellent impact strength (2500 J/m)[22].

As solubility of LHDPE, LLDPE and LDPE is only at higher temperature near to their melting point, hence melt spinning (melt-extrusion/cold-stretching methods) should be preferred to avoid any involvement of solvent or additive. LHDPE and LDPE can be used together or separately to make PE membrane in fibre form by melt spinning process or thermally induced phase separation (TIPS) method[8,9]. PE membranes are used in organic solvent filtration, sea water desalination by membrane distillation (MD), alkaline fuel cells, air filtration, environment monitoring, biomedical and biotechnology applications[25–27].

4.4. Polyvinylchloride (PVC)

PVC is a thermoplastic polymer having molecular weight in the range of 33 × 10^3–67 × 10^3 g/mol, with PDI of 2.01–2.44. It is a slightly hydrophilic polymer (water absorption (24 h) 0.03%–0.45%) and has a density of 1.26–1.5 g/cm^3[22]. It is a cheap polymer having very good mechanical strength and excellent chemical resistance towards halogens, inorganic acids, alkalis, and some of the organic solvents[10]. Some of the solvents that are used for making PVC solution are DMF, DMSO, NMP, DMAc, etc.[10,22]. Nonsolvent of PVC include alcohols, hydrocarbons, acetone, non-oxidizing acids, etc.[22]. PVC has low to very high degree of crystallinity (11.3%–84.2%). For making fibre of PVC polymer, a higher degree of crystallinity must be selected keeping processability factor in consideration. PVC has a very high melting temperature (473–573 K) but lower Tg value (344 K) and relatively high thermal expansion coefficient (4.7 × 10^{-4}–6.2 × 10^{-4} K^{-1})[22], so the operating temperature should be limited so as to avoid fibre failure. It shows good mechanical properties with average to excellent tensile modulus (276–75,884 MPa) and good tensile strength (55.5 MPa) making it suitable to deploy in applications requiring relatively high operating pressure[22].

PVC membrane in fibre form is prepared by non-solvent-induced phase separation (NIPS)[10,11]. PVC membrane in fibre form can be used in water treatment, oil-water separation and gas separation applications[11,28–30].

4.5. Polyvinylidene difluoride (PVDF)

PVDF is a thermoplastic fluoropolymer. The molecular weight of the polymer is 3.4 × 10^4–40 × 10^4 g/mol and PDI is 1.62–2.14. It is slightly hydrophollic polymer (water absorption (24 h) <0.04%; contact angle with water 82°)[22]. It is highly resistance to chemicals with no effect of inorganic acids; halogens; oxidants; weak bases; chlorinated solvents, etc.[22]. Common solvents of PVDF include benzaldehyde, DMF, THF, NMP, DMAc, etc. PVDF has high degree of crystallinity (50%)[22] which is desirable for making fibre. PVDF has high melting temperature (443–473 K) with low thermal expansion coefficient (0.7×10^{-4}–1.5×10^{-4} K^{-1}) and so operating at relatively higher temperature is possible. It shows good mechanical properties with moderate tensile modulus (1194 MPa) and average tensile strength (43 MPa). Thus, use of PVDF should be limited to applications requiring moderate operating pressure.

PVDF membranes in fibre form are prepared mostly by non-solvent-induced phase separation (NIPS)[12,13], and sometime using melt spinning method[31]. PVDF membrane in fibre form are used in vacuum membrane distillation (VMD)[12], water treatment, non-aqueous ultrafiltration applications, etc.[32,33].

4.6. Polypropylene (PP)

Polypropylene is a thermoplastic & hydrophobic polymer (water absorption (24 h): 0.01%, advancing contact angle for isotactic PP: H_2O; 116° at 298 K). It is a low-cost polymer having moderate mechanical strength and excellent chemicals resistance[22]. No common solvent can dissolve PP at room temperature and hence melt spinning process is usually used to prepare PP capillary/hollow-fibre membrane. PP can be of syndiotactic, atactic, elastomeric or isotactic macromolecular configuration. Atactic PP has some/none crystallinity and has poor mechanical properties with tensile strength: 1–2 MPa[22]. Hence atactic PP can't be used as it is to prepare membrane in fibre form but can be used along with syndiotactic or isotactic PP[14]. Atactic PP has a density of 0.855 g/cm^3 whereas syndiotactic PP has density in range of 0.91–0.989 g/cm^3. Syndiotactic PP has moderate degree of crystallinity (21%–27%) and hence can be used to prepare membrane in fibre form. It has melting temperature in the range of 398–421 K and has average tensile modulus (483 MPa). Thus, it can be operated at moderately high temperature and at moderate operating pressure. Elastomeric PP has density in range of 0.8683–0.8787g/cm^3 with low to moderate degree of crystallinity (9%–27%). Elastomeric PP has melting temperature in the range of 316.5–433 K which is low to moderate range and is influenced by the degree of crystallinity (as the degree of crystallinity increases it increases melting temperature of the polymer). It has average tensile modulus (23–359 MPa) and average tensile strength (3.2–39 MPa). Hence a proper choice of elastomeric PP having relatively higher degree of crystallinity should be made so as to obtain membrane in fibre form having good mechanical properties. Isotactic PP has density in range of 0.85–0.946 g/cm^3. It has very high degree of crystallinity (50%–70%) and hence is best suited for making membrane in fibre form but the pore sizes created will be expected to be smaller as compared to elastomeric or syndiotactic PP membrane. It has melting temperature in the range of 433–439 K which is quite high and has low thermal expansion coefficient (6.5×10^{-5}–14×10^{-5} K^{-1}). Thus, the membranes can be operated at higher temperature range. It has average tensile strength (23–36 MPa) with very low impact strength (23–36 J/m) and thus operating pressure has to be limited for applications involving PP membrane in fibre form.

