

Solvent-resistant porous membranes using poly(ether–ether ketone): preparation and application

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Abstract Poly(ether–ether ketone) (PEEK) is a linear aromatic macromolecule, which can form semi-crystalline aggregative status, allowing PEEK materials to have strong environment tolerance and excellent physicochemical properties. PEEK materials have become a promising alternative to fabricate particular membranes used in extreme conditions. In the past few decades, many researches and evolutions have emerged in membrane fabrication with PEEK materials and its applications for treating organic solvents and their mixtures; however, there are little systematic and comprehensive literature to summarize fabrication approaches, compile applications, and elaborate PEEK property–structure relationship. In this review, the main approaches to fabricate PEEK-based membranes are illustrated concretely, including conventional thermal-induced and non-solvent-induced phase separation, and novel chemical-induced crystallization; the representative applications in ultrafiltration, nanofiltration and membrane contactor containing organic solvents are demonstrated systematically. Meanwhile, the mechanism to tune PEEK solubility in solvents, which can be achieved by altering monomers in synthesis processes or changing membrane preparation routes, is deeply analyzed. Moreover, the existing problems and the future prospects are also discussed. This review provides positive guidance for designing and fabricating membranes using PEEK and its derivative materials for task-specific applications in harsh conditions.

Keywords PEEK, phase inversion, solvent-resistant membrane, nanofiltration, membrane contactor

1 Introduction

Membrane technology has been regarded as a significant green technology and boomed over the past decades. It has many advantages, e.g., low environmental impacts, energy-saving, low capital cost, small footprint, easy scale-up and incorporation into existing technologies [1–3]. Owing to the excellent performance in these aspects, membrane and membrane processes, have occupied strategic position to address the major difficulties being faced by humanity. In details, they are playing an irreplaceable role for industrial process reengineering, resource and energy reuse, and pollutant reduction, etc. Currently, membrane separation technology has been widely used in wastewater treatment, biomedicine manufacture, gas separation, food processing, seawater desalination and petrochemical industry. It has produced huge economic and social benefits and has become one of the most promising technology in the 21st century [4–6].

Membrane, the core element of membrane processes, is the key determinant of separation performance. Membranes can be manufactured from different materials; hereinto, most of those studied and commercially used are polymeric materials, owing to their lower cost, processing ability, flexibility and variable form. New polymeric membrane materials, which are expected to improve separation performance significantly, are developing rapidly [7,8]. The commonly used polymer materials, such as polyethersulfone, polyvinylidene fluoride, cellulose acetate, polyimide, and polyacrylonitrile, have relatively low chemical, thermal and mechanical resistance, thus limits the application in many industrial separation processes such as membrane extraction, membrane distillation, nanofiltration (NF) for organic solvent recovery and gas separation from hot gas flows [9–11]. Organic solvents in some complex and

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severe separation systems always cause polymer membrane porous structure collapse, chemical structure change, degradation of polymer chain aggregation, and even dissolution of membrane materials. As a result, the separation performance of the polymeric membrane is greatly reduced or even lost. Consequently, the design and development of novel high-performance membrane materials to overcome these problems and broaden the applications of membrane process have become a chief quest to manufacture membranes with optimum performance, high energy efficiency and relatively lower cost.

As a new type of high-performance membrane material, poly(ether-ether ketone) (PEEK) is considered to be the next-generation polymer membrane material that combines the excellent stability and durability of the inorganic membrane with the flexibility and low price of the polymeric membrane. PEEK has become one of the most interesting polymeric materials used in the industry, such as aerospace, nuclear reactors, biomedical applications like bone implants, and membrane separation [12–14]. The typical properties of PEEK are shown in Table 1. As a semi-crystalline polymer with a rigid aromatic backbone structure, PEEK's desirable properties like mechanical strength, chemical resistance, and high thermal stability make it a suitable polymer for membrane separation in harsh environments. It can not be ignored that the very low solubility of PEEK polymer caused by strong solvent resistance makes the fabrication process of membrane difficult, limiting its application in membrane separation [15]. To address this critical problem, many researchers have been trying to modify the PEEK polymer chain to realize the flexible adjustment of solubility and design different fabrication projects to

obtain PEEK membranes with various structures. So far, there is little comprehensive review on the research progress of PEEK in the field of membrane separation.

This article reviews and provides insights into the preparation and regulation of porous membranes based on PEEK polymers and their applications in extreme conditions such as organic solvent resistant, NF and membrane contactor. The solvent solubility of PEEK could be flexibly modified by altering monomers in the synthesis process or changing the route of membrane preparation. Meanwhile, the main challenges and future research prospects of preparing high-performance PEEK-based membranes are discussed. Therefore, this review aims to be used for designing and fabricating such membranes from PEEK and related materials with task-specific properties to extend their applications in membrane separation and technology.

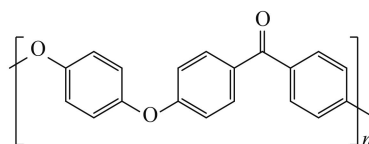
2 Preparation of PEEK membranes

There are two types of PEEK resin synthetic routes. The first synthetic route is conducted using diphenyl ether and isophthaloyl chloride as raw materials at low-temperature, along with side reactions such as polymer branching and cross-linking which may reduce the product yield [18]. The second and currently available industrialized production process is made from monomers difluorobenzophenone and hydroquinone through a nucleophilic aromatic substitution in polar aprotic solvents in the presence of alkali-metal carbonates [19]. The research groups of Zhang and Wu of Jilin University have conducted years of study on nucleophilic routes, and have made many major achievements such as PEEK resins with high heat resistance and good mechanical properties [20].

PEEK is a linear aromatic semi-crystalline thermoplastic polymer composed of repetitive units of one ketone bond and two ether bonds in the main chain structure. The molecular structure of PEEK is shown in Scheme 1. The conjugated double bonds existing in the main chain make the molecule good regularity, high modulus and good mechanical properties. At the same time, due to the strong intermolecular force and crystallinity of rigid molecules, the molecular chains are tightly packed and the penetration of solvent molecules is difficult, resulting in outstanding solvent resistance and chemical stability. The high chemical bond energy and

Table 1 Typical properties of PEEKs [16,17]

Physical property	Nominal value
Specific gravity	1.30 to 1.37
Molding shrinkage (flow 23 °C)	0.001 to 0.016 m·m ⁻¹
Water absorption (23 °C, 24 h)	0.049% to 0.21%
Mechanical	
Tensile modulus (23 °C)	2612 to 4770 MPa
Tensile strength (yield, 23 °C)	72 to 111 MPa
Tensile strength (break, 23 °C)	70 to 99 MPa
Flexural modulus (23 °C)	2909 to 4432 MPa
Flexural strength (23 °C)	116 to 155 MPa
Coefficient of friction	0.08 to 0.53
Thermal	
Glass-transition temperature (T_g)	143 °C
Melting temperature (T_m)	343 °C
Soluble	
Solubility parameters/(cal·cm ⁻³) ^{1/2}	
δ_d	10.07
δ_p	2.28
δ_h	3.03
δ	10.76



Scheme 1 The molecular structure of PEEK.

strong rigid chain endow the material with excellent thermal stability. T_m and T_g are 334 and 143 °C, respectively. The achievable crystallinity of PEEK is usually between 20% and 30%, a maximum of 48% [21]. The above properties endow PEEK with high heat-resistant grade, chemical resistance, and excellent electrical properties, coupled with outstanding wear resistance and easily serializable, which make PEEK polymer an indispensable key material widely used in the fields of aerospace, medical, energy, electrical and electronic.

