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## (Citation)

Journal of the Taiwan Institute of Chemical Engineers, 122:284-310

## (Issue Date)

2021-05

## (Resource Type)

journal article

## (Version)

Accepted Manuscript

## (Rights)

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## (URL)

<https://hdl.handle.net/20.500.14094/90008673>



# **Reinforced hollow fiber membranes: A comprehensive review**

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## **Abstract**

Reinforcing the HFMs provides appropriate mechanical and shear strengths and improves break at elongation. This comprehensive review paper first discusses the fundamental concept of HFMs fabrications, advantages and disadvantages of HFMs, fabrication methods and fabrication materials. Then, reinforcement methods are categorized into porous matrix membrane reinforced method, the fibers (use of threads or filament) reinforced method, and the use of tubular braids, and each one is discussed based on the concept of thermochemical compatibility of the supporting material and the base polymer. Such a compatibility leads to homogeneous- and heterogeneous-reinforcement method with different interfacial bonding state. A comparative study on the mentioned reinforcement methods is also presented based on the tabulated and charted tensile strength and elongation at break data. At the end, a brief look is taken into commercialized products and worldwide projects installed or under installation in the field of reinforced HFMs.

**Keywords:** Hollow fiber, Reinforcement, Braid, Polymer membrane, Interfaces, Strength

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## Nomenclature

CA	Cellulose acetate	PFA	Pore forming agent
CTA	Cellulose triacetate	PMIA	Poly(m-phenylene isophthalamide)
GO	Graphene oxide	PP	Polypropylene
HFM	Hollow fiber membrane	PPTA	poly(p-phenyleneterephthalamide)
IP	Interfacial polymerization	PS	Polysulphone
MBR	Membrane bioreactor	PTFE	Polytetrafluoroethylene
MF	Microfiltration	PU	Polyurethane
MSCS	Melt-spinning cold-stretching	PVA	Polyvinyl alcohol
NIPS	Non-solvent induced phase separation	PVC	Polyvinylchloride
PA	Polyamide	PVDF	Polyvinylidene fluoride
PAN	Polyacronitrile	PVP	Polyvinylpyrrolidone
PE	Polyethylene	SEM	Scanning electron microscopy
PEG	Polyethylene glycol	TIPS	Thermally-induced phase separation

PEGMA	Poly(ethylene glycol) methyl ether methacrylate	UF	Ultrafiltration
PES	Polyethersulfone	VC	Vinyl chloride
PET	Polyethylene terephthalate		

## 1. Introduction

Due to the expansion of industries and depletion of drinking and usable water in agriculture and industry, the reuse of wastewater has become increasingly important. Also, the rapid growth of the global population increases the demand for freshwater. Therefore, water and wastewater treatment technologies have attracted much attention in recent years (1, 2). One of the promising wastewater reclamation technologies is membrane technology, which is prevalently used in the home, industrial and scientific applications today (3). Due to their process flexibility and filtration capacity, the membrane technologies are being widely utilized in removing contaminants from wastewater to low levels to be reused as potable water or for agricultural consumption (4). The membrane technologies offer several important benefits: (1) less occupying space system, (2) excellent quality of treated water, (3) facile maintenance and operational control, (4) less use of chemicals, and (5) less sludge production (5). As well, in some cases, the membrane processes have lower energy consumption (6). Since there is no need for chemical additives and regeneration of spent medium requires low thermal energy consumption, pressure-driven membrane processes are the most desirable technology for water and wastewater treatment when compared to distillation, disinfection, and conventional filtration (7). Membrane separation technologies such as ultrafiltration (UF), microfiltration (MF), reverse osmosis (RO), nanofiltration (NF), and membrane bioreactors (MBRs) have been extensively employed in industrial wastewater

treatment (8-10). In these types of membranes, the size distribution of structural pores plays an essential role in membrane separation performance, as it causes the membrane to be used to remove certain species from water (see Figure 1).

**Fig. 1.** Comparison of filtration range of different membranes (11) (Adapted with permission from Elsevier)

The MF membranes have a relatively wide pore size distribution of 100 nm to 2  $\mu$ m and can therefore be used to reject large particles and various microorganisms. The UF membranes have pores in the range of 1 to 100 nm and therefore work effectively to remove bacteria and proteins as well as large particles and microorganisms. The RO membranes are usually considered as a nonporous medium with pores smaller than 1 nm. The NF membranes with nano-pores larger than RO's have a wide range of applications (12). As shown in Figure 2, the hollow fiber membranes (HFMs) are also easily assembled in modules, making them favorable for a wide variety of membrane applications (13). The HFMs are extensively utilized in the pretreatment of reverse osmosis (RO) in seawater desalination facilities (14), drinking and wastewater treatment (15, 16), solid-liquid separation in a septic tank (17), medicine (18), food (19) wastewater, and sewage treatment (17).

**Fig. 2.** A schematic illustration of MBR with HFM modules (Was reprinted from following website. <https://www.kobelco-eco.co.jp/english/product/gesui/makubunri.html>)

Nowadays, the HFMs are broadly used as the option for traditional separation processes in a wide variety of applications dealing with water quality, energy, environment, and health sciences (20). As another type of HFMs, mixed matrix HFMs with a wide use in gas purification is a main research topic in both academic and industrial communities due to their distinctive characteristics combining inherent properties of polymer and inorganic fillers (21). In this line, hollow fiber PS mixed matrix membrane exhibited a good performance for CO<sub>2</sub>/CH<sub>4</sub> separation (22). Further research indicated that the incorporation of GO into a hollow fiber PS mixed matrix membrane results in the improved gas permeation properties of CO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> (23). The mixed matrix HFM have also been used in filtration of human blood plasma (24) and desalination. Previous research showed that lanthanum cobalt oxide nanoparticle doped Mixed matrix HFM exhibits a NaCl rejection of 47% at transmembrane pressure drop 69 kPa. The same mixed matrix HFM also showed a rejection of 40% total dissolved solids when it was tested for actual seawater (25). The higher sodium sulfate rejection (40%–50%) was achieved by the GO-impregnated mixed matrix HFM (26). Despite the wide range of applications, the HFMs suffer from poor mechanical strengths and therefore need an internal support material to provide sufficient strength to the membrane while simultaneously improving its porosity and permeability as much as possible. One of the most promising methods to endow the HFMs with a high mechanical strength is braid reinforcement method. The voids of the supporting braid provide a desirable permeability for the ultimate HFM. The braids can be coated with a compatible resinous polymer to prevent fouling on the outer surface of the supporting materials. The supporting tubular braids may be twisted in different directions or be hybridized, resulting in an appropriate interfacial

bonding strength (27). The braid-reinforced HFMs are discussed in detail within the scope of the current review paper.

## 2. Scientometrics

### 2.1. Statistics on scholarly studies

Research on the HFMs has attracted global attention from both academic and industrial communications. The HFMs fabricated from a diversity of polymeric materials have found wide applications in various separation technologies. Figure 3 illustrates the number of scholarly studies in the field of HFMs, including books, journal articles, dissertations, etc. As clearly seen, the journal articles have the highest share of this research field. The number of articles have increased from 1960 to 2016 and then have found a declining trend. Among all the scholarly works accomplished over the years 1960 to 2020, the share of the journal articles, book + book chapters, and the other documents are 87.70%, 2.07%, and 10.23%, respectively.

**Fig. 3.** Scholarly works on the hollow fiber membrane over time (Reprinted from lens.org, updated on March 2020)

Figure 4 indicates the number of research works in the field of reinforced HFMs from 1973 to early 2020. The data have been collected by conducting a literature survey by using the keyword “reinforced hollow fiber membrane”. These research works have been reported in a variety of sources such as journal articles, books, book chapters, dissertations, and conference proceedings. The largest portion of the sources that authors chose to publish their

studies is the journal articles. From 2014 to 2018, more than 30 scholarly works were published each year, which shows the importance of this research field in this time period.

Decreasing the number of research works in 2019 can mean that the challenges of these membranes are largely solved. However, it is expected that research works in this area will again face an increasing trend by the end of 2020 and focus on new aspects of these membranes.

**Fig. 4.** Number of the published documents in the research field of reinforced HFMs

(Reprinted from lens.org, updated on March 2020)

## **2.2. Data collection and analysis methodology**

VOSviewer software (version 1.6.15) has recently been introduced by Leiden University as a popular tool for visualizing scientific landscapes. Using the Scopus database up to 25 October 2020, the most frequently terms were searched, including the words mentioned in the abstract, title and keywords of the published articles. Then, the database downloaded from the Scopus was imported into VOSviewer software and the co-occurrence parameter was adjusted at 2. This parameter tells the software to consider terms with a repeatability of 2 or more times to create a network and density map of this research field.

## **2.3. Bibliographic visualization**

Figure 5 shows the clusters network of HFMs. To specify more details of the cluster network shown in Figure 5, the software zooming tool was used, the result of which is shown in Figure

6. This tool provides deep navigation of the cluster network. From these charts, it can be seen that the polymers and reagents such as polyacronitrile (PAN), polyvinylidene fluoride (PVDF), polyethersulfone (PES), and cellulose acetate (CA) are the most widely used materials in membrane synthesis. Moreover, tensile strength, water flux, water permeability, interfacial adhesion and structure porosity are the most studied properties of the HFMs. It can be deduced that this field of research suffers from in-depth scientific discussions involved in the molecular mechanism of membrane microstructure formation. Also, this research area has received less attention in mass and heat transfer phenomena as well as energy consumption.

**Fig. 5.** Clusters network of HFMs

**Fig. 6.** Clusters network of HFMs with more details

A deeper navigation of the main cluster network is shown in Fig. 7. As shown, the “*tensile strength*” cluster is directly related to terms such as mechanical properties, homogeneous-reinforced, PVDF, water flux, interface, reinforce, braid-reinforced, reinforced, and porosity.

**Fig. 7.** Connection network of “tensile strength” term

A similar procedure revealed that the “*homogeneous-reinforced*” cluster is also associated with the terms “PAN”, “CA”, “interface”, “strength”, “tensile strength”, “PVDF”, and “surface modification”. The “*coating*” cluster includes the terms “interfacial adhesion”, “surface modification”, and “mechanical properties”. In general, this indicates that the

reinforcement of HFMs are majorly connected with interface and interfacial adhesion, tensile strength, and surface modification.

Figure 8 shows the co-occurrence density of each keyword in the conducted studies. It can be clearly seen that the tensile strength compared to the other properties has been investigated more and this has led to the creation of an important research field, such as reinforcement of HFMs.

**Fig. 8.** Density map of the most repetitive keywords in the field of HFMs (co-occurrence value $\geq$ 2)

Changing the keywords co-occurrence parameter into 1 in the software resulted in a density map shown in Figure 9. It can also be seen that all the previous discussions are clearly seen in this map. In addition to tensile strength, other properties such as “elongation at break” and “interfacial bonding” are also important.

**Fig. 9.** Density map of the most repetitive keywords in the field of HFMs (co-occurrence value $\geq$ 1)

Figure 10 shows the other keywords hidden in the sublayers of the main network. As can be seen, the keyword "hollow fiber membrane" has reappeared as the core of one of the main clusters, which is surrounded by the terms “braid tube”, “homogeneous-reinforced”, “reinforced”, “braid-reinforced”, “tubular braid”, “reinforced membrane”, “two-dimensional braid”, “heterogeneous-reinforced”, “braided”, and “tubular braid-reinforced”. Also the core "porous matrix membrane" is adjacent to “adhesion”, “reinforce”, and “reinforcement



mechanism” terms. It can be concluded that the density map of the two mentioned cores shows the main mechanisms of HFMs strengthening.

**Fig. 10.** Density map of the most repetitive keywords hidden in the sublayers of the main network

#### ***2.4. Definition of the scope of the study***

The discussion in this section necessitates a comprehensive review of studies on HFMs strengthening and their properties based on hot keywords in this research line. So, within the scope of the present paper, it is aimed to first discuss the different aspects of HFMs, including their advantages and disadvantages and fabrication methods. Then the main focus will be placed on the HFMs reinforcement methods. These methods are divided into three main categories, including porous matrix membrane reinforced method, the threads/filaments reinforced method, and the tubular braid reinforced method. A comparative discussion is conducted between the mentioned reinforcement methods from the viewpoints of interfacial bonding state, tensile strength, and elongation at break. For better comparison, the data reported in the literature were presented in tabulated and graphical forms. Also, the concepts of homogeneous and heterogeneous reinforcement methods are introduced and clarified. At the end of the article, the latest statistics of commercial applicant for the braid reinforced HFM and some of the great applications of the reinforced HFMs around the world are presented.

### **3. Advantages and disadvantages of HFMs**

The HFMs offer several benefits over conventional flat-sheet membranes, including higher packing density (28-30), excellent self-mechanical support to be durable against the backwashing process (28-30), and greater membrane surface area per unit volume of membrane modules (which leads to higher productivity) (28-30). The surface-area-to-volume ratio is in the range of 350 to 500 m<sup>2</sup>/m<sup>3</sup> for plate and frame, 650 to 800 m<sup>2</sup>/m<sup>3</sup> for spiral wound modules, and as high as 7000 to 13000 m<sup>2</sup>/m<sup>3</sup> for hollow fiber modules (31). In addition, the HFMs possess facile handling during module fabrication and operation control (32-35).

Owing to the above mentioned benefits, the hollow fibers have been regarded as an attractive option for diverse membrane applications (28, 30). Besides, the features mentioned above make HFMs interesting for industrial applications and also in production of MBR systems (36). It was reported that the HFMs utilized in the immersed MBR are easily damaged and destroyed by disturbance of the backwashing process and the aerated airflow (3, 37). Such damage also occurs in the membrane separation processes, where the HFMs are exposed to high-pressure water flow rate or turbulence for a long period of time (38). This problem which affects the quality of effluent and imposes high maintenance cost, has become one of the major limiting factors for developing the membrane technology, particularly in MBR systems (37). Moreover, application of the HFMs are sometimes restricted due to their weak tensile strength (1, 36). Thus, despite their noticeable separation and permeation performance, the HFMs are required to have high mechanical properties (3, 37). Such characteristics are more important in the use of HFMs in the MBR filtration applications (10). Besides, friction between the membranes because of aeration in the water treatment system necessitates high peeling strength for the HFMs (39). Therefore, there is a growing demand for development

of the composite HFMs that, in addition to having high stiffness and low dope permeation, can fulfill all the aforementioned requirements (39). In this regard, many endeavors have been done to reinforce the HFMs by utilizing a fabric or a tubular braid as a support of the membrane (39).

#### 4. Fabrication of HFMs

The density map shown in Figure 11, obtained using Scopus data on polymeric membrane synthesis methods, reveals that phase change-based methods and melt spinning methods have been used as the main methods for synthesizing polymeric membranes. However, the latter are less used than the former. These methods are briefly described in the following subsections.

**Fig. 11.** Density map of polymeric membrane fabrication methods based on Scopus database

For the HFMs, the most common fabrication methods are non-solvent induced phase separation (NIPS) as a wet spinning method (40, 41), melt-spinning cold-stretching (MSCS) method (42), and thermally induced phase separation (TIPS) method (43). Among these methods, the TIPS and NIPS methods are broadly employed for upscale and industrialization (44, 45). The MSCS and TIPS methods offer a more compact structure and narrow pore size distribution in the cross-sectional direction of the membrane, and consequently better mechanical property, compared to the NIPS method (36, 46-48). They could be suitable methods to fabricate membranes for different operational media.

#### ***4.1. Fabrication materials***

Recently, polymeric materials-based separation membranes have been used in a wide range of applications by improving their fabrication methods. Especially with the growing importance of environmental protection and demands for water supply used in various industrial, agricultural, and domestic sectors, applications of the polymeric membranes in water and wastewater treatment have been increased during the last couple of decades. The preparation of polymeric membranes with appropriate mechanical strength, as well as acceptable water permeability and pollutant rejection, is always of great interest. Parameters affecting membrane characteristics include the type of base polymer, the concentrations, the solvent and the non-solvent, the additives, the molecular weights (for both additives and base polymer), the coagulation bath, the mixing temperature, the coagulation bath temperature, the evaporation duration, etc. (49). In particular, in water and wastewater treatment processes, superior mechanical strength is essentially needed, simultaneously with high water permeability (50). Typically, the materials used to fabricate the HFMs include the dope solution and bore fluid. The dope is a viscous solution for the formation of the main backbone of the membrane. It is prepared by mixing a polymer resin, an organic solvent for the polymer being used, and an additive. The polymer resin is prevalently selected from polysulphone (PS), polyethersulfone (PES) (51), polyvinylidene difluoride (PVDF) (52), polyacrylonitrile (PAN) (53), polyvinylchloride (PVC) (54), polyimide, polyamide-imide, and polyesterimide. The organic solvent is preferably chosen from the group consisting of dimethyl acetamide (DMAc), N-methyl pyrrolidone (NMP), dimethyl formamide (DMF), or a mixture thereof. The use of additives in the dope solution could affect the phase inversion, membrane microstructure, separation performance, and the prevention of macrovoid formation and is

one of the ways to ameliorate hydrophilicity, porosity, anti-fouling properties, and mechanical strength. The additives can act as a pore former, increase viscosity of the dope solution, improve hydrophilicity, improve surface roughness and surface charge, accelerate the phase inversion process, enhance membrane morphology, flux, and selectivity (20). It is clear that the amount of additives can have a positive or negative effect on the properties of the dope solution. The additives used in the dope solution are divided into three categories: (1) low molecular-weight additives such as water, alcohols, ethylene glycol, glycerol, and inorganic salts (e.g. LiCl and LiClO<sub>4</sub>); (2) high-molecular-weight additives such as polyethylene glycol (PEG), polyvinylpyrrolidone (PVP); and (3) additives such as a mixture of water and LiCl or a mixture of PEG and LiCl (55, 56).