At present, PP capillary/hollow-fibre membranes are prepared by the melt spinning-cold stretching method (MSCS) and thermally induced phase separation method (TIPS) methods[34,35]. PP membranes in fibre form are used in membrane contactors, supported liquid membranes, gas separations, pervaporation, ultrafiltration, and microfiltration etc.[14,25,36].

4.7. Polyacrylonitrile (PAN)

Polyacrylonitrile is a thermoplastic and semi crystalline organic polymer. Although it is a thermoplastic polymer, it degrades before melting and hence melt spinning can never be used for preparing PAN membrane in fibre form. Common solvents of PAN include NMP, DMF, dioxanone, ethylene carbonate, DMSO, sulfuric acid, nitric acid, etc. PAN has moderate degree of crystallinity (18%–30%)[37] which is desirable for making fibre. PAN has high melting temperature (593 K)[22], but it degrades at lower temperature and hence operation temperature is restricted by degradation temperature of PAN. It has average tensile modulus (350 MPa) with average tensile strength (35 MPa)[27] and thus operation of the fibre made of PAN should be limited to moderate operating pressure. Due to the presence of highly reactive-CN group, the synthetic modification via post functionalization of PAN is an additional freedom for incorporation of improved properties in the membrane which can increase the number of targeted applications. The synthetic modifications can be the reactions such as nucleophilic addition, cycloaddition, and hydrolysis using various reagents.

PAN membrane in fibre form can be prepared by non-solvent-induced phase separation (NIPS)[16]. As polyacrylonitrile membranes are more hydrophilic compared to common polymeric membranes such as PVDF, PE, PP and PSf, they are less prone to fouling in aqueous solutions. PAN membrane in fibre form is used in pervaporation process, treatment of industrial wastewater, fabrication of the substrate of composite membranes and air filtration[38].

5. Summary & conclusions

Even though it was developed as early as 1960 s, but capillary/hollow fibres membranes have been prepared using a limited number of polymeric materials as on today. Various polymers namely, polysulfone (PSf), polyethersulfone (PES), polyethylene (PE), polyvinylchloride (PVC), polyvinylidene difluoride (PVDF), polypropylene (PP) and polyacrylonitrile (PAN) that are commonly used for preparing capillary/hollow-fibre membrane were reviewed with respect to their properties which qualifies them to be selected for making useful membrane along with their process of making and application areas. The membrane forming and the fibre forming properties of the polymer are essential for qualifying a polymer to be selected for making capillary/hollow-fibre membranes. The mechanical and physical properties of the polymer which are essential for forming fibre are directly influenced by crystallinity of the polymer which in turn is dependent on the chemical structure of the polymer. A general observation from the ‘degree of crystallinity’ data of selected polymers, which are presently used for preparing capillary membranes, suggests that the degree of crystallinity should be between 20%–50%. Lower value of degree of crystallinity may not lead to fibre formation while higher value may cause difficulties in fabrication. Higher values of tensile strength and tensile modulus of a polymer suggest better mechanical properties, which is desirable for making capillary membrane. From the observation of data of selected polymer, it can be concluded that the gross values of tensile strength should be more than 30 MPa and tensile modulus should be more than 150 MPa for making capillary/hollow-fibre membrane useful to operate at high pressure range. In addition to mechanical and physical properties of the polymer, thermal stability, chemical stability, hydrophilicity, etc. are also important parameters to be considered before selecting a polymer for making capillary/hollow-fibre membrane for a particular application. Based on the properties of the polymers, different methods are used for preparation of capillary/hollow-fibre membranes. Non-solvent-induced phase separation (NIPS) method is used for PSf, PES, PVC, PVDF & PAN membranes whereas PSf & PES membranes are prepared by vapor induced phase separation (VIPS) methods also. Thermally induced phase separation (TIPS) and melt-stretching method (MS) methods are used for PE & PP membranes.