Owing to good chemical stability, PEEK is insoluble in common organic solvents such as *N,N*-dimethylformamide (DMF), dimethylacetamide (DMAc) and *N*-methyl pyractyl anhydride (NMP), resulting in great difficulties in the preparation of membrane. PEEK is only dissolved in strong protic acid such as sulfuric acid (SA) and methanesulfonic acid (MSA) at room temperature, and soluble in high-boiling esters, benzophenone or diphenyl sulfone at a temperature close to the melting point [22–24]. In the following section, the PEEK is introduced and different membrane preparation approaches and mechanisms are reviewed.

2.1 Thermally induced phase separation (TIPS)

For many semi-crystalline thermoplastics, membrane fabrication using conventional solvent-based methods is difficult, owing to the chemical intractability of the materials. Accordingly, PEEK is insoluble in vast majority of solvents. The TIPS process has been proven to be an effective and versatile technique for the preparation of microporous membranes from advanced engineering thermoplastics such as PEEK [25,26]. In TIPS, the polymer is dissolved in a solvent, where the solubility between the polymer and solvent is temperature-dependent. The polymer-solvent blend is extruded or cast at a relatively high temperature, and as the temperature falls to ambient, the polymer phase separates from the solvent through solid-liquid or liquid-liquid phase separation and eventually solidifies. The solvent is subsequently removed in a leaching step and the selective extraction of the solvent provides the desired structure [27]. The TIPS approach is particularly advantageous for the high-performance polymers which cannot be prepared into membranes by solvent inversion methods smoothly due to poor solubility, so it is a good choice to fabricate PEEK porous membranes.

PEEK porous membranes were generally prepared with high boiling point solvents and plasticizers. Although several suitable low molecular weight diluents were studied in TIPS, the viscosity of PEEK/diluent homogenous solution formed at high temperature is too low to form membranes [28]. In the TIPS process, the casting solution formed after polymer/solvent blending must have a certain viscosity to form a usable and

effective membrane successfully. For example, a vast majority of PEEK (~70%) is required to meet the viscosity requirement after dissolution at a high temperature with the solvent of diphenyl terephthalate. Unfortunately, membrane with high polymer concentration usually shows poor permeability performance [29]. One remedy proposed for this problem is the introduction of a second, amorphous polymer as a plasticizer in the melt binary system mixture to increase the viscosity. The second polymer must be miscible with PEEK at the phase inversion temperature, while insoluble at room temperature, and able to be removed by dissolving in the extractant [30].

Polyetherimide (PEI) is an amorphous engineering thermoplastic material with a high glass transition temperature and excellent toughness. Unlike PEEK, PEI is soluble in varieties of common solvents and can be melted miscible with PEEK at all compositions to increase the viscosity of the solution system, suitable for preparing PEEK membrane as a diluent via TIPS [31,32].

Unlike the amorphous material PEI, PEEK is a semi-crystalline polymer. In the process of membrane formation, the semi-crystalline polymers undergo crystallization while amorphous polymers remain unchanged. The semi-crystalline solidification of homogeneously mixed polymer blends is a highly complicated process, and phase separation occurs during the crystallization of the PEEK component. The solid-liquid phase separation characteristics of the PEEK/PEI blends were investigated by microscopy and thermal analysis methods [33,34]. Mehta and Kalika [30] blended PEI as a diluent with PEEK to prepare PEEK microporous membranes by TIPS, and studied the effect of PEI on the PEEK membrane formation mechanism. The presence of PEI reduced the overall crystallization rate of PEEK in the process of forming membranes by solid-liquid phase separation, which could be exploited for improved control of the morphology of the fabricated membrane. During PEEK crystallization, amorphous PEI components exist in the interlamellar, interfibrillar and interspherulitic regions of the evolving crystallites, as shown in Fig. 1. PEI existing in the interfibrillar and interspherulitic regions can be removed completely by solvent extraction and result in porous membranes; however, PEI trapped in the crystal lamellae is extremely difficult to be extracted due to regular crystal barrier. In this instance, the residual PEI may reduce porosity and inhibit the pore connectivity of PEEK membrane, increase the mass transfer resistance and reduce permeability to some extent.

When the annealing temperature or the proportion of PEI in the mixture is relatively lower, the crystallization rate of PEEK is relatively fast and the diffusion rate of PEI is slow, thus the phase separation kinetics is controlled by the crystallization of PEEK, leading to the formation of a spherical grain structure with few



Fig. 1 Distribution models of the PEI in the PEEK crystalline region.

interspheroidal pores on the surface of the membrane. The PEI chain is mainly trapped in the interlayer region of the PEEK crystal, and the formed membrane has the characteristics of small pores, low porosity, narrow pore size distribution, compact structure, and low permeability. On the contrary, when the annealing temperature or the PEI content is higher, the PEEK crystallization rate is slower and the PEI diffusion rate is faster, thus the diffusion of PEI chains plays a dominant role in the phase separation. The PEI that exists in the interfiber and interspherulite regions quickly diffuses to form a large-sized pore with a loose structure and high surface porosity. Relatively regular pores are generated from the PEI between interfibrillar, while PEI in the interspherulite region is extracted to form relatively rough pore structures. Therefore, the structure and properties of PEEK membrane can be effectively controlled by adjusting the heat treatment conditions and the content of PEI. In addition, the molecular weight of PEI, related to the viscosity of the casting solution and the diffusion rate of PEI chain, is another influential factor to determine the residual amount of PEI in PEEK and regulate the pore structure of the membrane [30,35].

Dynamic mechanical thermal analysis (DMTA) can be used to study the distribution of PEI diluent in the crystallized blend matrix; however, this method does not give the information on the size scale of the extracted PEI to distinguish between interfibrillar and interspherulitic phase segregation, which is critical for establishing the pore size characteristics of membranes and developing strategies to optimize membrane separation performance. The special combination of semi-crystalline material (PEEK) and amorphous material (PEI) is an attractive system, due to not only the remarkable stabilities of this blend membrane, but also the improvement of solubility and crystallinity of PEEK by PEI. Bicakci and Cakmak [36,37] conducted a series of phase separation and crystallization behavior studies specifically for the crystallizable and amorphous blend of PEEK/PEI mixtures involving binary and ternary blend systems. An approximate ternary phase diagram of poly(ethylene 26-naphthalate) (PEN)/PEEK/PEI was drawn based on the results of differential scanning calorimetry (DSC) and DMTA techniques. PEEK and PEN are immiscible originally, while the addition of PEI facilitates the

miscibility. The addition of 10% PEI causes the domain sizes to decrease, and beyond 40% PEI concentration results in the homogenization of the three-component system, indicating that PEI in this ternary system acts as a special common solvent for PEN and PEEK [38].