#### ***4.2. Non-solvent induced phase separation (NIPS)***

The phase inversion utilizing a NIPS method is the most conventionally used process. Since the NIPS offers flexibility and simplicity to large scale membrane production, it is used for the preparation of the most commercially available membranes. However, laboratory-scale research on this method continues to achieve higher performance membranes (57-60). Moreover, the HFMs with diverse physicochemical characteristics and morphological structures can be achieved by controlling and optimizing the fabrication parameters and the chemistry of dope solution (20). Figure 12 schematically depicts a typical NIPS hollow-fiber spinning line for the fabrication of the polymeric HFMs.

**Fig. 12.** A typical NIPS hollow-fiber spinning line for fabrication of the polymeric HFMs

After the dope solution is homogeneously mixed and the bubble released well, a typical NIPS HFM spinning can be described as follows: the dope solution and bore fluid is first metered by various precision pumps. The dope solution and bore fluid are then extruded through a spinneret. In this step, internal coagulation may take place during the dope contact with the bore fluid flowing out the spinneret. Solvent evaporation densifies the outer surface of the emerging fibers in the air-gap region, and the moisture triggers phase separation. The fibers are stretched due to longitudinal tensions and gravity-induced by the take-up winder during the air-gap distance. An external coagulation bath is then used to complete the phase inversion, and the as-spun fibers are solidified. As-spun fibers are collected using rollers. The rollers control the take-up speed of the spinning process, and finally, solvent exchange or any appropriate post-treatment is employed to remove residual solvents/additives (20).

The HFMs fabricated by the NIPS method has been found to be usually asymmetric membranes with dense skin and a porous support layer. Such membranes have been extensively utilized due to their high permeability, excellent separation performance, and superior anti-fouling properties. However, their broad applications are limited due to the low mechanical strength (36, 61-63).

#### ***4.3. Melt spinning cold-stretching (MSCS)***

As schematically shown in Figure 13, the MSCS comprises extrusion of a hot polymer melt from a proper mold and then cooling and solidifying in the air prior to submerging in a quench tank. This technique can result in the fabrication of very fine fibers because the fibers can be stretched after they leave the mold. Also, compared to the solution-spun fibers, the melt-spun fibers have lower fluxes and are usually more compact. The MSCS also offers high-speed

generation of fibers. The MSCS technique is usually utilized to fabricate the HFMs for gas separation and high-pressure reverse osmosis applications. It is also applied for polymers such as poly (trimethyl pentane), which are insoluble in conventional solvents and are difficult to be used in wet spinning (64). Recently, Ji et al. (65, 66) used a solvent-free MSCS process for the fabrication of the PVDF loose NF HFMs with multilayer structure. The GO was used to coat the interface pores of the PVDF HFMs via vacuum filtration. The surface of the membrane was further modified by polypyrrole. The synergistic effect of GO and polypyrrole resulted in a multilayer structure. The modified HFM exhibited an improved hydrophilicity, a high dye rejection of more than >98.5%, and a low NaCl rejection of ~4%.

**Fig. 13.** A typical MSCS hollow-fiber spinning (67) (With kind permission from Elsevier)

#### ***4.4. Thermally-induced phase separation (TIPS)***

The TIPS is an extensively applied method to prepare well-interconnected porous scaffolds (68). Unlike the NIPS, the mechanism of phase separation in the TIPS technique is achieved by thermal energy removal from high temperature homogeneous polymer solutions. The TIPS typically includes the following steps for fabrication of the HFMs (69-71):

- 1) Firstly, the molten polymer solution is prepared by mixing the polymer with diluent at a temperature higher than the polymer melting temperature. The diluent must be a low molecular weight material and has a high boiling point. It must also be stable at the temperature in which the molten polymer solution is prepared.
- 2) The molten polymer solution is then extruded through a spinneret.

3) The thermal energy is removed from the extruded solution through either rapid cooling or controlled cooling the solution to achieve the phase separation.

4) Solvent extraction is finally performed to extract the diluent to generate microporosity in the structure of hollow fibers (20, 72).

Inasmuch as the membrane fabricated by the TIPS technique has homogeneous pore structure (i.e. narrow pore size distribution and uniform pore size), it is difficult to produce acceptable permeation performance for industrial water treatment (48, 73). Nevertheless, the fabrication of the HFMs with improved surface porosity and anti-fouling properties using the TIPS method has been reported recently (74-77).

#### ***4.5. Vapor induced phase separation (VIPS)***

Today, VIPS is a salient technology for the production of polymeric membranes. The non-solvent phase in the VIPS method is a gas and the non-volatile non-solvent is essentially present in the volatile solution, and therefore in the controlled solvent evaporation process, the casting solution is rich in non-solvent. Polymeric membranes produced by VIPS benefit from a possible morphology control with a relatively facile process, and therefore are extensively employed for different applications (78). In VIPS, the main phenomenon involved in the phase separation is a non-solvent intake rather than a solvent loss (79). In contrary to NIPS method, the VIPS technique is a relatively slow process that causes a more uniform diffusion of vapor into the polymer, making it possible to better control the phase inversion process (80). Typically for the VIPS systems, water vapor is a non-solvent such that the transfer of water molecules in the humid air exposure stage leads to phase separation.



The rate and extent of water transfer can be controlled by tuning the exposure time and the relative humidity, velocity, and temperature of the air (81).

The VIPS method is mainly used to fabricate HFMs for water filtration and gas separation applications, and so far no study has been conducted on the fabrication of reinforced HFMs by this method.

## **5. Reinforcement of HFMs**

The most commonly employed UF and MF HFMs nowadays, which are comprised of skin and support layers, are generally fabricated through the immersion-precipitation method (41). These HFMs usually have high permeability but suffer from low mechanical strength (62). Typically, the reinforced HFMs are prepared by integrating the separation layer with the porous supported matrix. The separation layer and the porous supported matrix lead to the superior separation efficiency and the high tensile strength, respectively (41, 82). In this line, researches have studied mechanical strength improvement of the HFMs (38, 83-85). Nowadays, three types of methods are usually used to improve the mechanical strength of the membranes, including the porous matrix membrane reinforced method (86), the fibers (use of threads or filament) reinforced method (50, 85), and the use of tubular braids. Table 1 provides a comparison of the advantages and disadvantages of these methods. These methods will be discussed in detail in the following sub-sections.

**Table 1.** Comparison of different methods of reinforcing the HFMs

HFM preparation method		Advantages	Disadvantages
<b>Porous matrix reinforcement</b>		<ul style="list-style-type: none"> <li>-Typically exhibits a tensile strength of more than 10 MPa.</li> <li>-Heterogeneous reinforcement can provide mechanical strength without adverse effects, such as being dissolved and swelled.</li> </ul>	<ul style="list-style-type: none"> <li>-Dissolution or swelling of the porous support layer due to the penetration of casting solution in homogeneous reinforcement method.</li> <li>-Heterogeneous reinforcement fabrication process is very costly and operationally complex.</li> </ul>
<b>Applying filaments or threads</b>		<ul style="list-style-type: none"> <li>-A relatively facile and low cost fabrication process</li> <li>-Possibility to use a variety of yarns</li> </ul>	<ul style="list-style-type: none"> <li>-A new failure mode may be created due to the movement of the longitudinal filaments within the softer membrane material.</li> <li>-The outer surface of the prepared membrane must be smooth.</li> </ul>
<b>Braid-reinforcement</b>	<b>NIPS-based braid reinforcement</b>	<ul style="list-style-type: none"> <li>-Easily applicable in industrial scale</li> <li>-A wide range of tensile strength</li> <li>-Possibility to use a variety of braids</li> </ul>	<ul style="list-style-type: none"> <li>-The fabrication of round-stable braids on braiding machines is a slow and costly operation.</li> <li>-Achieving a uniform polymeric coat on the braid is difficult.</li> <li>-A low peeling strength for heterogeneous-braid reinforced HFMs</li> <li>-The possibility of biofouling formation</li> </ul>
	<b>Electrospinning-based braid reinforcement</b>	<ul style="list-style-type: none"> <li>-No need of high temperatures and utilization of coagulation chemistry to generate solid threads from solutions.</li> <li>-Benefits from characteristics of both conventional solution dry spinning of fibers and electrospinning.</li> <li>-Usable when the fibers are insoluble and have ultrahigh melt viscosity.</li> </ul>	<ul style="list-style-type: none"> <li>-The limited control of pore structure</li> </ul>

From the scanning electron microscopy (SEM) micrographs shown in Figure 14, two separate layers are clearly observed in the porous matrix reinforced HFMs (Figure 14a), namely the coating layer with a finger-like structure and the matrix layer with a sponge-like structure. In the fiber-reinforced HFMs (Figure 14b), sufficient contact with filaments can offer larger attachment between the polymer and the filaments. In the braid-reinforced HFMs (Figure 14c), the separation layer is tightly bonded with the homogeneous reinforcing braids. The interfacial bonding strength of the braid-reinforced HFMs is a key factor in determining the mechanical properties of the reinforced HFMs, which is mainly attributed to material selection of the tubular braid and formation of the tubular braid-polymer composite (63). Each of these three reinforcement methods can be either homogenous or heterogeneous. This means that the reinforcement agent (sponge-like structured matrix layer or threads/filaments or braids) can be chemically homogeneous or heterogeneous with the base polymer (87).

**Fig. 14.** Common methods of reinforcing the HFMs (Reprinted from (37, 41, 88).

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### ***5.1. Heterogeneous reinforced HFMs***

In the heterogeneous-reinforced HFMs, the reinforcement agent/layer and the base polymer used in the fabrication are chemically different and exhibit different thermochemical behaviors (e.g. miscibility). In these reinforcement methods, the casting solution penetrates through the porous supported matrix that provides mechanical strength without adverse effects, such as being dissolved and swelled. However, different thermochemistry of the

reinforcement layer and the base polymer cause apparent changes in the gradient in the chemical and structural composition of the interface among them. The gradual penetration of the casting solution to the porous support could induce restricted interfacial bonding strength, which may bring about exfoliating the separation layer from the porous support during the high-pressure cleaning process or by perturbation of the aeration in the MBR filtration process. In addition, when the heterogeneous-reinforced HFMs are exposed to pressing and stretching effects, the deformation rate becomes different between the porous support and the separation layer. Thus, the interfacial interactions of the heterogeneous-reinforced HFMs have become a vital factor in limiting their applications (89).

## ***5.2. Homogeneous reinforced HFMs***

Unlike the heterogeneous-reinforced HFMs, in the homogenous-reinforced HFMs, the reinforcement agent/layer and the base polymer used in the fabrication are chemically the same and possess similar thermochemical behaviors. Such homogeneity can overcome the defects of the heterogeneous-reinforced HFMs (37). The use of the same materials in the two layers of homogenous-reinforced HFMs offers better adhesion (and consequently improved interfacial bonding strength) of the support layer to the separation/coating layer compared to the heterogeneous-reinforced HFMs in which two different polymers are used (3, 36).

In the fabrication process of the homogenous-reinforced HFMs, the casting solution penetrates through the porous support layer, which may be accompanied by dissolution or swelling of the layer. Although dissolution and swelling of the porous support layer have inherently negative effects, they can provide superior interfacial bonding strength after solidifying the homogenous-reinforced HFMs. The adhesion between the porous support

layer and the separation layer plays a crucial role in the composite materials. Appropriate interfacial bonding states that guarantee the load transfer from the matrix to the reinforcement is a primary prerequisite for the efficient utilization of reinforcement properties (90).

In this line, multibore homogeneous HFMs have exhibited a high mechanical/chemical strength, high permeation fluxes, enhanced long-term operation reliability, a large surface area, and a facile module fabrication. These types of HFMs benefit from the properties of both flat sheet and HFMs and have demonstrated superior stability and a proper performance compared with the conventional single-bore HFMs for different applications, especially for membrane distillation. The multibore HFMs are usually fabricated through phase inversion spinning process utilizing specially designed multi-needle spinnerets of various geometrical shapes (e.g. blossom geometry) (91, 92).

### **5.3. Porous matrix reinforced HFMs**

The porous matrix in this type of the reinforced HFMs is achieved by the TIPS or MSCS methods as the reinforcement, and the functional surface layer is generated by the NIPS method (63, 93). As mentioned before, the membranes fabricated by the TIPS and MSCS methods have a more compact structure than those prepared by the NIPS method. This, in turn, provides superior mechanical strength for the homogeneous-reinforced HFMs (43, 47). The porous matrix membranes prepared by the TIPS or MSCS methods typically exhibit a tensile strength of more than 10 MPa (37, 89). However, this fabrication process is high cost and operationally complex.

Liu *et al.* prepared homogeneous-reinforced PVC HFMs through the coating process. The porous matrix of the homogeneous PVC membrane was first fabricated by the MSCS method.

The blends of polymer solutions were then uniformly coated on the prepared porous matrix of the homogeneous PVC membrane. The prepared membranes exhibited desirable interfacial bonding strength between the membrane matrix and the coating layer. The results showed that the prepared membranes have a tensile strength of around 19 MPa, which experiences a slight decrease (~3 MPa) compared with the uncoated matrix membrane. However, break elongation increases from about 93% to ~102% (86). In another work, they fabricated the porous matrix reinforced PVC HFMs, including a porous support layer and separation layer via the dry–wet-spinning process. The PVDF or PVC polymer solutions were uniformly coated on the MSCS-prepared PVC matrix membrane. The effects of polymer concentration and pre-wetting solutions on the performance and structure of the homogenous-reinforced PVC HFMs were investigated. The results revealed that the pure water flux of the pre-wet homogeneous reinforced HFMs is higher than that of the no pre-wet ones. The reason is formation of a dense interface between porous support layer and separation layer. In the pre-wet homogeneous reinforced HFMs, the pre-wet solution temporarily fills the pores on the outer surface of the matrix. During the coating stage, the pre-wet solution is extracted from the pores and a porous interface is finally formed. The homogenous-reinforced PVC HFMs possess more desirable interfacial bonding strength than the heterogeneous-reinforced PVDF HFMs. The fabricated reinforced PVC HFMs showed tensile strength of more than 12 MPa but lower than that of the original unreinforced PVC HFMs (~21 MPa). The decrease in tensile strength after reinforcement is due to dissolution of the PVC HFMs in the polymer solution which contains high concentration (80 wt%) of solvent (DMAc) (89). It seems that composition of the polymer solution needs to be optimized. Liu *et al.* prepared homogeneous-reinforced PVC HFMs using the method the

same as the one applied in the previous studies and then investigated the effect of ethanol mass fraction in water coagulation bath on structure of the prepared membranes. The results indicated that by increasing the ethanol mass fraction from 0 to 45%, pure water flux of the homogeneous PVC HFMs increases from  $\sim 90$  L/m<sup>2</sup>h to  $\sim 127$  L/m<sup>2</sup>h, whereas porosity is slightly reduced. Tensile strength of around 9.5 MPa and break elongation of higher than 97% were reported (93, 94).

Zhang *et al.* prepared a new design of HFMs with controllable performance and reinforced mechanical property. The PVDF HFMs fabricated by the TIPS method were used as porous support. The PES layers generated by the NIPS method and the polyamide (PA) top skins created by the interfacial polymerization (IP) were coated one after another. The experimental results revealed that when the PES concentration increases from 13% to 28%, the mean pore size of the PVDF-PES membrane decreases from 15.5 to 7.1 nm, tensile strength at break experiences an increase from 11.6 to 17.3 MPa, and the prepared membranes exhibits a sharp and drastic decrease in pure water permeability. After the PES layers (PES concentration=16%-28%) were coated, the molecular weight cut-off of the PVDF-PES membranes was about 200 kDa, and the mean pore size decreased to 10 nm. The results indicated that at the PES concentration of 28%, when the PA layers as the second coating layer were added, the final HFMs exhibit salt rejection up to 94.1%. The overall conclusion was that the proposed fabrication process could promisingly prepare HFMs with the improved mechanical strength and the controllable filtration performance (95).