Conflict of interest

The authors declare no conflict of interest.

References

1. Ahmed I, Yusof ZAM, Beg M. Fabrication of polymer-based mix matrix membrane—A short review. *International Journal of Basic & Applied Sciences* 2010; 10(2): 17–27.
2. Prabhakar S, Ghosh AK, Bindal RC, Tewari PK. Outside skin tubular ultrafiltration membranes for separation of proteins and polysaccharides and removal of turbidity from seawater. *Desalination and Water Treatment* 2011; 27(1–3): 231–236. doi: 10.5004/dwt.2011.2578
3. Mulder M. *Basic Principles of Membrane Technology*, 2nd ed. Springer; 1996.
4. Anokhina T, Raeva A, Makaev S, et al. Express method of preparation of hollow fiber membrane samples for spinning solution optimization: Polysulfone as example. *Membranes* 2021; 11(6): 396. doi: 10.3390/membranes11060396
5. Plisko TV, Bildyukevich AV, Zhao L, et al. Formation of polysulfone hollow fiber membranes using the systems with lower critical solution temperature. *Fibers* 2021; 9(5): 28. doi: 10.3390/fib9050028
6. Alsalhy QF, Salih AH, Simone S, et al. Poly(ether sulfone) (PES) hollow-fiber membranes prepared from various spinning parameters. *Desalination* 2014; 345: 21–35. doi: 10.1016/j.desal.2014.04.029
7. Uebele S, Johann KS, Goetz T, et al. Poly(ether sulfone) hollow fiber membranes prepared via nonsolvent-induced phase separation using the green solvent Agnique® AMD 3 L. *Journal of Applied Polymer Science* 2021; 138(37): e50935. doi: 10.1002/app.50935
8. Matsuyama H, Hayashi K, Maki T, et al. Effect of polymer density on polyethylene hollow fiber membrane formation via thermally induced phase separation. *Journal of Applied Polymer Science* 2004; 93(1): 471–474. doi: 10.1002/app.20461
9. Kim J, Kim SS, Park M, Jang M. Effects of precursor properties on the preparation of polyethylene hollow fiber membranes by stretching. *Journal of Membrane Science* 2008; 318(1–2): 201–209. doi: 10.1016/j.memsci.2008.02.050
10. Mei S, Xiao C, Hu X. Preparation of porous PVC membrane via a phase inversion method from PVC/DMAc/water/additives. *Journal of Applied Polymer Science* 2011; 120(1): 557–562. doi: 10.1002/app.33219
11. Lu F, Liu H, Xiao C, et al. Effect of on-line stretching treatment on the structure and performance of polyvinyl chloride hollow fiber membranes. *RSC Advances* 2019; 9(12): 6699–6707. doi: 10.1039/c9ra00265k
12. Yan J, Xiao C, Ji D. Robust preparation and reinforcement mechanism study of PVDF hollow fiber membrane with homogeneous fibers. *Polymer Testing* 2022; 108: 107488. doi: 10.1016/j.polymertesting.2022.107488
13. Ji D, Gao Y, Wang W, et al. Green preparation of PVDF hollow fiber membranes with multiple pore structure via melt spinning method for oil/water separation. *Journal of Environmental Chemical Engineering* 2022; 10(5): 108337. doi: 10.1016/j.jece.2022.108337
14. Gu B, Du Q, Yang Y. Microporous hollow fiber membranes formed from blends of isotactic and atactic polypropylene. *Journal of Membrane Science* 2000; 164(1–2): 59–65. doi: 10.1016/S0376-7388(99)00204-5
15. Qiu Z, He C. Polypropylene hollow-fiber membrane made using the dissolution-induced pores method. *Membranes* 2022; 12(4): 384. doi: 10.3390/membranes12040384
16. Nouri M, Abbasi M, Aghebati T, Shirzadkhan M. Preparation and characterization of nanoclay loaded polyacrylonitrile hollow fiber membranes. *The Journal of the Textile Institute* 2022; 113(5): 952—960. doi: 10.1080/00405000.2021.1909862
17. Hill R, Walker EE. Polymer constitution and fiber properties. *Journal of Polymer Science* 1948; 3(5): 609–630. doi: 10.1002/pol.1948.120030501
18. Rein H. Fibres from synthetic polymers, herausgeg. von R. Hill. Elsevier Publishing Comp. Amsterdam, 1953, 1. Aufl. XV, 554 S., 179 Abb. gebd. sh. 80. *Angewandte Chemie* 1954; 66(4): 120. doi: 10.1002/ange.19540660415
19. Sinha R. *Outlines of Polymer Technology: Manufacture of Polymers*. PHI Learning Private Limited; 2004.
20. Perepechkin LP. Methods for obtaining polymeric membranes. *Russian Chemical Reviews* 1988; 57(6): 539. doi: 10.1070/RC1988v057n06ABEH003370