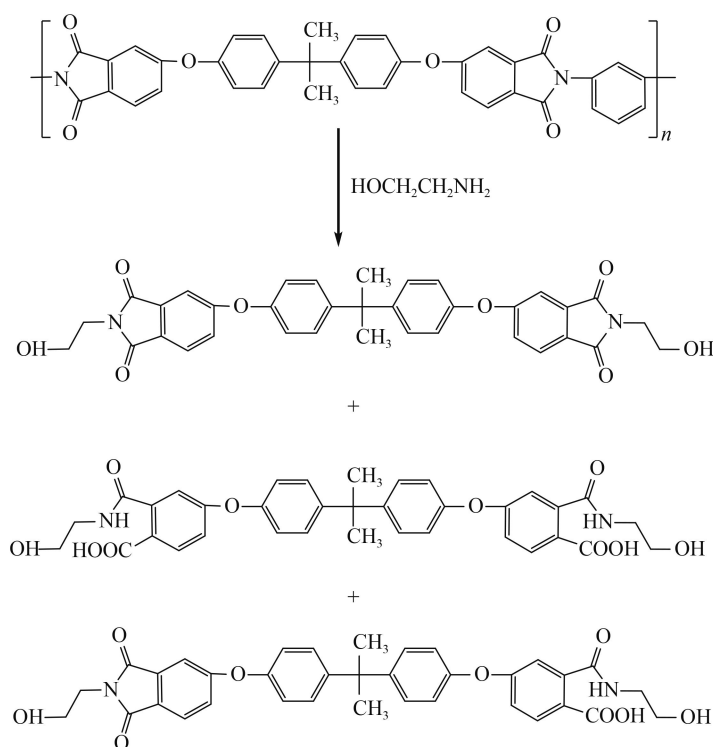
Sonnenschein [29] blended diphenyl isophthalate with diphenyl terephthalate in a certain proportion as a solvent, polysulfone, polyethersulfone and PEI acts as a plasticizer to increase the viscosity of the PEEK casting solution. Diphenyl isophthalate delays the recrystallization of the system in the process of membrane fabrication, which allows easy handling of the membrane. The blend casting system here exhibited a concentration-independent recrystallization temperature, demonstrating that the liquid–liquid phase separation occurred before solid–liquid phase separation, which was beneficial to obtaining a membrane with narrow pore size distribution and high flux. As the second polymer, polyethersulfone exhibited a relatively rapid phase separation from the molten polymer blend and formed a highly coarsened structure with relatively large maximum and mean pore sizes. PEI is too miscible with PEEK and there was still residue after multiple extractions, leading to dense membrane pores along with difficult control of the membrane pores shrinkage. Polysulfone shows moderateness between the two extremes. Subsequently, polysulfone was chosen as the second polymer, methylene chloride as the extractant, and HB-40 (a blend of hydrogenated terphenyls from Monsanto Corporation) as pore shrinkage agent to reduce the pore size of the membrane, ultimately asymmetric PEEK microfiltration (MF) and ultrafiltration (UF) membranes were prepared [22,39]. The membrane structure assumed a certain asymmetry through virtue of the differential quenching, but the degree of asymmetry is significantly much less than that obtained via non-solvent induced phase separation (NIPS). The performance of the PEEK MF membrane prepared by TIPS was similar to that of other polymers at the time, while the UF membrane suffered from relatively low permeation performance. The lower membrane asymmetry caused by a relatively high density of membrane led to insufficient membrane surface porosity and denser membrane pores, which was responsible for the membrane performance. It's a feasible solution to reduce the concentration of PEEK and

polysulfone to improve the membrane porosity, but at the same time, the very low viscosity of the casting solution will hinder the fabrication of membrane.

Due to the entanglement of PEEK and PEI chains, complete removal of PEI phase is almost impossible by conventional leaching extraction during the PEEK membrane preparation process with TIPS method, which affects the property of membrane to some extent as mentioned earlier. Ding and Biston [40] prepared PEEK porous membranes by selective chemical decomposition to remove PEI, and called this novel membrane preparation process as reactive porogen removal (RPR) process. Precursory PEEK/PEI blend hollow fibers were heated to 250 °C to form a semi-crystalline PEEK network and then submerged into an NMP solution containing 5 vol % mono-ethanolamine and 5 vol % water, among which the non-toxic, harmless and inexpensive primary amine reagents was used to selectively decompose the PEI phase, as shown in Scheme 2. As expected, the PEI polymer chain was decomposed into small fragments and then quantitatively removed, leading to high porosity, relatively loose and porous semi-crystalline PEEK hollow fiber membrane structure with high permeability. The average pore size of PEEK/PEI (50/50) membrane is smaller than that of the PEEK membrane obtained by solvent extraction of PEI by Mehta and Kalika with the traditional TIPS method [30]. The pore size of PEEK membrane prepared by the RPR method was in the mesoporous range with a remarkable material surface area of 264 m²·g⁻¹ [41]. The

fabricated porous hollow fiber membrane behaved with a uniform pore size distribution, and outstanding thermal and chemical resistant capability, expecting to serve as the ideal supporting substrates of composite membranes applied in organic-resistant NF and membrane contactor.

Researches about the PEEK membrane preparation via TIPS have shown that solvent-induced crystallization occurs when PEI is extracted from PEEK/PEI blends, which further leads to the solid–liquid phase separation of PEEK and PEI [30,42]. Chen and coworkers [43] studied the effect of solvent-induced crystallization on the structure and properties of PEEK hollow fiber membranes by changing the composition of extractants during the extraction process. DSC analysis showed that the melting point and crystallinity of the PEEK membrane after extraction were increased, confirming the solvent-induced PEEK crystallization, which increased the size of the PEEK crystalline region and promote further phase separation of PEEK and PEI to increase the size of the PEI phase domain and pore size of the membrane. In general, the stronger the polymer-solvent interaction, the higher the crystallinity. Ethanolamine can form hydrogen bonds with PEEK, and the polarities of dichloromethane and PEEK are similar, while the polarity of NMP is quite different from that of PEEK. As a result, the extraction ability and solvent-induced crystallization of the composite extractant (80 vol % NMP, 10 vol % ethanolamine and 10 vol % water) were the strongest, while the extraction ability of NMP was stronger than that of dichloromethane, but the crystallization of PEEK



Scheme 2 Mechanism of PEI chemical decomposition by ethanolamine.

induced by NMP was the weakest. These results indicated that the extraction ability of the extractant and the solvent-induced crystallization in the extraction process has a remarkable influence on the pore structure, permeability, and mechanical property of PEEK membranes.