Zhang *et al.* examined the fabrication and properties of the homogenous-reinforced PVDF and PAN HFMs through the dry-wet spinning process (Figure 15). The process typically includes three main stages: 1) coating the PVDF matrix membrane with the polymer solutions,

2) guiding coated matrix through a coagulation bath to establish a microporous layer, and 3) taking-up. The results disclosed that the tensile strength of the homogenous-reinforced PVDF membranes decreases slightly compared with that of the matrix membrane, but elongation at break greatly increases. The prepared HFMs possess better flexibility performance. The homogenous-reinforced PVDF HFMs had desirable interfacial bonding between the matrix membrane and the coating layer (36).

**Fig. 15.** A schematic diagram of the dry–wet spinning process for fabricating the homogenous reinforced membrane (Reprinted from (36). Copyright 2013, with kind permission from Elsevier)

#### ***5.4. Applying filaments or threads***

The fibers reinforcement method has attracted widespread attention due to its relatively facile fabrication process and low cost (38, 41, 82, 96). One method of reinforced HFMs preparation is the use of composite yarns. As shown in Figure 16a, a composite yarn consists of at least two different yarns. The yarns are mostly composed of continuous longitudinal filaments and other wrapped filaments with loose ends (Figure 16b) (97).

**Fig. 16.** (a) A typical composite yarn, (b) typical architecture of a yarn



In a filament- or yarn-reinforced structure, the yarns or the continuous longitudinal filaments are formed around the outer surface of a core, such as a needle, mandrel, or fiber (97).

In the filament-reinforced HFMs, the reinforcement is performed using filaments in a longitudinal direction or in the wrapped form around the membrane. In the wrapped filament-reinforcement, the wrap angle (relative to the vertical axis) is greater than  $0^\circ$  or less than  $90^\circ$ . The wrapped filaments can be either mono-filaments or multi-filaments or a mixture of both. The filaments can be made from polymeric fibers (e.g. PE, PP, polyester, nylon, PVDF, etc) or natural fibers (cotton, wool). Filaments can be bi-component filaments, with an outer layer adapted for filament-to-filament bonding where filaments intersect (97).

Yoon *et al.* [14] and Murase *et al.* (82) described embedding mono or multi-filament yarns longitudinally within the wall of an HFM as a way of reinforcing the membrane. However, considering flexibility and movement of the hollow fiber, the longitudinal filaments were likely to see within the softer membrane material and thus created a new failure mode. The inventors were not aware of any use of such a membrane in the industry (97).

Yoon *et al.* disclosed an external pressure-resistant HFM having a reinforcing supporter for gas separation and water treatment. The reinforcing supporter was woven only with nylon- or polyester-based mono-filaments by the mixed spinning of mono-filaments and multi-filaments. The HFM of the present invention showed superior pressure resistance and high tensile strength, owing to the use of the rigid and tubular supporter (98). Quantitative results of external pressure resistance (resistance against fluid flow subjected to the outer surface of the HFM) were not reported.

Fabrication of polyester threads reinforced PVDF HFMs was investigated by Liu *et al.* (41). As shown in Figure 17, the polyester threads were incorporated in the support layer of HFM

in the axial direction. It was discovered that the tensile/break strength of the threads reinforced membranes considerably increases up to 11 MPa when the number of polyester threads increases to 3. However, this type of HFMs suffered from weak interfacial bonding between the threads and the coated polymer. Thus, the coated polymer layer detached from the threads due to incompatibility between reinforcement filament and coated polymer. To solve the incompatibility issue, they used the same materials for the thread and the coated layer to fabricate a homogeneous reinforced HFM.

**Fig. 17.** SEM micrograph of the interface between polyester multi-filaments and PDVF

(Reprinted from (41). Copyright 2009, with kind permission from Elsevier)

Chen *et al.* (99) prepared reinforced cellulose triacetate (CTA) HFM via the melt spinning method employing a twin-screw spinning machine. The reinforcement was performed by A poly(p-phenyleneterephthalamide) (PPTA) twisted fiber bundle as a new type of supporting layer. PPTA is an aromatic PA fiber with outstanding thermal stability, excellent hydrophilicity, and mechanical strength. The prepared PPTA-reinforced CTA HFM was suitable for reverse osmosis application. A desirable interfacial bonding state between the PPTA twisted fiber bundle supporting layer and the CTA separation layer was observed. The PPTA twisted fiber bundle reinforcement could overcome the facile vulnerability of the CTA membrane at moderate or high pressure operational conditions. After reinforcement, tensile strength increased from ~9 to ~97 MPa due to the larger interfacial stress transfer coefficient.

Figure 18 shows the microstructures of different regions of a typical fiber bundle CTA reverse osmosis membrane.

**Fig. 18.** Membrane structure illustration and morphologies of a typical fiber bundle CTA reverse osmosis membrane: (a) enlarged interfacial bonding morphology, (b) interfacial bonding morphology, (c) surface of supported PPTA twisted fiber bundle morphology, (d) cross-section morphology, (e) outer surface morphology, (f) cross-section of supported PPTA twisted fiber bundle morphology, (g) inner surface morphology, (h) digital photograph. (Reprinted from (99). Copyright 2019, with kind permission from Elsevier)

Figures 18a and 18b show suitable adhesion of the CTA separation layer to the PPTA twisted fiber bundle supporting layer. Figures 18c and 18f show the interspace between the PPTA twisted fibers and cross-section morphologies of the bundle. Figures 18d and 18g depict morphologies of the inner surface and cross-section of the fabricated membranes, respectively. As seen, a dense and smooth structure is formed on the outer surface of the PPTA twisted fiber bundle supporting layer. Also, a desirable interfacial bonding between the PPTA twisted fiber bundle supporting layer and the CTA separation layer is clear. The smoothness of the outer surface of the prepared membrane is clearly seen in Figure 18e. Figure 18h depicts the digital photograph of the prepared membranes. As can obviously be seen, the prepared membranes possess appropriate flexibility. The light yellow color is due to the inclusion of the light yellow PPTA twisted fiber bundle supporting layer.

### **5.5. Braid-reinforcement structures**

A thorough understanding of the braid-reinforcement requires sufficient information about the braid and the braiding process. Therefore, this section first deals with concepts of braid, braiding technology, and hybrid braids and then discusses the braid-reinforced HFMs.

#### *5.5.1. Braiding*

Braid is defined as a structure that is fabricated by combining three or more strands of parallel yarns (100), in a diagonal direction in which the yarns string intermittently pass through or across each other in the opposite direction (101). As shown in Figure 19, the main constituent element of braid is the braided yarn; however, warp yarns and cores can be used to enhance the strength of braid structures for different applications. The braid angle ( $\theta$ ) is the most important geometrical parameter which affects mechanical behavior of the braids. Due to different direction of the yarns, the braids can simultaneously improve the hoop strength and longitudinal strength of tubes or pipes reinforced with the braids.

**Fig. 19.** Different parts of braid

From a typical illustration and SEM image shown in Figure 20, it is evident that the braid has a cylindrical shaped textile structure that is formed by weaving the diagonal threads around the axis (102).

**Fig. 20.** SEM image of a cylindrical braid (Reprinted from (87). Copyright 2015, with kind permission from Wiley)

The complex structure of braids makes them as fabrics with unique characteristics such as appropriate impulse, axial, and compressive membrane mechanical strengths (103, 104). In this way, today, braid structures are widely used in various industries such as aerospace, automotive, medicine, and so on, by the production of various composites (103). The synthetic fibers are made from polyester, PA, polyvinyl alcohol (PVA), PAN, polypropylene (PP), PVC, or polyurethane (PU) (2).

The braiding process is a typical technique that has been used for ornamental purposes that is well progressed and developed its usage in industrialization. This impressive technology can be applied in many industries for a variety of applications (103, 105, 106). Meanwhile, its application for membrane technology has some gaps that require more studies. The braiding process is performed by moving the diagonal bobbins, or the pulleys, and the strands are threaded when both pulleys (in two opposite directions) pass apart (104). The braiding process offers several advantages, including simplicity of the process, high efficiency of production and diversity of application, durability, and flexibility of the final product, and structural characteristics. Such benefits have proven the importance of the braiding process in a variety of applications, from very simple processes (decorative textiles used in clothing and furniture, shoelaces, fishing wire, etc.) to more complex processes (medical equipment, composite materials, parachute ropes, etc.) (103).

### 5.5.2. Braid-reinforced HFMs

One of the common reinforcements, that are currently applied to reinforce HFMs that is currently applied in industrial applications is a hollow textile braided sleeve coated or impregnated with a polymeric membrane layer (97, 107). A general idea of a composite HFM utilizing a tubular braid was patented for the first time by Hayano *et al.* in 1977. In this idea, the tubular braid was not used as a support for a coating, but it was completely embedded in the membrane in order to prevent the reduction of water permeability due to the shrinkage occurred when an acrylonitrile HFM was solely treated one time with hot water at 80° C. Such a composite membrane had larger thickness than the thin film coated on a support, while the embedded braid membrane resulted in an increase in the membrane compaction and thereby the membrane water permeability did not decrease (108). It was found that to improve both water permeability and mechanical strength, the polymer thin film thickness is better to be less than 0.2 mm and also the amount of the polymer thin film penetrated into the reinforcing substance should be less than 30% of the thickness of the reinforcing substance (96).

The braids as the reinforcing substance are usually fabricated from multi-filament. Each mono-filament can be even 0.01-0.4 denier in fineness. Such a braid can possess a peeling strength of 1 to 10 MPa (50). The braid can provide the strength needed to use MF/UF membranes for filtration of water suspension or mixed liquor. In such an application, the hollow fibers are in exposure to continuous or intermittent agitation (with air or otherwise) to prevent membrane fouling (97, 107).

As schematically shown in Figure 21, a braid-reinforced composite HFM typically comprises a reinforcing material of a tubular braid and a polymer solution or a porous layer coated on

the surface of the tubular braid (38, 83, 85, 96). Compared with a self-supporting HFM, in the fabrication of a braid-reinforced HFM, the tubular substrate is used instead of the bore fluid.

**Fig. 21.** A schematic illustration of self-supporting and braid-reinforced HFM fabrication

Coating the tubular braid makes it possible to enhance tensile strength and pressure resistance of the composite HFM. The polymeric thin film consists of a compact structured skin layer and an inner high porosity sponge-like layer, resulting in high water permeability and filtration reliability (39). To improve both mechanical strength and water permeability, it is preferable that penetrating length of the polymeric thin film into the tubular braid to be within a range of 10% ~ 30% of the tubular braid thickness. If the penetrating length of the polymeric thin film into the tubular braid is less than 10% of the tubular braid thickness, it has a disadvantage of low mechanical strength due to possible delamination. Meanwhile, if the penetrating length of the polymeric thin film into the tubular braid is above 30% of the tubular braid thickness, water permeability is reduced (39).

The coating layer can be facilely detached from the braid during filtration in the case that the coating layer and the reinforced fiber are not the same substance, and this results in thermodynamics incompatibility of the heterogeneous-reinforced membranes. Such problems restrict applications of these membranes in engineering practice (90, 109, 110). This implies the importance of interfacial bonding state. This importance even surpasses the importance of tensile strength due to the harsh nature of aeration and backwashing in the

filtration process. The interfacial bonding state between the braid and the polymer matrix plays a major role in the mechanical behavior of composite materials. An appropriate interfacial bonding state that guarantees the load transfer from the polymer matrix to the reinforcement is a primary requirement for the effective use of the reinforcement properties (90). For this reason, researchers have tried over time to explore different improvement techniques to address such problems.

Mailvaganam *et al.* revealed a method for the fabrication of a braid-reinforced selectively permeable membrane. The invention uses multi-filaments of 16-60 yarns of 150-500 deniers to produce a tubular braid. However, the method suffers from a drawback, originating from the thick tubular supporter formed by the multi-filament of a single sort. Due to the formation of such a thick tubular supporter, the membrane softness decreases. In addition, there is a possibility for the formation of a selectively permeable membrane coated on the braid due to some curvy parts of the braid surface. Another problem is related to the difficult control of inner pore size of the membrane. This problem originates because of not using an internal coagulating solution during coating of the selectively permeable membrane (38). Adequate research work is still needed to propose solutions to these problems.

Bottino *et al.* fabricated PVDF HFMs by immersion of PVDF-solvent solutions into water cast on the outer surface of glass fiber braids as very cheap support. The benefit of these HFMs lies in their improved mechanical properties owing, clearly, to the support (111). However, the prepared HFMs need to have better PVDF coating distribution along the braid length, especially to produce longer membranes for industrial applications.

Jung *et al.* (112) reported a new method to fabricate microfiber aligned HFMs with an extremely high pore connectivity via phase inversion. The microfiber aligned HFMs were



fabricated using a polymer mixture consisting of PVDF and polysulfone in PolarClean® as a green solvent. The prepared HFMs demonstrated a six-fold higher water productivity compared to the best electrospun membranes reported in the literature.

It was found that polyester braid-reinforced polytetrafluoroethylene (PTFE) HFMs exhibit good toughness and strength. However, due to the complexity of the preparation process, industrialization is challenging (113). Unfortunately, no further details were reported on the amounts of strength and toughness.

In the field of asymmetric capillary membranes, Beckers *et al.* (55) longitudinally reinforced the membranes using internal braids. The capillary membranes developed in their work could be employed as UF and MF membranes for MBRs. They suggested a multistage fabrication process including pulling a tubular braid through a spinneret, impregnation of the braid with a non-coagulation liquid and coating the braid with a polymer dope. The viscosity of the liquid should be high enough to hold it in the braid pores during the coating process. As a result, the pores and internal channels of the braids cannot be filled with the dope solution. Using a non-coagulation liquid, prior to the coating stage, may provide a two-fold benefit: first, preventing excessive penetration of the dope solution through the braid pores, and second, achieving outer-skinned coating without the need for special braids or special nozzle design on the spinneret.

Lee *et al.* revealed a composite HFM and a tubular braid. The tubular braid was prepared by combining thin and thick filaments. The thin filament consisted of mono-filaments having fineness of 0.01 to 0.4 Den., and the thick filament was comprised of at least one mono-filament having fineness of 3 to 50 Den. The prepared HFM could exhibit superior water

permeability, great mechanical and peeling strengths, low dope permeation, and high stiffness (39).

The interfacial adhesive strength could be improved by the addition of a macromolecule polymer to the transition layer. To further tailor the bonding between the separation layer and the braided support, the corona electric shock treatment was applied to the braided support. The corona treatment is to use high-frequency high voltage (high-frequency AC voltage up to 5000~15000 V/m<sup>2</sup>) on the plastic surface to initiate free radical crosslinking reaction of the polymers (2). In this line, the effects of acrylate adhesive and silane coupling agent KH570 on the performance of the tubular and knitted polyester braid-reinforced PVDF HFMs were studied by Liu *et al.* (114). The results demonstrated that both tensile strength and the bursting strength of tubular braid-reinforced HFM treated with acrylate adhesive increased by 15.2% compared with the untreated tubular braid-reinforced HFM. Also, the tensile strength and the bursting strength of the knitted tubular reinforced HFM increased by 9.9% and 19.1%, respectively compared with the untreated knitted tubular reinforced HFM. These results indicate that silane coupling agent has an evident effect on the knitted tubular reinforced HFM, while acrylate adhesive is more suitable for the tubular braid-reinforced HFM (114).

Quan *et al.* prepared two-dimensional braid heterogeneous-reinforced PVDF HFMs through the dry-wet spinning process. The results showed that the prepared reinforced HFMs exhibit better flexibility performance with the tensile strength of around 75 MPa. The membrane benefited desirable interfacial bonding between the two-dimensional braid and the coating layer. Further experiments proved that enhancement of the polymer concentration decreases pure water flux, while increases rejection (115).

Fan *et al.* prepared homogeneous braid reinforced CA HFMs through the dry–wet spinning process. The prepared membranes consisted of the CA separation layer and CA hollow tubular braids. Such membranes exhibited a tensile strength of more than 11 MPa, which mainly due to the tubular braids. The tensile and bursting strengths of the membranes experienced improvement due to increasing the CA concentration (3, 116). Figure 22 shows structural differences between the homogeneous and heterogeneous interfaces in the braid-reinforced CA HFMs. In the fabrication of the braid-reinforced CA membranes, the coating solution penetrates into the interspace between the fibers owing to the capillary adhesion. Such a penetration causes the CA fibers to swell easily and thus form a dense region outside the braid (Figure 22a). An appropriate interfacial bonding strength is achieved, which is related to thermodynamic compatibility between the coating layer and the braids. However, permeability decreases because of preventing the pore connection from the outer surface to the inner surface. A space between the PAN braid and the separation layer is evident in Figure 22b. This occurs due to the partial shrinkage of the CA solution, which easily results in the interfacial debonding. All of these are shown schematically in Figure 22c.