21. Grosberg AY, Khokhlow AR, de Gennes PG. *Giant Molecules: Here, There, and Everywhere*, 2nd ed. World Scientific Publishing; 2010.
22. Mark JE. *Polymer Data Handbook*, 2nd ed. Oxford University; 1999.
23. Voicu ŞI, Aldea F, Radut M, Nechifor G. Nanostructured polysulfone composite membranes. *UPB Scientific Bulletin, Series B: Chemistry and Materials Science* 2008; 70(3): 39–46.
24. Kheirieh S, Asghari M, Afsari M. Application and modification of polysulfone membranes. *Reviews in Chemical Engineering* 2017; 34(5): 657–693. doi: 10.1515/revce-2017-0011
25. Scott K. *Handbook of Industrial Membranes*, 2nd ed. Elsevier Science; 1995.
26. Sherazi TA, Sohn JY, Lee YM, Guiver MD. Polyethylene-based radiation grafted anion-exchange membranes for alkaline fuel cells. *Journal of Membrane Science* 2013; 441: 148–157. doi: 10.1016/j.memsci.2013.03.053
27. Zuo J, Bonyadi S, Chung TS. Exploring the potential of commercial polyethylene membranes for desalination by membrane distillation. *Journal of Membrane Science* 2016; 497: 239–247. doi: 10.1016/j.memsci.2015.09.038
28. Behboudi A, Ghiasi S, Mohammadi T, Ulbricht M. Preparation and characterization of asymmetric hollow fiber polyvinyl chloride (PVC) membrane for forward osmosis application. *Separation and Purification Technology* 2021; 270: 118801. doi: 10.1016/j.seppur.2021.118801
29. Bhran A, Shoaib A, Elsadeq D, et al. Preparation of PVC/PVP composite polymer membranes via phase inversion process for water treatment purposes. *Chinese Journal of Chemical Engineering* 2018; 26(4): 715–722. doi: 10.1016/j.cjche.2017.09.003
30. Ghosh AK, Mamtani VS, Adak AK. Carbon based nanofillers embedded fouling resistant polyvinyl chloride nanocomposite membranes for oil-water separation. *International Journal of Scientific Research in Science, Engineering and Technology* 2023; 10(3): 394–398.
31. Ji D, Gao Y, Wang W, et al. Green preparation of PVDF hollow fiber membranes with multiple pore structure via melt spinning method for oil/water separation. *Journal of Environmental Chemical Engineering* 2022; 10(5): 108337. doi: 10.1016/j.jece.2022.108337
32. Maiboroda AB, Petrov DV, Kichik VA, Starikov EN. Polyvinylidene fluoride hollow fiber membrane and its use for treatment of natural water. *Petroleum Chemistry* 2014; 54(7): 562–567. doi: 10.1134/S0965544114070081
33. Li Y, Nulens I, Verbeke R, et al. Tuning the porosity of asymmetric membranes via simple post-synthesis solvent-treatment for non-aqueous applications. *Separation and Purification Technology* 2019; 217: 147–153. doi: 10.1016/j.seppur.2019.02.012
34. Shao H, Wei F, Wu B, et al. Effects of annealing stress field on the structure and properties of polypropylene hollow fiber membranes made by stretching. *RSC Advances* 2016; 6(6): 4271–4279. doi: 10.1039/C5RA21785G
35. Yan SY, Wang YJ, Mao H, Zhao ZP. Fabrication of PP hollow fiber membrane via TIPS using environmentally friendly diluents and its CO_2 degassing performance. *RSC Advances* 2019; 9(33): 19164–19170. doi: 10.1039/C9RA02766A
36. Guo X, Li Y, Liu Z, Xiao C. A new superhydrophobic polypropylene hollow fiber membrane preparation method and its application in the treatment of brine with high salt concentration. *Journal of Environmental Chemical Engineering* 2023; 11(1): 109054. doi: 10.1016/j.jece.2022.109054
37. Beevers RB. The physical properties of polyacrylonitrile and its copolymers. *Journal of Polymer Science: Macromolecular Reviews* 2003; 3(1): 113–254. doi: 10.1002/pol.1968.230030103
38. Wang LY, Yu LE, Lai JY, Chung TS. Effects of Pluronic F127 on phase inversion and membrane formation of PAN hollow fibers for air filtration. *Journal of Membrane Science* 2019; 584: 137–147. doi: 10.1016/j.memsci.2019.05.001