In summary, PEEK could be fabricated into a homogeneous or a weak anisotropic membrane structure with pore size in the range of MF and UF via TIPS method without any use of strong corrosive and sulfonated acid. The produced porous membrane can be used as organic solvent-resistant MF/UF membranes for solvent-phase filtration and membrane contactor for ions extraction and gas capture. Although the membranes have open pores on the surfaces thereof, the permeability and fractionating characteristics of the membrane cannot reach an excellent balance, which is a great limitation on the subsequent industrial application.

2.2 Non-solvent induced phase separation

The NIPS, known as the immersion precipitation phase inversion and shortened for the L-S phase inversion, is an efficient membrane preparation method introduced by Loeb in the 1960s [44]. In a typical NIPS process, an appropriate non-solvent is induced into a homogeneous polymer-solvent solution, where the solvent and non-solvent exchange through mutual diffusion in the mixture, forming a porous membrane. The asymmetric membrane structure prepared in this way has the advantages of excellent permselective properties, and the membrane pore structure is easy to regulate [45,46]. Owing to many advantages such as versatility, simplicity and processing ability at room temperature, NIPS has become one of the most powerful methods for preparing porous polymer membranes in current research and commercial production process [47,48].

Despite strong solvent resistance, a German patent [49] proposed for the first time that PEEK can be prepared into porous membrane via NIPS when dissolved in concentrated SA. However, the membrane formed is no longer the original PEEK but rather has been sulfonated. As a consequence of the change of chemical structure, the membrane loses the advantageous properties of PEEK and is known to swell upon prolonged exposure to water [50]. Lawrence et al. [51,52] proposed to use non-sulfonated acids such as MSA and trifluoromethanesulfonic acid as solvent, and SA as a diluent, to prepare porous PEEK membrane via NIPS, avoiding the sulfonation of PEEK. Compared with the PEEK membrane prepared by TIPS, it has excellent water permeability and separation performance. Restricted by strong corrosive acidic solvents, the PEEK membrane pore structure is maintained in the UF range and is not easy to alter, mainly suitable for use as a UF membrane or reverse osmosis supporting substrate.

Livingston et al. [23,53] dissolved PEEK powder in a mixture of MSA and SA (weight ratio of 3:1), deionized water used as non-solvent, to fabricate PEEK asymmetric membranes via NIPS. The pore size of the PEEK membrane prepared is in the UF range, and further solvent exchange and drying process could narrow the pore structure to obtain NF performance with a molecular weight cut-off (MWCO) range of 350–500 g·mol⁻¹. The membrane selectively holds excellent resistance to polar aprotic solvents, acids and bases. The solvent exchange from water to isopropanol, methanol, ethanol, *n*-hexane, acetone, or tetrahydrofuran (THF) was considered to be an effective method for regulating membrane pores, which was confirmed in experiments, and the porosity of the dried membrane was found to be inversely proportional to the solvent surface tension and the solvent boiling point [54]. Polymer membranes in organic solvent system generally suffer from increased brittleness, decreased permeability and enthalpy, and alterations in other properties, due to the aging phenomenon caused by re-arrangement of the polymer chains. With a rigid aromatic backbone structure constituted of hydroquinone and benzophenone segments, PEEK appears to stay in a stabilized equilibrium state following membrane formation and does not undergo free volume collapse or become brittle even under extreme conditions of high-temperature air annealing and high-temperature solute filtration with aggressive solvents [55]. The possible reason is that PEEK has a strong tendency for a uniplanar lamellar orientation in its growing spherulites, and the amorphous phase trapped within these spherulites would be substantially immobilized and hardly susceptible to ageing.

Huang et al. [56] measured the linear cloud point curve of the PEEK/MSA/SA/H₂O quaternary system, showing that water is a strong non-solvent of PEEK. Due to strong hygroscopicity of the mixed acidic solvent of PEEK casting solution, phase separation occurs even when water vapor is absorbed from the air. They attempted to separate liquid–liquid separation and solid–liquid separation during membrane formation, but failed. From a thermodynamic point of view, these two separations may occur at the same time. The fabricated PEEK membrane was utilized in a membrane contactor to strip lithium-ion from lithium-contained organic solvent with 7 mol·L⁻¹ HCl, exhibiting outstanding solvent resistance and stable mechanical property. To further increase the ion diffusion flux, sulfonated PEEK (SPEEK) was blended with PEEK to optimize the membrane structure [17]. During the phase inversion process of the SPEEK/PEEK blend membrane, when the SPEEK content is lower than 50%, the rigid structure formed by PEEK crystallization dominates, and the interference of SPEEK is not important; when the SPEEK content is higher than 50%, the amorphous SPEEK disrupted the crystal formation of PEEK in the secondary phase separation, resulting in

open membrane pore structure and lower permeation resistance. Their studies broadened the application scope of PEEK membrane and introduced new stable polymeric materials for membrane contactors.

Shimoda and Hachiya [26,57] proposed a two-step phase inversion method for the preparation of solvent-resistant PEEK membranes in the patent to diversify the morphology of the membrane. After the PEEK resins were completely dissolved, it was exposed to a small amount of thickener with low solubility or a poor solvent with low compatibility to achieve microphase separation conditions, then immersed in the second coagulation bath for complete phase separation, and finally passed through the heat treatment to produce PEEK MF membrane with larger pores. The heat treatment process is to improve the crystallinity of the PEEK membrane and ensure that it still maintains excellent solvent resistance at high temperature. Li et al. [58] used this improved NIPS method to design a porous PEEK membrane with a uniform sponge-like structure by delaying the phase separation process, and investigated its application in lithium-ion battery for the first time. Compared with the traditional NIPS process, they altered the mass ratio of MSA and SA mixture to 10:1, reducing the content of strong water-absorbing SA with sulfonation function. Firstly, a homogeneous fluid gel-like precipitate, composed of polymer, solvent and non-solvent throughout the whole membranes, was obtained after the casting solution was cast and transferred to water for about 10 min. Subsequently, it was completely immersed in water for curing, and the whole gel-like substance was solidified at a similar time to form a sponge-like structure throughout the membrane cross-section. The polar oxygen atoms and carbon–oxygen double bonds in the PEEK polymer showed strong interaction with the carbonate electrolyte, so the obtained sponge-like porous

PEEK membrane had a high affinity with the electrolyte. As a consequence, the electrolyte absorption rate reached 251% with high thermal stability, no decomposition occurring even at 350 °C.