**Fig. 22.** Interfacial structures existing in braid-reinforced CA membranes; (a) homogeneous interface, (b) heterogeneous interface, and (c) a schema of homogeneous and heterogeneous interfaces (Reprinted from (116). Copyright 2015, with kind permission from Elsevier)

The interfacial bonding state of the PAN HFMs reinforced by PAN and polyester fibers was probed by Quan *et al.* (87). The findings showed that the interfacial bonding state of the PAN tubular braid-reinforced HFMs is better than that of the polyester tubular braid-reinforced ones. In the fabrication process of the PAN braid-reinforced HFMs, the casting solution cannot penetrate through the tubular braids due to the swelling of the tubular braids, and consequently, a dense interface is easily formed between the tubular braids and the separation layer. As a result, membrane permeability decreases. The results also indicated that the breaking strength of the braid reinforced PAN HFMs is higher than 80 MPa.

Hao *et al.* fabricated the braid-reinforced PVDF/graphene HFMs by coating PVDF/graphene solutions on poly(ethylene terephthalate) (PET) tubular braids. After incorporation of graphene into the casting solutions, the as-fabricated membranes exhibited narrow pore size distribution. Graphene had a positive effect on the improvement of water contact angle and water entry pressure of the membranes. The results disclosed that the as-produced membranes reject water completely during an 8 h continuous oil/water separation process, owing to their high water entry pressure and hydrophobicity. The membranes could be potentially applied for continuous separation of kerosene-water mixtures. The experiments proved that the addition of 0.5 wt.% graphene results in an optimum oil/water separation performance for the prepared braid-reinforced HFMs. The membrane separation efficiency did not change by increasing cycle times, indicating the prominent durability performance (84). El-badawy *et al.* (117) treated the PET braids with NaOH and KOH to investigate the pure water flux, water contact angle, tensile strength characteristics of the reinforced HFM. The HFM reinforced with the KOH-treated braids exhibited the highest water flux of 1388 LMH and a negligible decline in tensile strength of only about 0.9%. This HFM sample

indicated a better interfacial adhesion between polymer and braid in comparison to the control. Investigating the surface morphology of the braids disclosed a washing effect and augmentation of braid interspaces. As a result, the braids demonstrated more porosity and hence enhanced permeability, with a contact angle of  $0^\circ$  with water.

Chu *et al.* (118) fabricated a reinforced PES loose NF HFMs with polyester twisted fiber bundle through a dry-wet spinning process. A desirable interfacial bonding state was observed between the separation and supporting layer. The highest tensile strength of the reinforced HFMs was achieved 185.7 MPa. The fabricated reinforced HFMs exhibited stable pure water flux of 52.3 LMH under 0.6 MPa. Moreover, the reinforced HFMs demonstrated a superb separation efficiency for dye/NaCl mixtures, with a high dye rejection of 99.9% and a low NaCl rejection of  $<7\%$ , indicating a remarkable potential application for textile wastewater treatment.

Fan *et al.* modified the braid-reinforced CA HFMs by doping graphene oxide (GO). The GOs of different sheet sizes and content were integrated into the separation layer to optimize the anti-fouling and permeability performance of the membranes. The microstructural observations by SEM micrographs indicated that the fabricated membranes exhibit well-established interfacial bonding state between the braids and the separation layer. The GOs modification resulted in emergence of more and longer finger-like macro-void and thinner skin layer in the separation layer. The membrane pure water flux increased from  $\sim 130$  to  $\sim 158$  LMH by incorporating 1 wt% GO (with sheet size of  $30\text{--}50\text{ }\mu\text{m}$ ). Furthermore, the GOs modification led to enhanced protein solution permeate flux and flux recovery during the filtration process. Tensile strength of about 30 MPa was achieved which mainly depended on the braids. Such a tensile strength was much greater than that of the conventional solution

spinning HFMs. Meanwhile, bursting strength of the GOs-modified membranes was also promoted (119).

Liu *et al.* fabricated novel braid-reinforced PVC HFMs through the dry-wet spinning process. The blends of PVC polymer solutions were uniformly coated on the polyester/PAN hybrid tubular braids. The PVC HFMs that were produced by the polyester/PAN hybrid tubular braids possessed appropriate interfacial bonding strength compared with the sole polyester or PAN tubular braid-reinforced HFMs. The polyester/PAN hybrid tubular braid-reinforced HFMs exhibited pure water flux less than those of the pure polyester or PAN tubular braid-reinforced HFMs, but their bovine serum albumin (BSA) rejection was higher. The fabricated PVC HFMs showed a tensile strength of more than 50 MPa. Both elongation at break and tensile strength decreased with increasing the PAN filaments content in the polyester/PAN hybrid tubular braids (63).

Chen *et al.* prepared the braid-reinforced poly(m-phenylene isophthalamide) (PMIA) HFMs with good mechanical strength. Exploring the effect of PMIA concentration on water permeability disclosed that by increasing the PMIA concentration from 5 wt% to 15 wt%, water permeability decreases from ~297 to ~76 LMH. Tensile strength and breaking elongation of the PMIA HFMs at all the PMIA concentrations were higher than 170 MPa and 63%, respectively. In addition, the PMIA HFMs possessed a desirable interfacial bonding state of ~0.4 to ~1 MPa between the reinforcement braids and the separation layer (1).

Zhou *et al.* produced the braid-reinforced HFMs with high mechanical strength and remarkable anti-fouling characteristics by mixing PVC with poly(vinyl chloride-co-poly(ethylene glycol) methyl ether methacrylate) (poly(VC-co-PEGMA)) copolymer through the NIPS method. The good interfacial bonding state showed good compatibility

between the PET braids and the coating materials. According to the surface segregation phenomena, enhancement of the poly (VC-co-PEGMA)/PVC mixing ratio led to increasing the surface coverage of the membranes with PEGMA. As a result, higher hydrophilicity and BSA rejection were achieved. The tensile and bursting strengths of the braid-reinforced HFMs exceeded 170, and 2.1 MPa, respectively, which were considerably higher than those of the self-supporting HFMs and the various PVC HFMs reported in the literature (120).

In another work, Zhou and colleagues prepared the mechanically stable hydrophilic braid-reinforced HFMs by utilizing an amphiphilic copolymer/PVC mixture, and alkaline treated PET braids via the NIPS method. In this work, an easy, effective, and low-cost modification method was claimed to enhance the bonding strength between the braids and the coating layer. By applying the proposed modification method, no alteration in water permeability and microstructure of the coating layer of the braid-reinforced HFMs occurred. The modification method was based on the alkaline treatment of the PET braids. The alkaline treatment resulted in the formation of more polar functional groups on the PET braids surface, becoming the braids more hydrophilic. As a result, the interfacial bonding strength between the braids and the coating layer was improved due to the generation of stronger polar–polar interaction between the hydrophilic coating layer and the hydrophilic braids surface. According to the reported results, for the 3 wt% KOH-treated PET braids at 90 °C for 1 h, bonding strength between the modified PET braids and the hydrophilic coating layer was 1.1 MPa, while bonding strength between the original PET braids and the coating layer was 0.6 MPa (121).

Wu *et al.* fabricated the reinforced PVDF HFMs by the concentric circles spinning method. Polyester filaments were used to prepare braided tubes by the two-dimensional braided

technique using polyester, while PVDF was coated by the NIPS method. Investigating the influence of vapor bath time on structural and morphological properties of the HFMs proved that the prolonged vapor-bath time induces roughness to the coated surface. At a vapor-bath time of 18 h, the static water contact angle was 139.2°. Enhancement of vapor-bath time increased not only porosity but also the mean pore size of the HFMs. However, liquid inlet pressure was declined clearly. As another result, the morphology of pores was changed from finger-like to sponge-like (122).

Wu *et al.* produced the polyester braid tubular reinforced PU HFMs by the concentric circular spinning method. The inclusion of the polyester tubular braids into PU foam resulted in improved mechanical strength. The toluene isocyanate index (RNCO/OH) was found to affect interfacial adhesion strength. The results indicated that with the isocyanate index of 1.05, the interface bonding strength is 0.37 MPa (123).

Xia *et al.* investigated the feasibility of utilizing a reinforced HFM as a substrate to produce a thin film composite (TFC) membrane for NF application. A commercially available braid-reinforced UF HFM from Koch Membrane System Inc. was employed to support a piperazine-based PA selective layer. This support membrane consisted of polyester braids and PVDF coating layer. The PA selective layer was formed on the outer surface of the substrate, using the conventional IP technique. No failure was observed at pressures up to 70 psi. This braid-reinforced HFMs exhibited great normalized water permeability of 12 LMH/bar and salt rejection of 92%. The prepared membranes also exhibited low NaCl rejection of <30%. The results indicated a sharp selectivity for divalent/monovalent salts (124).



Turken *et al.* (125) prepared a braid reinforced UF HFM using the wet spinning process. The blends of 16 wt.% polysulfone and different molecular weights of PVP as the pore forming agent was used. The polyester braid was utilized as a support layer and coated with the polymer. The effects of fiber take-up speed, coagulation bath temperature, and polymer solution temperature on the properties of membrane were probed. The results showed that the PVP with the lowest molecular weight resulted in the narrower and smaller pore size distribution. Inasmuch as the PVP is highly hydrophilic, adding it to the dope solution brings about the increased water penetration into the dope solution, resulting in the formation of larger macrovoids. The higher molecular weight PVP with a low diffusivity suppresses the formation of aggregated polymer molecules in the surface layer, leading to the increased porosity in the surface layer. The fiber take-up speed had an outstanding effect on the thickness of the polymer layer coated on the braid support. The results revealed that at the take-up speed of 1 m/min, the coating layer could not cover the braid support homogeneously. The take-up speed of 3.5 m/min resulted in a thick coating layer with a non-uniform shape. Therefore, it is necessary to optimize the take-up speed to achieve a uniform and homogeneous coating layer.

The application of hybrid braids in the reinforcement of HFMs also has attracted the attention of researchers. The concept of hybrid systems has been well known for improving materials or functions of certain structures in engineering design. Hybridization is inspired by natural materials that lead to the design of innovative materials and structures. Studies on natural materials show how to obtain high structural performance through optimal hybridization of conventional materials (126). Hybrid braids consist of two or more different types of yarns (127); and are important when appropriate mechanical behaviors or arbitrary features (e.g.,

stiffness, energy absorption, nonlinear elastic behavior) cannot be achieved by single materials (128).

As an example, the application of hybrid braids in the reinforcement of HFMs was reported in the braid-reinforced cellulose acetate (CA) HFMs. Figure 23 shows cross-section SEM images of the braid-reinforced CA HFMs with various braid compositions. As clearly seen in all the braid compositions, a separation layer is formed at the outer surface of the HFMs. Figure 23a belongs to the homogeneous reinforced membrane owing to the same materials in the reinforced braid and the separation layer. In the homogeneous braid-reinforcement, the separation layer firmly adheres to the reinforced braid (CA fibers). In the ‘hybrid’ braids (i.e. CA braid + PAN braid) reinforced CA membranes (Figures 23b and 23c), both homogeneous and heterogeneous interfaces exist, and inner penetration of the coating solution is observed in the membrane sample in Figure 23c rather than the membrane sample in Figure 23b. Figure 23d is related to the heterogeneous reinforced membrane because of using different materials in the braid and the separation layer. In contrast to the homogeneous braid-reinforcement, in the heterogeneous braid reinforcement, a weak interfacial bonding state is observed between the braid (PAN fibers) and the separation layer due to their thermochemical incompatibility. As can be seen, the interfacial bonding state between the braid and the separation layer in the homogeneous and heterogeneous reinforced membranes are different from each other. This could be reflected to some extent by measuring bursting strength. Bursting strength of the homogeneous and heterogeneous reinforced membranes were  $\sim 0.71$  and  $\sim 0.20$  MPa, respectively, while the HFMs reinforced with hybrid braids exhibited bursting strength of  $\sim 0.30$  to  $\sim 0.50$  MPa.

**Fig. 23.** Cross-section SEM images of braid-reinforced CA HFMs with various braid compositions; (a) CA/PAN=3/0, (b) CA/PAN=2/1, (c) CA/PAN=1/2, and (d) CA/PAN=0/3) (Reprinted from (116). Copyright 2015, with kind permission from Elsevier)

### 5.5.3. *Disadvantages of braided supports*

Despite all the benefits of the braid reinforcement method discussed in detail in the previous sections, this method also has some shortcomings. As a matter of fact, the fabrication of round-stable braids on braiding machines is a slow and costly operation. Because the braiding machines usually contain a large number ( $>16$ ) of braiding carriers. Several bobbins feed all the carriers. These bobbins must cross paths in the braiding machines. During the operation, the speed of the bobbins must vary as needed, and the carriers must be reversed radially every time cross each other. Small diameter braids ( $<2$  mm) are generally fabricated at a speed of lower than 0.5 m/min. Conversely, impregnation operation or braids coating is typically performed at a much faster speed of higher than 15 m/min. This necessitates the need for separate operations with a spool transfer step. Unwinding a large spool of braids at constant tension for membrane coating is also challenging, and the coating process must be stopped at certain times to replace the spools.

Furthermore, the braids employed as membrane support generally have a relatively large diameter (higher than 1.5 mm). This is because braiding speed are usually independent of diameter, but surface area increases proportionally to diameter. In addition, to have large diameters, braids, therefore, have thick wall, which is needed to make them round-stable. Consequently, the inner-to-outer diameter ratio is typically smaller than 0.5. This ratio is a

normalized parameter that specifies the pressure drop for conducting permeate flow through the lumen. A high lumen pressure loss in thick wall braids restricts the length of hollow fibers, which is applicable in a module. Fiber diameter is also an influential factor on the overall cost of the prepared membranes. Because the volume of a fiber is proportional to the square of its diameter, while the dependence of developed surface area on diameter is direct. Thus, at fixed inner-to-outer diameter ratio and constant packing density of hollow fibers in a module, enhancement of the outer diameter of a fiber lessens specific surface area and increases mass of applied polymer per unit surface area, both of which raise the cost of membrane system designed to treat a specified flow of water (97, 129).

#### *5.5.4. Electrospinning*

Electrospinning is an electric force-based fiber manufacturing method. The electric force is used to draw charged threads of polymer melts or polymer solutions up to fibers with diameters in the order of a few hundred nanometers. Electrospinning benefits from characteristics of both conventional solution dry spinning of fibers and electrospraying. The method does not need high temperatures and utilization of coagulation chemistry to generate solid threads from solutions. The importance of the electrospinning method is especially evident where fabrication of fibers or membranes by common solution- or melt- spinning techniques are difficult due to insolubility and ultrahigh melt viscosity of the fibers (e.g. PTFE fibers) (130, 131). Preparation of the PTFE HFMs is even more difficult. In these membranes, ultrafine fibrous PTFE membranes act as separation layers, while porous glass-fiber braided tubes act as support layer. Electrospinning has made it possible to prepare ultrafine fibrous PTFE HFMs. Such membranes possess great effective membrane surface

area, appropriate mechanical strength, and simplicity of handling compared with the PTFE flat-sheet membranes (132-134).

In a typical ultrafine fibrous PTFE HFMs preparation method (as schematically illustrated in Figure 23), the membranes are first fabricated through electrospinning the PTFE/PVA polymer solution on fiberglass braids, then PVA is removed during the sintering process, while the attained ultrafine fibrous PTFE membrane experiences an inward shrinkage to some extent that it is further integrated with the support layer. The resulting ultrafine fibrous PTFE membranes exhibit superior interfacial bonding strength with the support layer. SEM micrographs of the supporting matrix and the PTFE ultrafine fibrous layer in Figure 24 obviously depict that the membrane exhibits desirable hollow fiber structure and the supporting braided tube is coated by the PTFE layer completely. The ultrafine fibrous PTFE HFMs possess excellent properties such as high porosity, strong hydrophobicity, and narrow pore size distribution. It is anticipated that the ultrafine fibrous PTFE HFMs attract more attention in both applications of wastewater treatment and membrane contactors (135).