Niu et al. [59] prepared a sponge-like PEEK/poly(vinyl pyrrolidone) (PVP) (referred to as S-PEEK/PVP) membrane by vapor-induced phase separation using water-soluble polymer additive PVP as a pore-forming agent. As a comparison, an F-PEEK membrane with a finger-like structure was prepared by immersion directly into water and a pure S-PEEK membrane without PVP with a sponge-like structure was fabricated via vapor-induced phase separation, respectively. As shown in Fig. 2, the initial liquid PEEK/PVP solution film was first exposed to a water vapor environment with a humidity of $37\% \pm 3\%$ for 10 min, due to the hygroscopicity of SA/MSA solvent blend, the water vapor in the environment slowly diffused into the polymer solution to cause phase separation. The semi-finished membrane was then soaked into a water bath, completely removing the acidic solvents and most of the PVP additives, to form an S-PEEK porous membrane with a much open structure. On the contrary, an obvious asymmetric figure-like morphology was obtained in the F-PEEK membrane from the typical NIPS. The vapor absorption process was slow and the mutual-diffused acid/water mixture acted as a mild precipitation media to induce a slow demixing process, favorable for the membrane pore growth. Compared with the pure S-PEEK, owing to the obstruction for PEEK chains to form a regular crystalline structure brought by PVP polymer chains, the solid–liquid demixing was delayed in PEEK/PVP system, allowing large pores to form with the growth of the polymer-lean phase. The high open interconnected pore structure was ascribed to the absence of entanglement between PVP and PEEK during the secondary

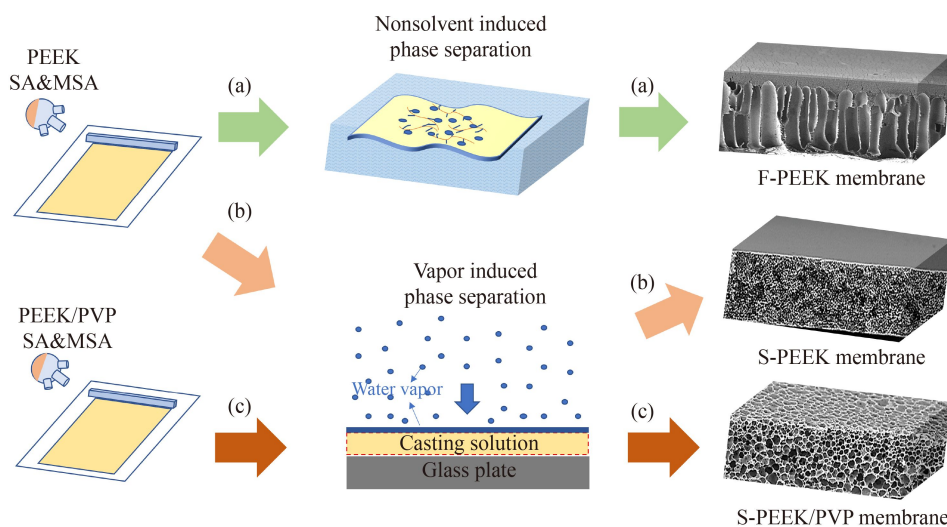


Fig. 2 Membrane preparation process via NIPS and a two-step NIPS (temperature = 25 °C, relative humidity = $37\% \pm 3\%$). Reprinted with permission from Ref. [59], copyright 2022, Springer.

solid–liquid phase separation. On the other hand, the polymer-lean phase increased by approximately 20% with the addition of PVP to generate more connected pores in membrane, which is meaningful to the separation performance of membrane.

From this section, it could be summarized that PEEK porous membrane with asymmetric structure can be prepared via conventional NIPS with the blend solvent of SA and MSA. The pore size of the prepared membrane is in the range of UF and NF, which can be adjusted by the variation of polymer concentration, solvent exchange and drying process. The membranes with asymmetric structure have excellent permeation flux and selectivity simultaneously, which can be used for solvent-resistant UF, NF and membrane contactor. On the other hand, PEEK membranes with tunable symmetric sponge-like structures could be obtained by a two-step NIPS method, providing more options for high-power battery separators such as sodium batteries and lithium–sulfur batteries. It should be mentioned that further systematic research on the unique phase separation mechanism in NIPS process is necessary and significant in the following work.

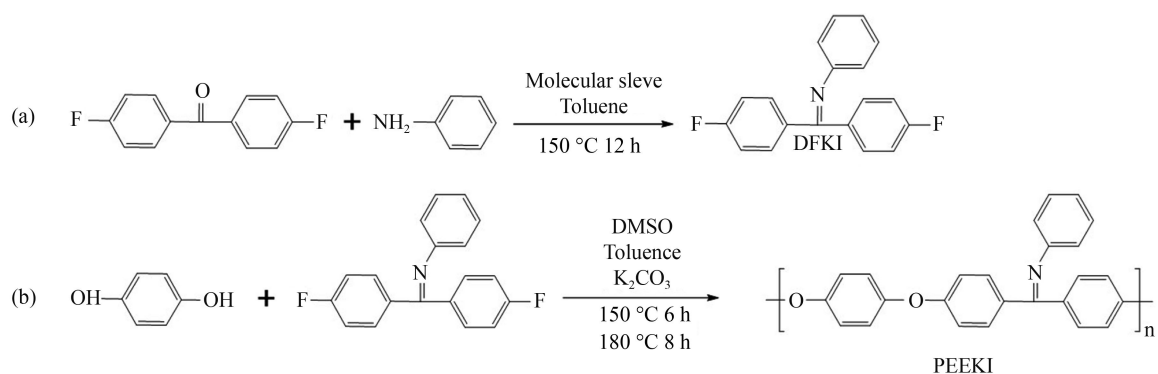
2.3 Chemical-induced crystallization

In the fabrication of PEEK asymmetric membranes, although researchers have improved the traditional NIPS phase separation, the use of strong corrosive acid solvents has always been unavoidable. The sulfonic acid solvent always causes more or less sulfonation and backbone degradation of PEEK, which destroys the crystallinity of PEEK and reduces its inherent chemical resistance, meanwhile bringing difficulty to regulate the membrane structure. Considering the industrial fabrication in continuous machines, the risk of corrosion caused by strong acid cannot be ignored, the production of PEEK asymmetric membranes with common solvents is valuable and practical, thus the chemical-induced crystallization (CIC) method was proposed [24,60].

Under an acidic environment, amorphous polymer precursors can be easily transformed into the semi-crystalline structure by Schiff base hydrolysis. In the

process combined the traditional NIPS and one-step heat treatment, the amorphous precursor polymer poly(ether-ether ketimine) (PEEKI), which can be dissolved in conventional organic solvent, was synthesized first; then the PEEKI asymmetric membrane was prepared by NIPS, and finally the HCl heat treatment was carried out to convert PEEKI membrane to PEEK counterpart [61]. The synthesis route of *N*-phenyl (4,4'-difluorodiphenyl) ketimine (DFKI) monomer and amorphous PEEKI is outlined in Scheme 3 and the conversion process from PEEKI membrane to PEEK membrane is depicted in Fig. 3. During the transition process, the polymer chains were rearranged in the membrane, and the aggregated state changed from amorphous to semi-crystalline. This method not only solves the insoluble problem during the traditional preparation of PEEK membranes, but also maintains various excellent properties of PEEK materials. The obtained membranes kept stable after being soaked in organic solvents for 120 h [60]. More interesting is that the pore size of the membrane can be regulated by adjusting the temperature since the hydrogen bond between the hydrogen atom of the acid and the oxygen atom of the polymer is affected by temperature. In addition, the structure of the final semi-crystalline PEEK membrane could be varied by regulating the morphology of the PEEKI membrane, resulting in various solvent-resistant nanofiltration (SRNF) membranes that meet the requirements of different circumstances.