**Fig. 24.** Top: Schematic diagram of the PTFE HFMs fabrication process; Bottom: SEM micrographs of (1) porous glass fiber braided tube; (2) nascent membrane; (3) sintered membrane; (4) the whole cross-section of sintered membrane (Reprinted from (135))

## 6. Comparative study

### 6.1. Tensile strength and elongation at break

The higher mechanical strength values, which originated from the introduction of reinforcement materials during the fabrication stage, increase the life span of the HFMs (136). Generally, selectivity and permeability of such HFMs depend on properties and microstructure of the resulting thin-film layer (137). Based on the results reported in the literature, the reinforced HFMs exhibit a variety of mechanical behaviors. To achieve a better realization of tensile strength and elongation at break values of the reinforced HFMs, a comparative discussion is provided in this section. Table 2 and Figure 25 provide a comparative overview on traditional and reinforced HFMs based on the reported experimental data. The comparative Figure 25 is based on the data in Table 1 and some experimental results extracted from the literature.

**Table 2.** A comparative overview on traditional and reinforced HFMs

Traditional reinforced HFMs								
Polymer	Coating layer	Tensile strength (MPa)	Elongation at break (%)	Breaking strength (MPa)	pure water permeability (PWP) $\frac{L}{atm\ m^2\ h}$	Rejection (%)	Year of report	Ref.
PVDF/PVA	Not applicable	0.17-3.67	-	Not reported	27.86-141.85	56- 80 (Egg Albumin Protein)	2010	(62)
PVDF		1.19	54		30.4- 172.25	60- 96	2009	(41)
PVC		1.97- 3.96	57.6-83.78		10.13- 212.78	(PVP K90)	2012	(138)

PVC		4.16	28.12					2017	(63)
						10- 85			
PAN		0.03- 0.92	-			152- 354.64	(Dextran T250)	2001	(139)
PVC		-	8.7- 46.7	1.8- 4.3		23.3- 203.66	99 (BSA)	2002	(140)
Porous matrix reinforced HFMs									
Polymer	Coating layer	Tensile strength (MPa)	Elongation at break (%)	Breaking strength (MPa)	pure water permeability (PWP) $\frac{L}{atm\ m^2\ h}$	Rejection (%)		Year of report	Ref.
						67.5- 80			
PVDF	PVDF	8.75- 22.67	56.7- 67	Not reported	141.85- 898.75	(Egg Albumin Protein)		2013	(36)



PVDF	PVDF	8.8-11.5	57-100	108-864	97- 99 (Ink solution)	2013	(37)
PVDF	PAN	10.4	63	270-486	95 (Ink solution)	2013	(37)
PVC	PVC	18.75- 19.5	101- 104	2.45- 10.11	56.23- 76.12 (BSA)	2013	(86)
PVC	PVC	9.5- 9.7	97- 100	92.2-125.94	34.75- 74.1 (BSA)	2014, 2015	(93, 94)
PVC	PVC	14.93- 16.19	31.83- 48.6	20.3- 192.5	63 -92 (BSA)	2014	(89)
PVC	PVDF	12.75	35.73	101.32- 187.45	55.25- 74 (BSA)	2014	(89)

PVDF	PES, PA	11.64-20.16	49.7- 65.3		1-175- 1436.76	5- 94 (dextran and PEO)	2014	(95)
Filament or threads-reinforced HFMs								
Polymer	Threads/Filament	Tensile strength (MPa)	Elongation at break (%)	Breaking strength (MPa)	pure water permeability (PWP) $\frac{L}{atm\ m^2\ h}$	Rejection (%)	Year of report	Ref.
PVDF	PET	5.8- 11.15	25-42	Not reported	7.6-48.12	1	2009	(41)
CTA	PPTA	9.2-96.8	-		0.43-0.49	82.5- 87 (salt)	2019	(99)
Braid-reinforced HFMs								
Polymer	Braid	Tensile strength (MPa)	Elongation at break (%)	Breaking strength (MPa)	pure water permeability	Rejection (%)	Year of report	Ref.

					(PWP)			
					$\frac{L}{atm \cdot m^2 \cdot h}$			
PAN	PAN	-	33.8	86.3	50.66-354.63	84-91.5 (BSA)	2014	(87)
PAN	PET	-	42.2	188	101.32- 476.22	80-92 (BSA)	2014	(87)
PMIA	PMIA	178.76- 179.15	63.2- 68.2	-	91.19-699.14	78- 98 (BSA)	2017	(1)
CA	CA	11.3- 14.3	-	-	60.79- 172.25	73- 90 (BSA)	2015	(3)
CA	CA	-	-	0.75	10.13	-	2015	(116)
CA	CA/PAN	31.5-33.8	40.4- 47.2	0.29- 0.65	202.65- 319.17	90- 99 (BSA)	2015	(116)
CA	PAN	-	-	0.2	50.66	-	2015	(116)
PVC	PET	106	54.37	-	~ 100	34 (BSA)	2017	(63)

PVC	PAN	51.13	39.37	-	~ 40	55 (BSA)	2017	(63)
PVC	PET/PAN	65.3-66.5	39.37- 47.5	-	~ 60	58- 70 (BSA)	2017	(63)
PVDF	PAN	75	-	-	323.46- 561.22	74- 95 (BSA)	2014	(115)
PVC/PEGMA	PET	170	50	-	470- 1200	■	2017	(120)

**Fig. 25.** Tensile strength and elongation at break range of traditional and reinforced HFMs

As can be clearly seen, the traditional HFMs exhibit lower tensile strength values compared to the reinforced HFMs. Among the reinforced HFMs, the braid-reinforced ones possess a very wide tensile strength range from ~15 to as high as ~170 MPa. In other words, the tensile strength of higher than 100 MPa is achievable only by incorporating braids into the matrix of HFMs. Such a wide range of tensile strength depends on various factors such as material and type of braid, type and concentration of polymer, thermochemical compatibility of the braid with the base polymer, and so on. The filament/threads-reinforced HFMs exhibit tensile strength in the range of ~5 to ~100 MPa, while the porous matrix reinforced HFMs possess tensile strength in the range of ~6 to ~20 MPa.

Introducing braids into the HFMs matrix offers three unique advantages over traditional membranes: first, the braids as the support for the filtration layer substantially increase mechanical strength of the membranes. The higher tensile strength results in the higher membrane durability in high pressure filtration processes; second, the reinforced membrane filtration layer can be thinner than the traditional membrane filtration layer, which in turn reduces filtration resistance and increases flux; and third, choosing a cheap PVC resin as the main matrix of the filtration layer can offset some part of the cost incurred by introducing the braids.

Contrary to tensile strength, the traditional HFMs possess a wide elongation at break range, between ~28% and a little bit lower than 85%. The highest (102%) and the lowest (25%) breaking elongation values have been measured for the porous matrix HFMs and the

threads/filament-reinforced HFMs, respectively. In this respect, the braid-reinforced HFMs are in the middle range.

## **6.2. Separation performance**

As can be seen in Table 2, the performance of the reinforced HFMs in some cases is higher than that of traditional membranes and in some cases less. It is very important that the simultaneous improvement of mechanical strength and separation performance requires optimal adjustment and selection of membrane fabrication conditions. Moreover, many factors affect the separation performance (permeability and rejection) of the reinforced HFMs and various interpretations can be provided about the results, which is beyond the scope of the present article, the main focus of which is on the reinforcing the HFMs.

## **6.3. Bursting pressure**

The bursting test can be a realistic measure of the mechanical strength of flat sheet and HFMs (141, 142). This is a proper mechanical test method to measure the force required to rupture membranes under planar stress. In this experiment, the membrane is exposed to increasing pressure until failure takes place. At this point, pressure is considered as bursting pressure or bursting strength (142). The bursting strength of the HFMs can be determined by employing an apparatus with nitrogen cylinders and pressure gauge (3). The bursting pressure can be related to the tensile stress of HFM by applying Barlow's formula for isotropic tubes (143):

$$P=2t\sigma/(d_0.S_f) \quad (1)$$

where  $\sigma$  is the HFM tensile strength,  $t$  is the hollow fiber wall thickness,  $d_0$  is the outer diameter, and  $S_f$  is the safety factor. The  $S_f$  is usually assumed to be 1. Equation (1) indicates

that the bursting strength of HFMs strongly depends on the tensile stress, outer diameter, and wall thickness of the membrane.

The bursting strength is affected not only by concentration and composition of the polymer, but also by the porosity (62). The bursting strength typically increases with the increase in polymer concentration in the doping solution. The reason is the tighter stack of molecule chains in the membrane with a higher polymer concentration (41, 144).

Increased porosity has a negative effect on the bursting strength of the membrane (62). Smaller cavities exhibit higher resistance to water penetration which can lead to a higher bursting strength (62, 144). Figure 26 demonstrates a comparison of the bursting pressure of two types of reinforced HFMs with the traditional one.

**Fig. 26.** Bursting pressures of three types of hollow fiber membranes

As can be seen, the bursting pressure of the traditional HFMs is in the range of 0.1 to 0.65 MPa, with the highest reported range being in the range of ~0.3 to ~0.5 MPa.

The bursting pressure of the filament-reinforced HFMs shows more spread in the range of 0.15 to 0.45 MPa. The bursting pressure of braid-reinforced HFMs with the highest numbers reported in the literature is in the range of 0.25 to 0.98 MPa. However, the bursting pressure up to 2.1 MPa has also been reported (120) The bursting strength is a vital parameter in the backwashing process, especially for the braid-reinforced HFMs. The bursting strength could be a criterion of the interfacial bonding strength between the coating layer and tubular braid to a certain extent (116).

In the filament-reinforced HFMs, adding threads leads to their axial distribution over the membrane. Inasmuch as the diameter of threads is very small compared to the membrane girth, threads cannot affect the microstructure of the membrane and as a result have a slight effect on the bursting pressure (41).

### *7. Commercialized products*

The superior mechanical and separation properties of the reinforced HFMs have convinced several large companies to produce or use them in their projects. HIFIL TECH INC. recently claimed its Cleanfil-S product is the world best durable reinforced PVDF HFM. The Cleanfil-S is claimed to exhibit high tensile and peeling strengths properties, high permeability & rejection rate, low fouling properties, and a high resistance against cleaning chemicals. This commercial product benefits from easy-to-storage in dry conditions and easy handling & maintenance (145). Koch Membrane Systems, Inc. developed a single-header UF PURON MBR, which is claimed to be high flow rate, energy-efficient and cost-effective, and exhibits an effective air scouring and no fiber breakage. The developed UF MBR can effectively removes phosphorous and operates based on outside-to-inside filtration. This patented module is a kind of reinforced PVDF HFMs that are fixed only at the bottom. The single-header UF PURON MBR has a wide range of primary applications including municipal wastewater solutions, food & beverage water solutions, metal finishing, oil & gas water reuse, produced water, oil & gas wastewater treatment, pulp & paper, semiconductor wastewater treatment, and water recovery (146). MegaVision developed HYPER™ PVDF, a high-packing MBR, using the PE braid-reinforced HFM, delivering excellent tensile strength, fouling resistance, high & stable flux, high chemical resistance, stability and elimination



effectiveness (147). Figure 27 indicates the latest statistics of applicant for the braid reinforced HFMs. Kolon Industries, Inc. fabricated a braid-reinforced HFM using tubular braids and a polymer thin film coated onto the reinforcement braids surface (96). However, such a reinforced HFM suffered from easily surface layer peeling problem. The problem originated from thermodynamic incompatibility between the reinforcement fiber and the porous membrane (3).

Mitsubishi Rayon Co. Ltd. invented a porous membrane consisting of a porous body and a reinforcement fiber. The reinforcement fibers were aligned linearly between the two ends, perpendicular to permeation direction of the membrane (82).

Zenon Environmental Inc. fabricated a braid-reinforced HFM with a microporous structure, termed as Zeeweed 500. This membrane consisted of a microporous supporting matrix and a thin tubular asymmetric semipermeable polymeric film as a coat (38). This braid-reinforced HFM exhibited superior mechanical property, reliable separation and favorable water permeability.

**Fig. 27.** Statistics of applicant for braid reinforced hollow fiber membranes (Reprinted from lens.org, updated on March 2020)

Koch Separation Solutions (KSS), a global leader in membrane filtration and ion exchange technology, recently mentioned that it is expanding the production capacity of PURON® reinforced HFM technology by 50%. KSS's reinforced HFM solutions include PURON MP, PURON HF, PURON MBR, and PULSION MBR (148). Koch Membrane Systems Inc.

produced “PURON PULSION” MBRs. These MBRs used PVDF HFMs with minimal downtime which were reinforced using polyester fabrics. The PULSION MBR modules could supply an alternative source of desirable water for the golf course in Pacific Grove through the city sewer water treatment. In another project in China’s electricity industry for the first time, the PURON MBRs were used to recycle the water. In Sao Paulo, these MBRs are being used in an industrial wastewater treatment plant. The first large MBR installation facility in North America, in Santa Paula, CA, uses the PURON membrane filtration modules. They set up a new treatment plant to meet current and future sewage needs. Koch Membrane Systems Inc. also produced other kinds of polyester braid-reinforced HFMs, termed as PURON HF and PURON MP. In 2013, General Electric Company was able to produce high-durability membranes by focusing on the method of providing tubular braids for HFMs. In 2015, they fabricated a braid-reinforced HFM consisting of ordinary and core-sheath filaments. Also in the same year, they introduced a new tool and process for producing the reinforced HFMs, in which the minimum stress required to pull the fibers from the spinneret reduced distortion of the membrane cross section in coagulation bath. Also in 2016, they developed an apparatus for fabricating the braid-reinforced HFMs using ultrasonic welding of filaments. Membrane modules prepared in this way were used specifically in MBRs. They did not break in the MBR system despite the intense movements of these membrane systems (149-152). Some of the great applications of the reinforced HFMs around the world are presented in Table 3.

**Table 3.** Projects installed or under installation in the field of reinforced HFMs (153)

<b>Installation place</b>	<b>Country</b>	<b>Capacity (m<sup>3</sup>/day)</b>	<b>Year of installation</b>	<b>Application(s)</b>
Wenyuhe River Water Treatment	China	130000	2010	Drinking water treatment
Reverside	USA	186000	2014	Urban wastewater
Nanaimo River	Canada	72000	2015	Drinking water treatment
Casa Grande	USA	10000	2016	Industrial wastewater/food industry/beverage and dairy products
Blackfoot	USA	4900	2016	Industrial wastewater/food industry/beverage and dairy products
Shunyi	China	234000	2016	Urban wastewater
Gaoyang Textile Industrial Park	China	260000	2016	Textile industry/dye-related industries
Canton	USA	333000	2015-2017	Urban wastewater
Euclid	USA	250000	2018	Urban wastewater

Tuas	Singapore	80000	2025	Urban wastewater
Henriksdal	Sweden	864000	2025	Urban wastewater

## 8. Conclusions and perspectives

This review first discussed the traditional hollow fiber membranes (HFMs) and their advantages and disadvantages, followed by concise explanations and illustrations of fabrication methods and materials. The main problem with HFMs is their poor mechanical strength in high-pressure water flow rate or turbulence flow for a long period of time, and this necessitates the need for reinforcement methods. Therefore, the next focus was on the reinforcement methods and on the different aspects of the reinforced HFMs, including substantial concepts and common methods of the reinforcement. Three types of reinforcement methods were discussed which included the porous matrix membrane reinforced method, the fibers (use of threads or filaments) reinforced method, and the use of tubular braids. Also, the concept of homogeneous and heterogeneous reinforcement was elucidated, which was generally related to the thermochemical compatibility of the reinforcement substance and the base polymer. A careful literature survey revealed that many direct and indirect factors affect the quality of the interfacial bonding strength, the most important of which are the type of HFM fabrication method, thermochemical compatibility of the reinforcing material and the base polymer, contact area between reinforcing material and the base polymer, porosity of the reinforcing material, viscosity and penetration rate of the casting solution to the porous support, dissolution and swelling of the porous support layer, polymer concentration and pre-wetting solutions, composition of the polymer solution,

the use of hybrid filament/braid, roughness/smoothness of the surface, thickness of polymer coating, braid thickness and toughness, the addition of a macromolecule polymer to the transition layer, pretreatment of braids (such as alkaline treatment, the corona electric shock treatment), and the use of additives (e.g. acrylate adhesive, silane coupling agent, GO). The

comparative study by tabulating and graphically presenting the tensile and elongation at break data indicated that among the reinforced HFMs, the braid-reinforced ones exhibit a wide tensile strength range and appropriate breaking elongation. Due to the high importance of interfacial bonding state, a great deal of research conducted on the braid-reinforced HFMs to propose practical and useful improvement techniques. Further research guarantees a privileged future for these membranes. So, the current paper suggests the following study topics for future research:

- The use of homogeneous or heterogeneous coating polymer and braid reinforcement seems to require further research.