Kelsey et al. [62] proposed a poly(ether ketal ketone) by the polycondensation of a “protected” monomer of 4,4-difluorobenzo-phenone with 4,4-dihydroxy benzophenone in DMAc. After modification, the carbonyl group can be recovered in 85%–98% H₂SO₄ or HCl at 160 °C. Karimi et al. [63] used *N*-bromosuccinimide to promote the substitution of aliphatic diols for 1,3-dithiones for a short period at room temperature. Manolakis et al. [64] reported that polyetheretherdithione can generate quantitatively hydrolyzable cyclic acetals that form the same PEEK as the pre-modified polymer. Another reversible derivatization of PEEK has been reported to protect the carbonyl group to form the corresponding cyclic dithioketone by heating in HCl in the presence of



Scheme 3 The synthetic route of (a) DFKI monomer and (b) PEEKI polymer.

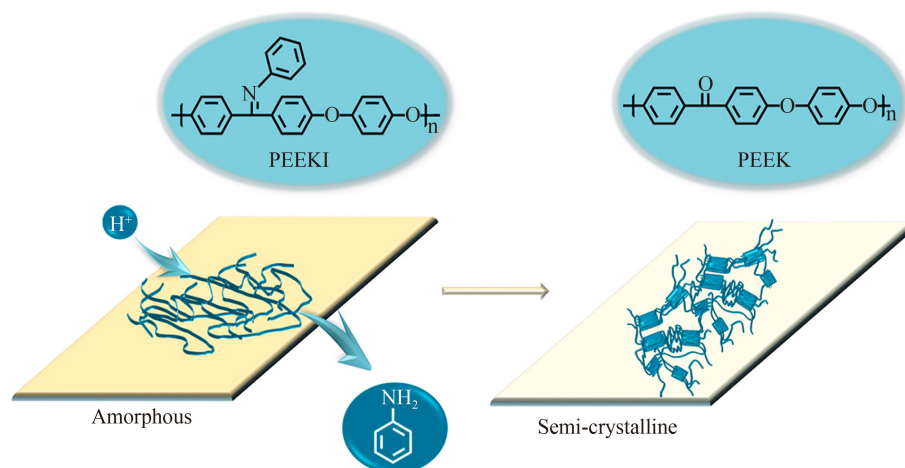


Fig. 3 Schematic illustration of PEEKI membrane transformed to PEEK counterpart. Reprinted with permission from Ref. [24], copyright 2021, Elsevier.

dimethyl sulfoxide and tertbutyl iodide for 48 h [65]. Based on previous studies above, Aristizábal et al. [66] proposed a “protection–deprotection method” to prepare PEEK membranes through a reversible chemical modification. First, the ketone groups in PEEK are chemically modified into dithione, and then exchanged with aliphatic diols in the presence of *N*-bromosuccinimide to obtain soluble precursors PEEK-1,3-dioxolane. Finally, the soluble precursors are prepared into membranes via NIPS and then deprotected by acid heterogeneous hydrolysis post-treatment to regenerate the PEEK membrane with formic acid or HCl. The resulting PEEK membranes have higher permeation flux for THF and DMF than the membranes fabricated via strong acids, along with high stability in organic solvents and at high temperatures (up to 140 °C).

The CIC method does not involve strong corrosive acid or high-temperature conditions, opening many possibilities for the formation of PEEK membranes with various morphology and structure by using common solvents. The PEEK porous membrane prepared by this technique largely retains the properties of the original PEEK materials such as organic solvent resistance, high temperature and mechanical stabilities, which endows it with unique performance advantages in the applications of solvent resistance UF, NF and high-temperature fuel cell membranes. However, the reactions between various polymers would result in different insoluble impurities, which could appear in the casting solution to affect the quality of the formed membrane and the polymer content of the final PEEK membrane is not easy to control. The last heterogeneous hydrolysis step of the conversion process may cause the problem that the groups converted incompletely and narrow the crystalline region, forming imperfections or defects in the crystals or creating a different polymer arrangement, which needs to be solved urgently in the future.

3 Applications of PEEK-based membranes

The separation process plays a more and more significant role in industries such as chemicals and pharmaceuticals, accounting for about 40%–70% of capital and operating costs, among which membrane technology is a necessary means to achieve efficient separation and energy conservation [4]. With the expansion of the application range of membranes, membranes have to face a more and more complicated separation environment due to the rapid development of industrialization and the increasingly serious crisis of energy, resources and environment. Currently, various complicated puzzles cannot be ignored in membrane separation which impeded its practical applications, among which the performance of membrane materials is the most critical. The crucial problem is the durability of membrane polymer in the challenging circumstances including combinations of organic solvents, acid, alkaline, high pressure and high temperatures could hardly be satisfied without any process [67,68]. Most of the currently available polymeric membranes require a cross-linking step to obtain membrane stability in harsh environments, such as cross-linked polyimide [69], polyacrylonitrile [70], and polybenzimidazole (PBI) [71]. As expected, insoluble in almost all organic solvents inherently, PEEK has very stable solvent resistance, thermal stability and excellent mechanical properties without any cross-linking step, making itself or functionalized derivatives suitable in various severe fields [72–74].

3.1 Special UF and MF membranes

In the field of membrane separation, low-pressure MF and UF can remove the particles above nanometers (including microorganisms) in wastewater, which is the most widely used membrane separation technology. With

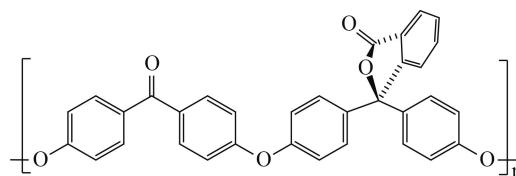
the instant development of industrialization, the composition and circumstance of wastewater are becoming more and more complex and severe. What followed is the increasing demand for porous membranes with high-performance and excellent stability used in extreme circumstances. As stated previously, the structure of PEEK endows it with invaluable stability in various complex and extreme environments without any cross-linking steps. Accordingly, PEEK-based materials were proposed as a perfect alternative class of polymer for membrane separation in harsh conditions, where almost all common polymeric materials cannot survive.

The early reports on PEEK for membrane applications were on its potential use in MF and UF, because the porous membranes prepared by PEEK polymer according to different fabrication methods fell into this range due to some kind of restriction [51,75]. In the early stages, research scholars focused on the formation mechanism and structure regulation of PEEK porous membrane via TIPS, NIPS or other derived technologies. Shimoda and Hachiya [57] proposed a NIPS process including two steps to prepare a porous PEEK membrane with excellent heat resistance, chemical resistance and a balance of water permeability and rejection performance. Mehta and co-workers investigated the preparation of MF and UF PEEK membrane from fully miscible PEEK/PEI blends by TIPS and studied the corresponding solid-liquid phase separation in detail [30,42]. Sonnenschein and his partners prepared the PEEK hollow fiber MF membrane and UF membrane using a mixture solvent of 75% diphenyl isophthalate and 25% diphenyl terephthalate, PEI, PS and polyethersulfone as a plasticizer [22]. The produced MF membranes exhibited a general performance comparable to the commercial polymer membranes, while the UF membranes suffered from relatively low permeability. The reasons for this phenomenon were ascribed to relatively low asymmetry degree and insufficient surface porosity of the membrane. Macroporous and mesoporous PEEK membranes with pore sizes in the range of 10–200 nm were prepared utilizing a two-step TIPS process, which displayed good thermal stability (stable up to 250 °C) and excellent resistance in most solvents such as NMP, toluene, and isopropanol [41]. Improved membrane separation performance can be realized by solvent-induced crystallization, which could promote further phase separation of PEEK and PEI to form larger pores in membrane [25].

There are many difficulties to overcome for the membrane preparation of native or non-sulfonated PEEK owing to difficult solubility and processability, limiting its development and large-scale application to a great extent. Designing new molecular structures with different functional groups is expected to enhance the solubility and possibility of membrane fabrication. In 1987, Zhang et al. [76,77] proposed a new amorphous glassy PEEK derivative, poly(oxa-*p*-phenylene-3,3'-phthalido-*p*-phenylene-

noxo-*p*-phenylenoxy-*p*-phenylene) with Cardo groups, abbreviated as PEEKWC (shown as Scheme 4, WC refers to the cardo group) in patent CN85108751, and then PEEKWC was used to prepare UF membrane firstly. Buonomenna et al. [78] presented a series of systematic studies on the preparation of PEEKWC UF membranes via dry and wet NIPS techniques and found that the membrane morphology and properties could be regulated by changing various parameters such as polymer concentration, exposure time of the cast film to the air before coagulation, type of solvent and non-solvent, and coagulation bath composition during the membrane preparation process. The employment of “softer” coagulation made different effects on specific systems. For the PEEKWC/DMA cast solution, the introduction of DMA solvent to the water coagulation bath promoted the sponge-like character of the membrane and increased the permeability, due to the strong interaction between water and DMA. While for PEEKWC/DMF solution, the addition of DMF to the isopropanol coagulation bath reduced the larger average pore size brought by isopropanol and the corresponding permeability of PEEKWC membrane decreased. Hollow-fiber UF membranes were fabricated from PEEKWC under different conditions, including polymer concentration in the spinning solution, height and humidity of the air gap, and PVP additives [79,80]. It is worth mentioning that owing to the short residence time of the nascent fiber in the air gap, only the air humidity close to 100% can affect the morphology and performance of the PEEKWC membrane. PEEKWC hollow fiber UF membranes have been successfully applied in the clarification of juice processing [81,82]. During the clarification of kiwifruit juice, the PEEKWC membranes exhibited a steady-state permeate flux of about 26 L·m⁻²·h⁻¹ and a nearly complete restoration of the initial hydraulic permeability was then reached after a chemical cleaning treatment with NaClO solution, benefiting from its excellent chemical stability.

In addition to direct application as UF membranes, PEEK UF membrane also can be used as solvent stable supporting substrate to prepare thin film composite (TFC) SRNF membrane due to inherent solvent-resistant stability and mechanical stability. Jimenez Solomon et al. [83] used PEEK UF membrane as a supporting substrate for the first time to fabricate TFC SRNF membranes by interfacial polymerization (IP) and confirmed that the addition of polyethylene glycols and treatment of



Scheme 4 The molecular structure of PEEKWC.

membranes with DMF would enhance solvent flux for TFC-PEEK membranes. Cao et al. [11] coated SPEEK on PEEK UF membranes to obtain a PEEK-SPEEK NF membrane after heat treatment under a $2 \text{ mol} \cdot \text{L}^{-1}$ HCl solution. The prepared membranes were used in the complex textile wastewater industry and showed outstanding organic solvents resistance and antifouling properties apart from excellent separation performance.

Applied in the field of water treatment, MF and UF membranes always face biofouling problems [84]. The non-polar aromatic backbone composed of alternate aryl ether and benzophenone groups endows PEEK with certain hydrophobic surface characteristics, which hinders its application in aqueous phase separation because of non-specific adsorption of foulants such as proteins and natural organics on the membrane surface. In general, increasing the hydrophilicity of membrane is an effective method to improve the antifouling performance of the membrane [85,86]. The hydrophilic modification methods of membranes mainly include chemical grafted hydrophilic groups, blending nanoparticles, and coated with a hydrophilic layer, among which the surface graft modification has been extensively studied and applied owing to the advantages of maintaining the bulk properties and lasting modification effect. Due to the existence of a benzophenone-like structure in the molecular structure of PEEK, ultraviolet (UV) grafting can be carried out to inarch various functional groups in the absence of free radicals generated under UV irradiation which is simple and effective for various monomers. A series of studies have been conducted on the hydrophilization modification of PEEK membranes by photografting technology to improve their antifouling performance [86,87]. What's more, the UV grafting proceeds only on the surface of the PEEK substrate, retaining the inherent properties of PEEK membrane, which is very important in the application of harsh elevated temperature or organic solvent systems. Yousaf et al. [88] grafted various polymer groups on the PEEK surface such as styrene, butyl acrylate, vinyl phosphonic acid, acrylic acid, polyacrylic acid and monomethoxy terminated oligo (ethylene glycol) methacrylate (MeOEGMA) via UV irradiation technique. The graft of MeOEGMA endowed PEEK membrane enhanced surface hydrophilicity and antifouling characteristics by preventing bioadhesion. Thermal analysis of pristine PEEK membrane and membrane grafted with any reactive monomer using TGA and DSC showed similar thermal behavior, indicating that the UV irradiation did not affect the stability of PEEK membrane. Apart from hydrophilicity, electrostatic interaction also has a certain influence on the anti-fouling performance of the membrane. Liu and coworkers [86,89] grafted negatively charged acrylic acid, neutral ethyl hydroxyacrylate, polyethylene glycols and positively charged acryloxyethyl trimethylammonium chloride (DAC) as hydrophilic

monomers respectively onto the PEEK hollow fiber membrane surface via UV irradiation polymerization. The neutral hydroxyacrylate monomer improved the permeability, hydrophilicity as well as the antifouling performance of the PEEK membrane obviously, while the introduction of two charged monomers reduced the permeability owing to the stretched conformation of the charged grafting chain caused by the mutual repulsion interaction of the graft chains. Compared with the unmodified membrane, the antifouling performance of PEEK membranes grafted with hydroxyacrylate and DAC was decreased to bovine serum albumin (BSA). Yet the detailed influencing mechanism of grafted charged monomers on the antifouling performance of PEEK membranes is still not completely clear.