- Water permeability of reinforced hollow fiber membranes also needs further improvement.

- Interfacial bonding state has a critical effect on the mechanical strength of these membranes and therefore thermodynamics of the miscibility of polymers needs to be included in the scientific discussion of these membranes.

- Further research is also needed to answer the question of whether the use of braid restricts mass transfer in liquid-liquid systems.

- The possibility of biofouling formation in these membranes can be an interesting area of research.

- The life cycle and cost advantages of using braids are needed to be investigated.

- Modeling and simulation of reactions between polymer and reinforcing agent at the molecular scale can lead to an improved understanding of the mechanisms of microstructure formation and reinforcement.
- The study of pressure drop and energy consumption in the reinforced HFMs systems has not received much attention, and so it can become an important area of research.
- An in-depth study of microstructural properties such as porosity and the binding of the polymer and the reinforcing agent can provide valuable information on the adoption of the appropriate polymer and the reinforcing agent as well as the appropriate experimental conditions.
- The use of multidimensional or hybrid braids in HFMs reinforcement requires further research in terms of mechanical and functional properties of the resulting membranes.
- Pilot-scale experiments are required to be performed over a long period of time for different types of water and wastewater to determine the performance limitations of these membranes and to study and resolve probable challenges.

## **Acknowledgment**

Prof. Toraj Mohammadi would like to thank Iran National Science Foundation (INSF) for supporting the research (Grant No. 96008182).

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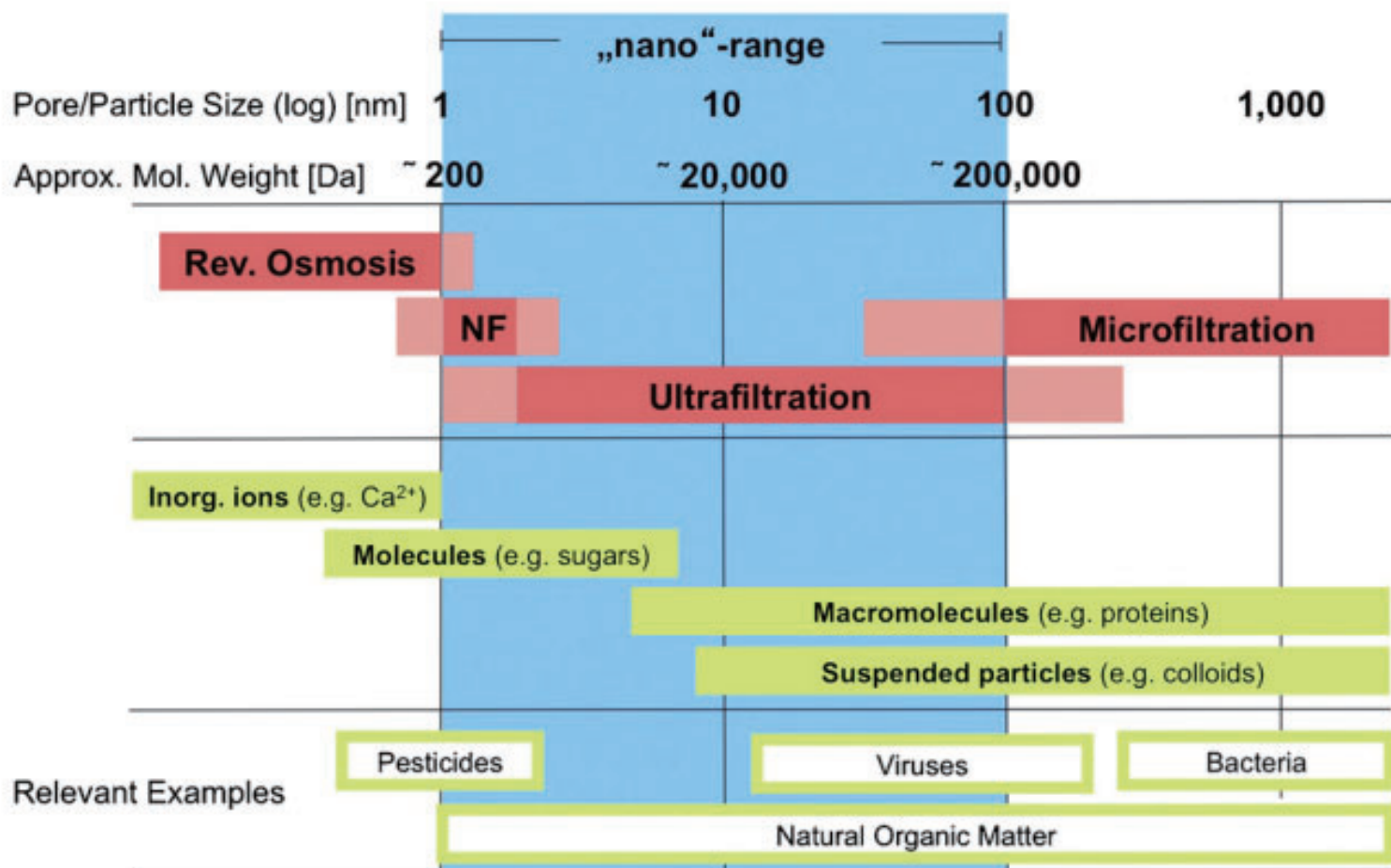
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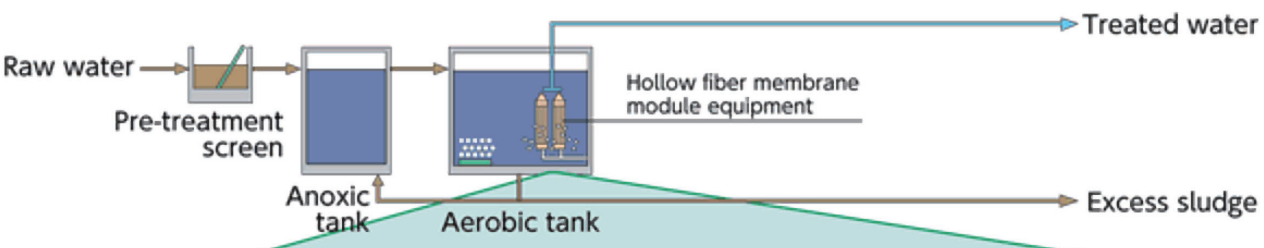
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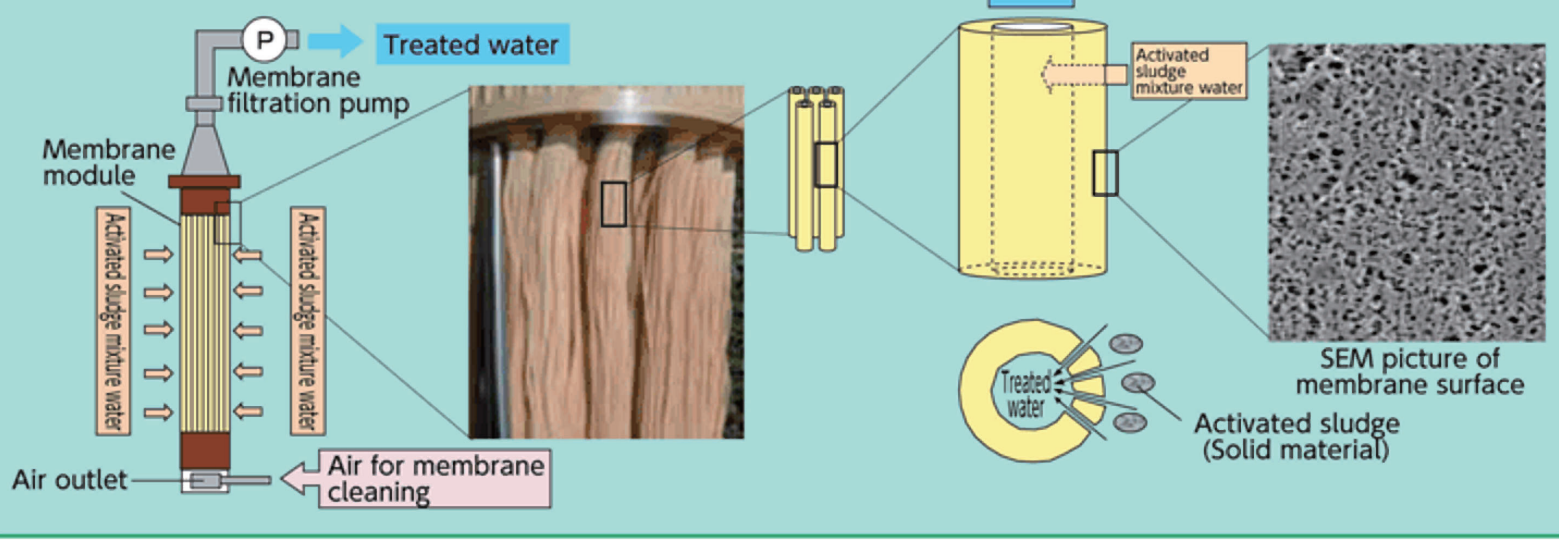
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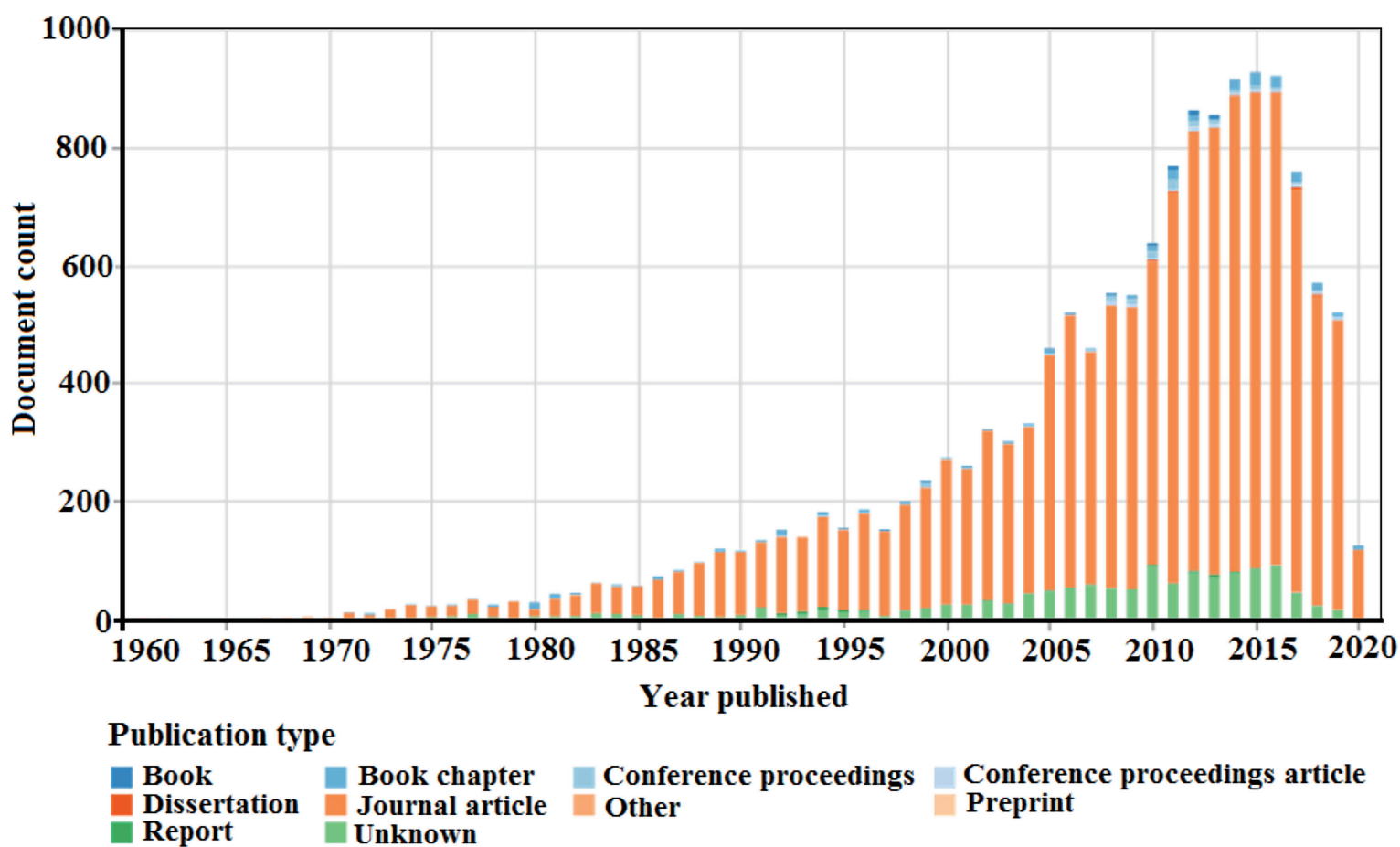


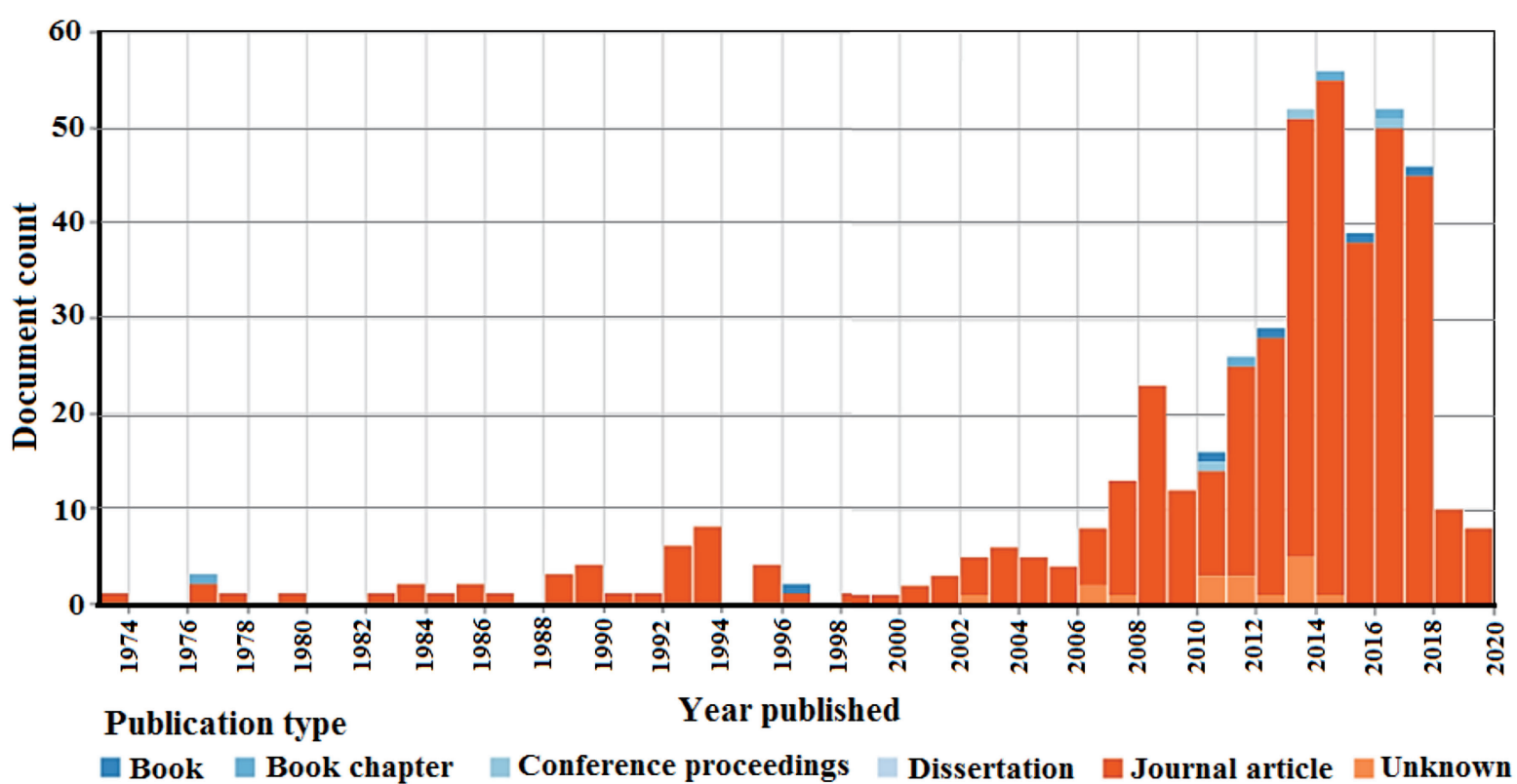


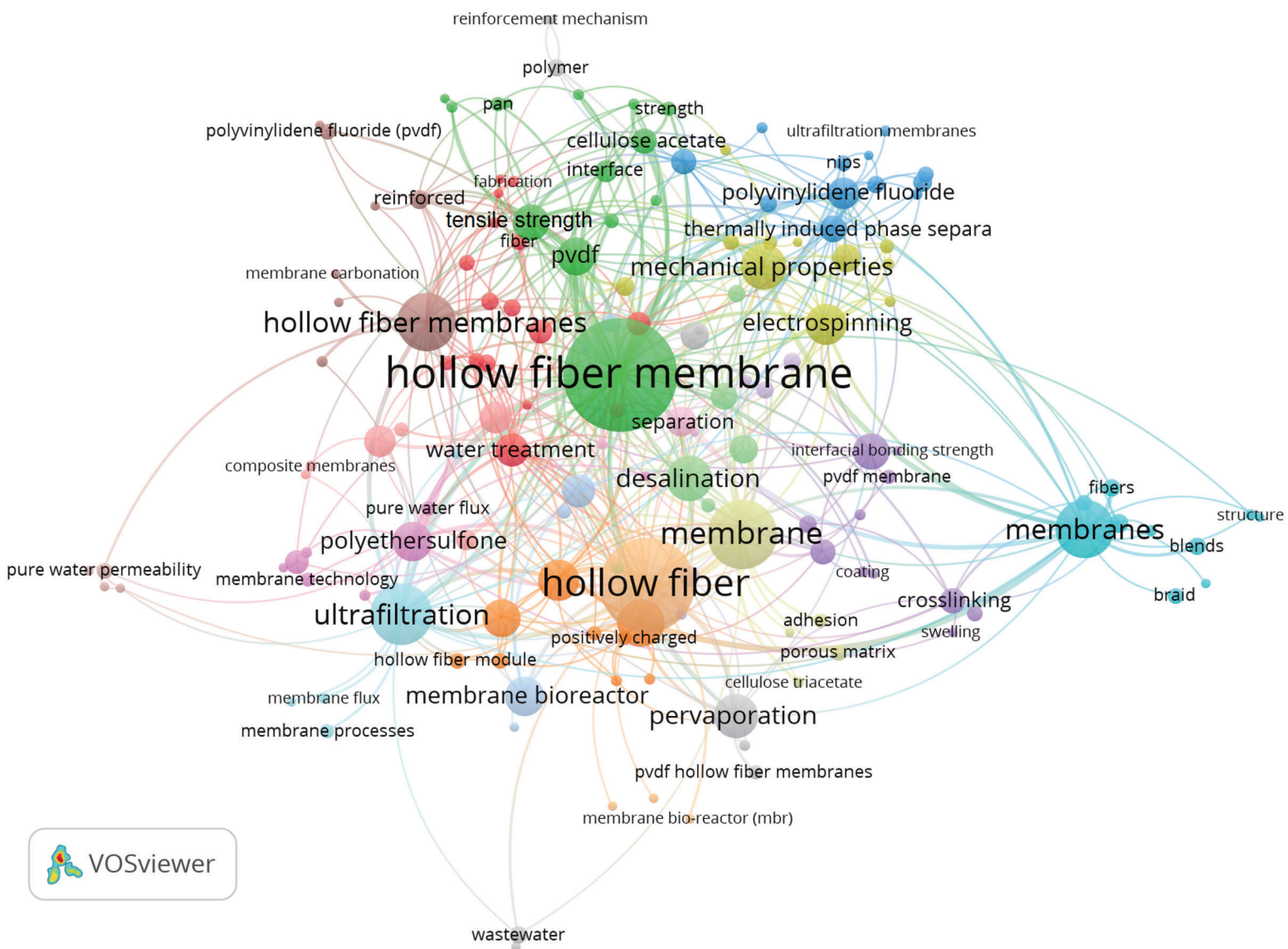
# Hollow fiber membrane module

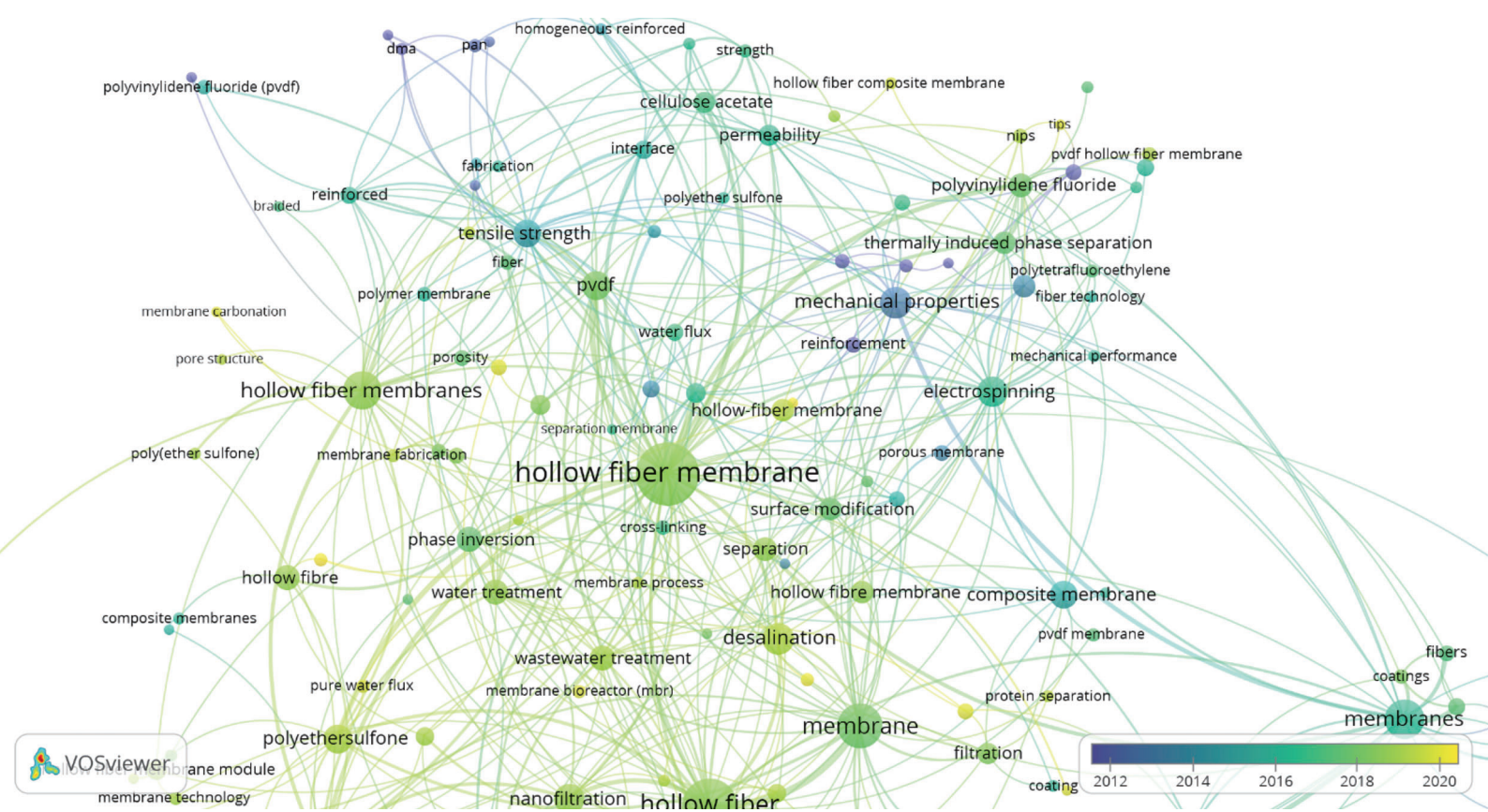


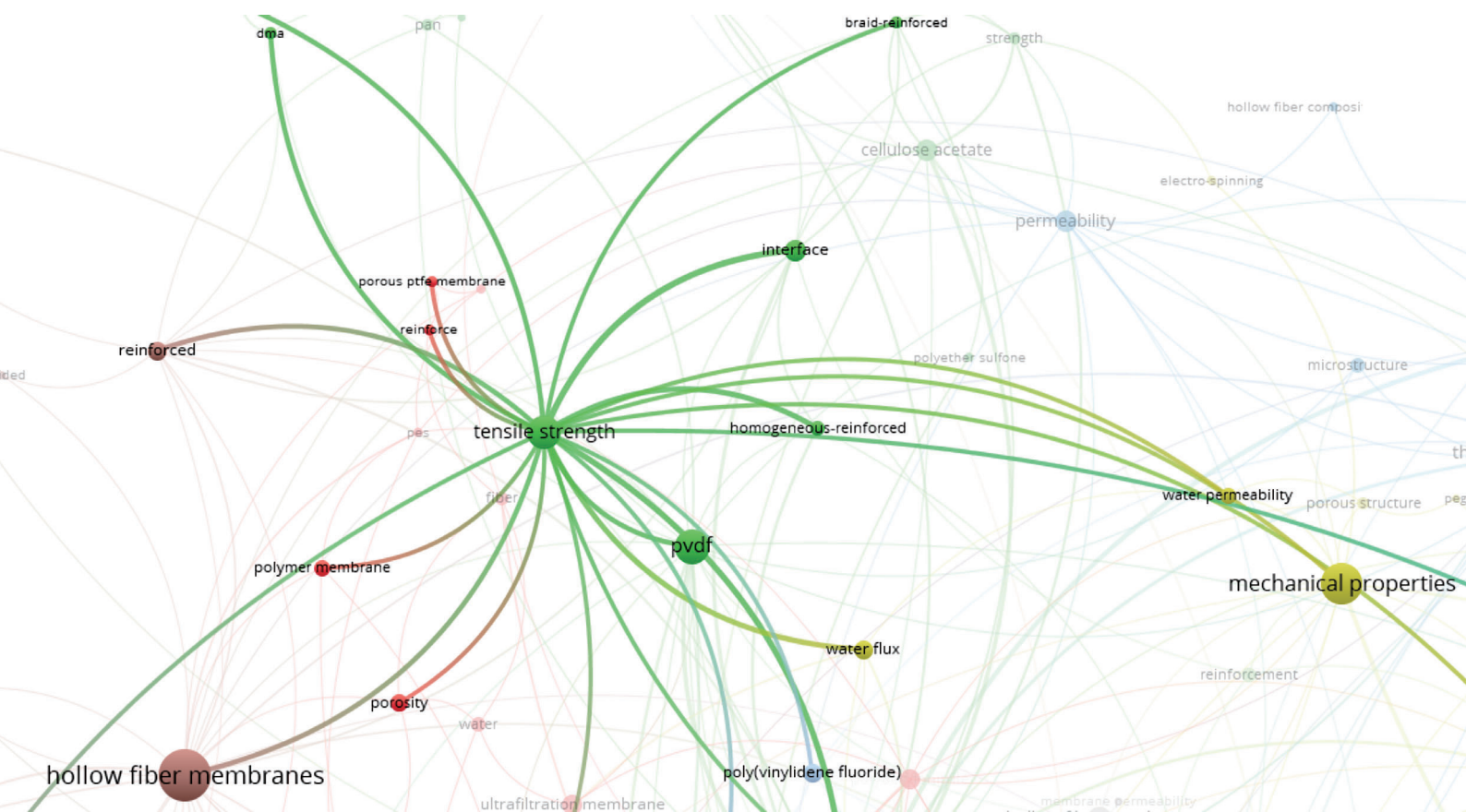




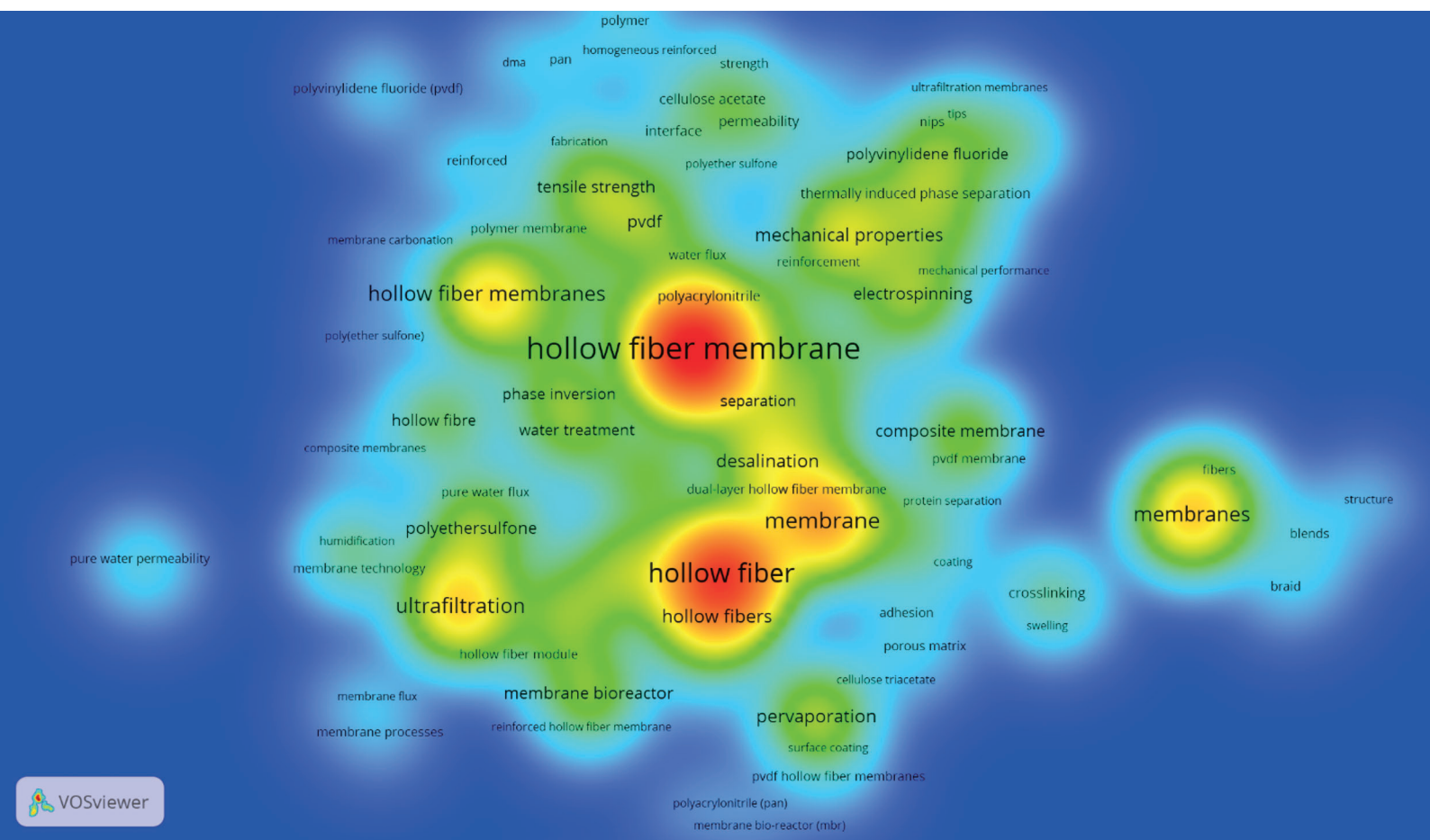


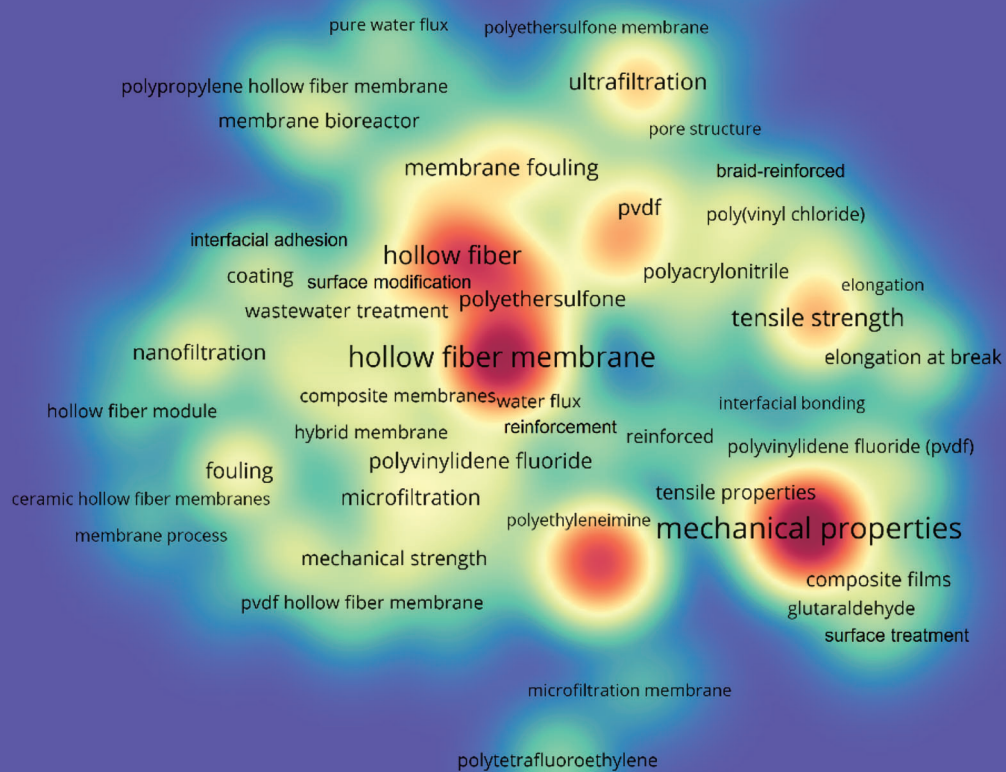


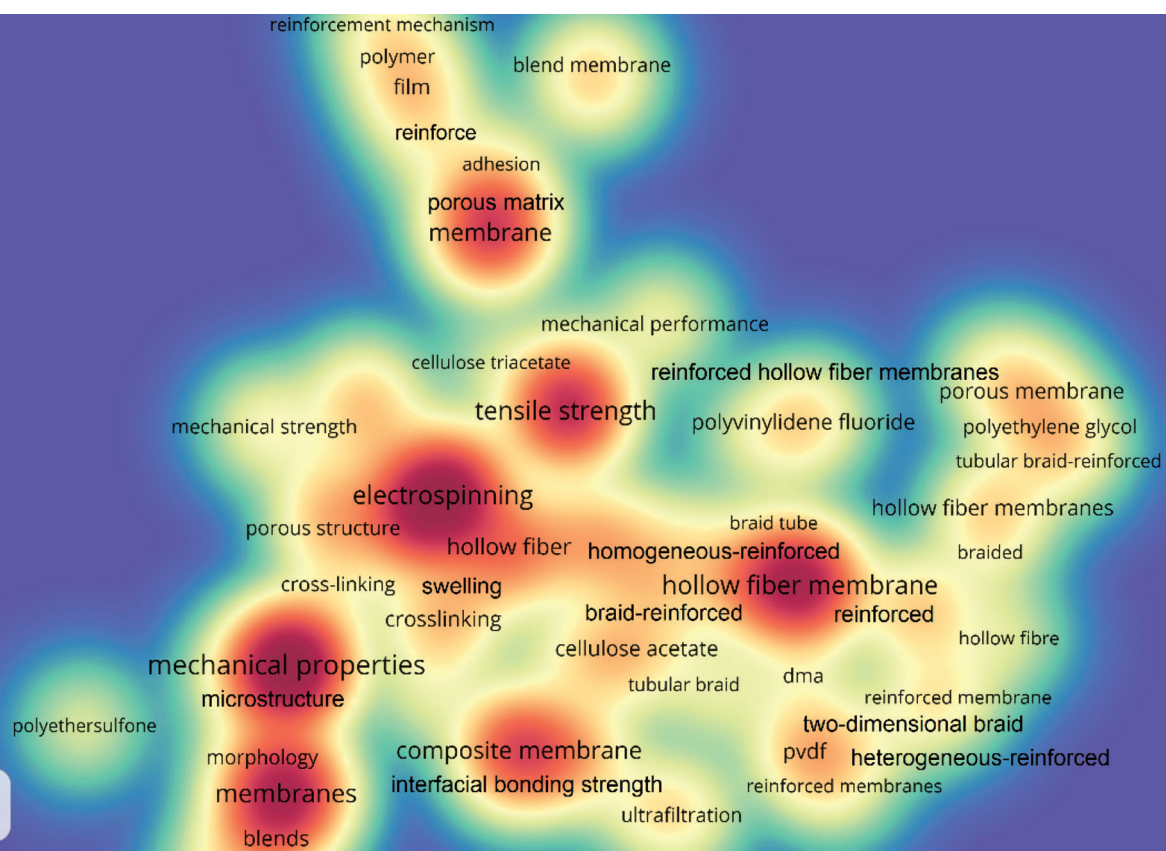




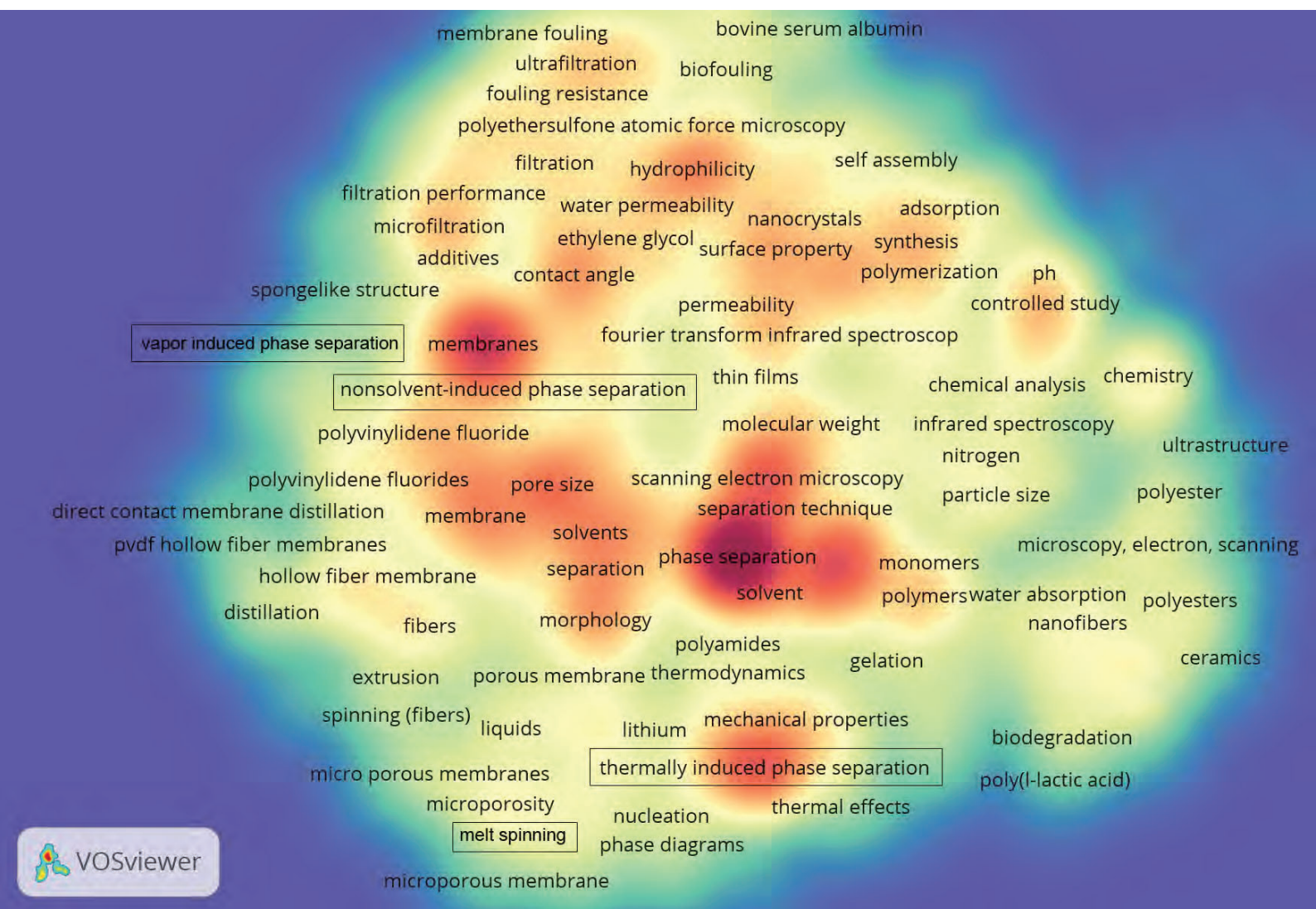


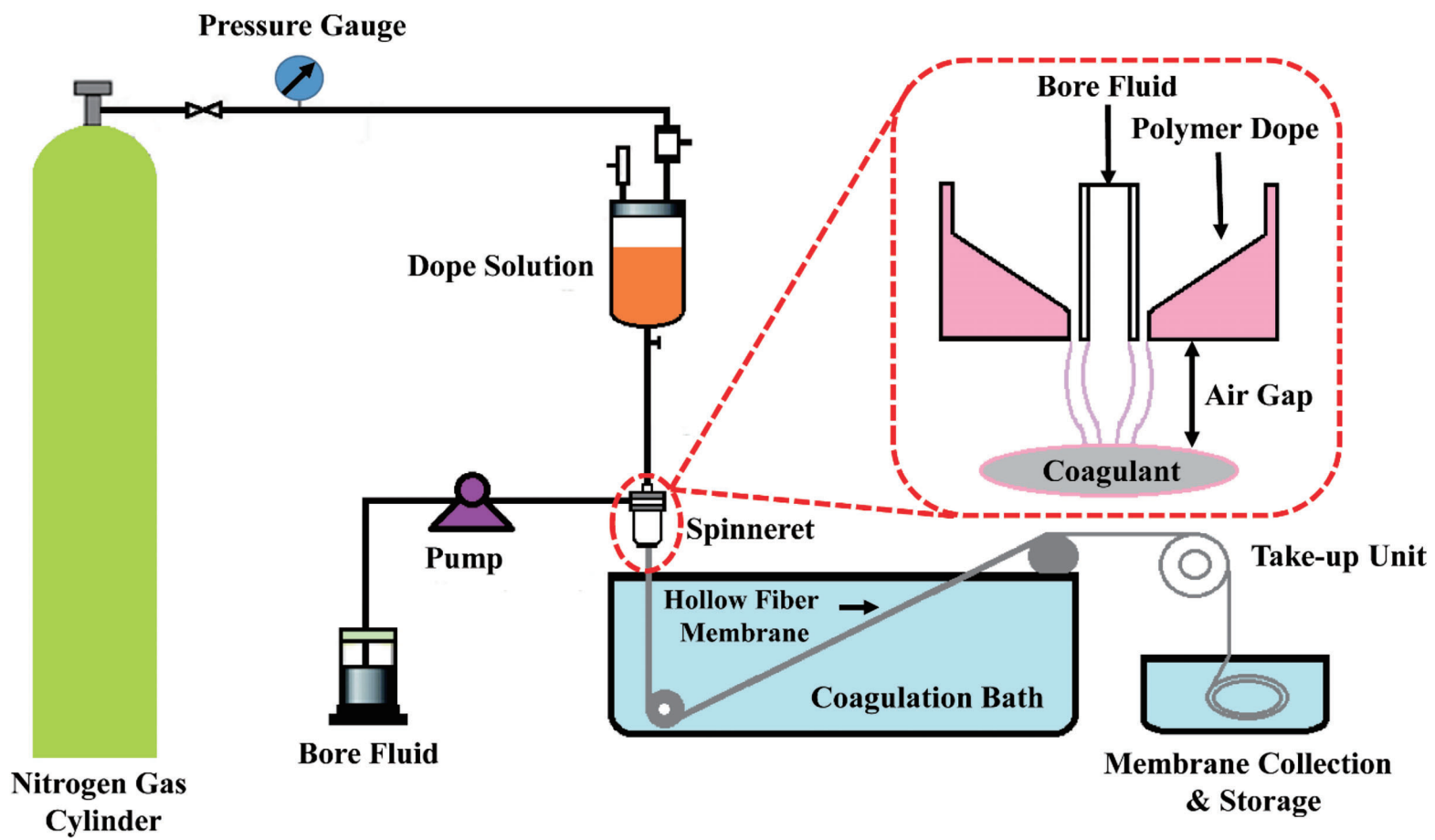


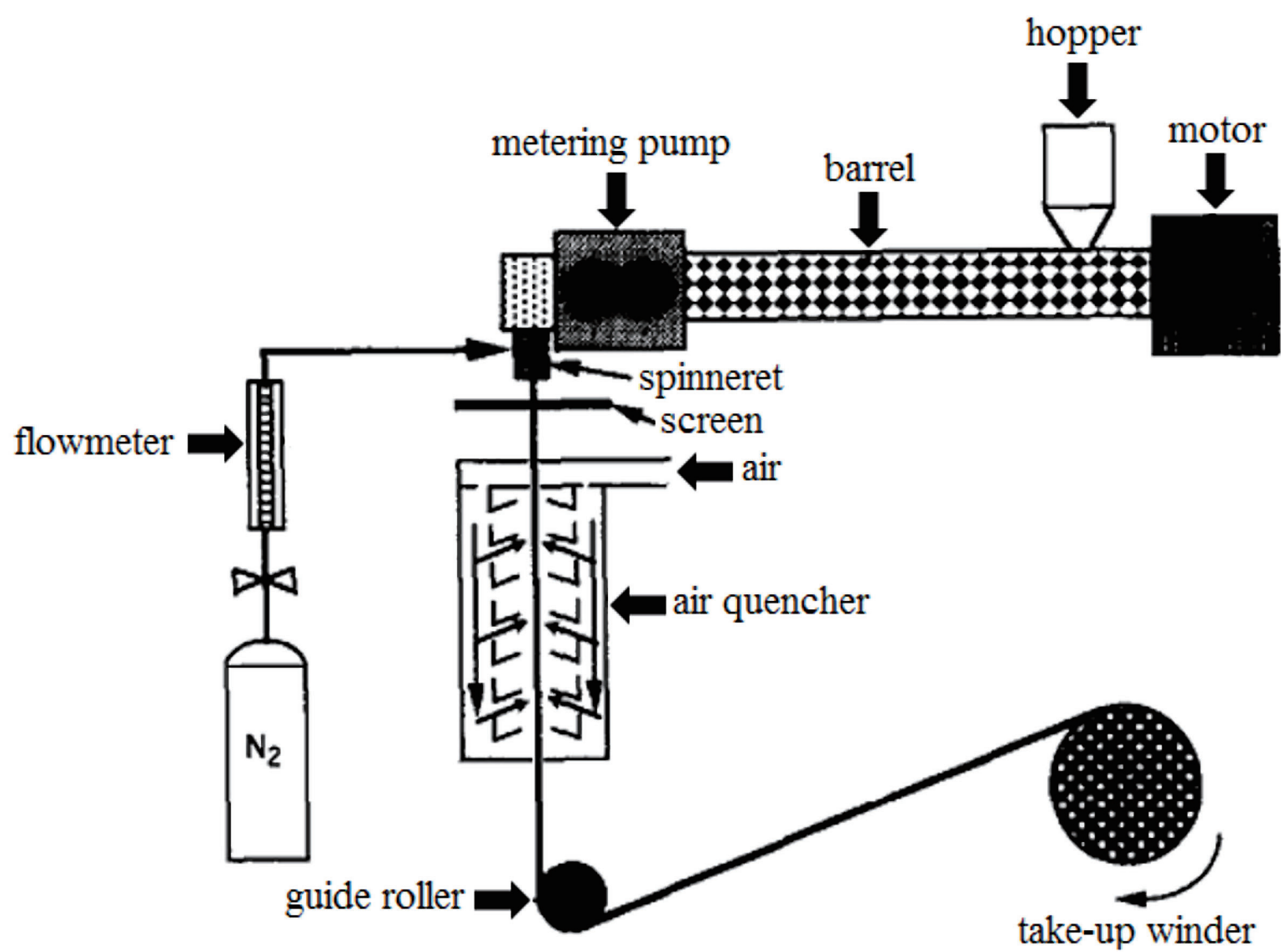








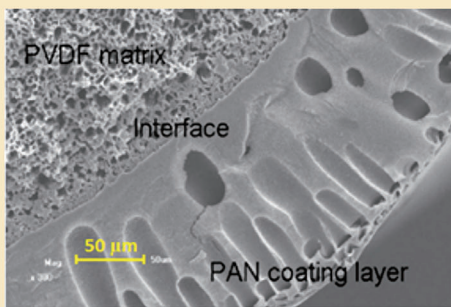




## Common methods of reinforcing HFMs

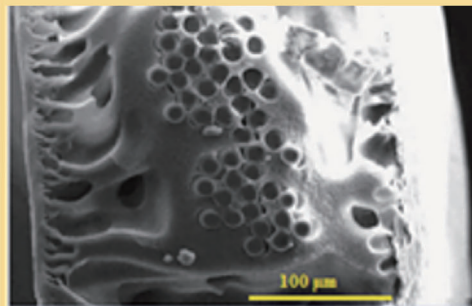
Porous matrix membrane reinforcement

(a)



Use of fibers (threads or filaments)

(b)



Use of tubular braids

(c)