As a brief perspective in this section, it can be concluded that the PEEK-based materials can be used to prepare porous MF and UF membranes by NIPS and TIPS methods, which can be further transformed into NF membranes through the post-fabrication solvent exchange, the addition of volatile co-solvent and coating procedures. The permeability and anti-fouling properties of membranes can be significantly improved via UV modification by grafting neutral monomers. According to the summarized studies, it is apparent that the high-performance PEEK-based membranes with excellent thermal and chemical resistance can be applied in high-temperature circumstances for separation in aqueous phase containing organic solvents, acids and alkali with the control of membrane pore size.

3.2 SRNF membranes

SRNF, also known as organic solvent nanofiltration (OSN), has received increasing attention since its inception in the 1990s, where small solvent molecules permeate through the membrane, while the solutes with an MWCO between 200 and 1000 Da are rejected [90]. The SRNF has been applied in a variety of complex systems due to relatively low energy consumption, significantly milder operating conditions, and no additional additives or chemical treatments are required compared to the conventional organic solvent separation technologies [91]. What's more, SRNF can be operated continuously and combined with other chemical techniques to form a coupled hybrid process, which gives it valuable advantages applied in various industries including the homogeneous catalysis [92], pharmaceuticals [93], food processing [94] and petrochemical industries [95].

It is worth noting that the scarcity of high-performance SRNF membranes able to operate stably along with effective separation performance under challenging operating conditions such as harsh organic solvents, extreme pHs, high temperatures and oxidative environments always impedes the further widespread of

SRNF in various applications [96]. Up to now, the available SRNF membranes are mainly based on polymers including polyimide [69], polyacrylonitrile [97], polydimethylsiloxane [98] and PBI [99], which required further complex chemical cross-linking process, always resulting in environmental damage and additional costs. It is known from the previous content that PEEK is a good candidate without any chemical cross-linking steps. Thence, some of PEEK-based materials have been used in the fabrication of SRNF membranes. Table 2 summarizes the properties of NF membranes based on PEEK and its derivatives.

Most of the PEEK NF membranes with organic solvent resistance are fabricated from UF membrane through multiple solvent exchange procedures, which can decrease the surface tension and minimize the risk of collapses upon consecutive drying. The post-fabrication drying process is found to be the vital reason for the transformation of separation performance from UF to NF for PEEK membrane. Bursal and coworkers [54] prepared PEEK NF membranes via NIPS method using an MSA/SA mixture solvent with 3:1 wt %, and the MWCO of the membrane varied from 295 to 1400 g·mol⁻¹ by adjusting the polymer concentration in the dope solution and change of solvent filling in the membrane pores. The introduction of volatile co-solvent to the stock solution can also adjust the pore size and structure of the membrane, leading to membranes suitable for different application systems with various morphology. A high mutual affinity solvent/non-solvent DMF/water couple resulted in a nearly symmetric spongy structure and the combination of DMA/water obtained asymmetric membranes applied in MF and UF, while the high volatility of THF and low miscibility of THF/water pair

allowed the formation of asymmetric membranes with a dense permselective top layer, suitable for NF or gas separation applications [102,106]. As expected, the pure PEEK membranes showed outstanding resistance to polar aprotic solvents, acids and bases with a relatively low degree of sulphonation.

Peeva et al. [100,107] first reported the application of PEEK membranes in OSN in 2013. The PEEK membrane was applied in a continuous Heck coupling reaction to recover palladium catalyst from aggressive solvent DMF and organic basic with high concentration (> 0.9 mol·L⁻¹ triethylamine) at 80 °C. The unit ran continuously for more than 1000 h, during which the PEEK membranes maintained their integrity and excellent stable performance with 20 times lower contamination of product than the conventional process in the same conditions, demonstrating the potential of PEEK membranes in SRNF such as continuous catalytic process and pharmaceutical industry. In another report [53], the PEEK NF membranes were compared with the commercial polyimide membrane in terms of the production process, waste treatment and economic cost at the bench and industrial scales. To sum up, the overall greenness of the PEEK membrane was much better than the polyimide-based membrane with the solvent intensity of 8.3 vs. 35–224 and the waste cost of 46 vs. 189 £·kg⁻¹ for PEEK membrane and polyimide-based membrane, respectively. At last, a scale-up of PEEK membranes to spiral-wound modules were carried out successfully with the permeation flux of THF ranging from 0.26 to 0.47 L·h⁻¹·m⁻²·bar⁻¹ and MWCO of ~300 g·mol⁻¹.

Apart from the above-described NIPS method to obtain pristine PEEK membrane by strong acid solvent, Cao et al. [60] reported a facile route combining NIPS and

Table 2 Properties of PEEK-based NF membranes

Polymer abbreviation	Solvent	Permeance ^g /(L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Solute (MWCO, Da)	Rejection	Ref.
PEEK ^{a)}	DMF	0.07	Polystyrene (480)	90%	[100]
PEEK ^{a)}	THF	0.47	Polystyrene (300)	90%	[53]
PEEK ^{a)}	DMF	0.97	RD 80 (1373)	99.9%	[66]
PEEK ^{a)}	Water ^{h)}	225	BSA (66446)	92%	[60]
		225	RB (1017)	90%	
		170	Methyl blue, MB (800)	90%	
PEEK ^{a)}	DMF	4.19	PB (305)	71.7%	[24]
		4.19	SY (452)	96.2%	
		7.68	RB (1017)	97.5%	
PEEKWC ^{b)}	Isopropanol	1.00	RB (1017) Safranin (351)	99.8% 52%	[101]
TBPEEK ^{c)}	Isopropanol	0.77	RB (1017) RA (479)	88.3% 49.6%	[102]
BPAPEEK ^{d)}	Isopropanol	0.78	RB (1017) RA (479)	89% 63.6%	[103]
Hexane diamine (HDA) Crosslinked VAPEEK ^{e)}	Acetone	0.19	RB (1017)	90%	[104]
	Isopropanol	0.11			
BPAVAPEEK ^{f)} (cross-linked polyallylamine, PAA)	Isopropanol	0.03	RB (1017)	90%	[105]
	Acetone	0.17	Sunflower oil	94%	

a)–f) Molecular structure of the PEEK-based polymers is depicted in Fig. 4. g) Permeance was tested by filtration of pure solvent. h) Permeance was tested by filtration of water after being exposed to NMP, ethanol, and THF for 120 h.

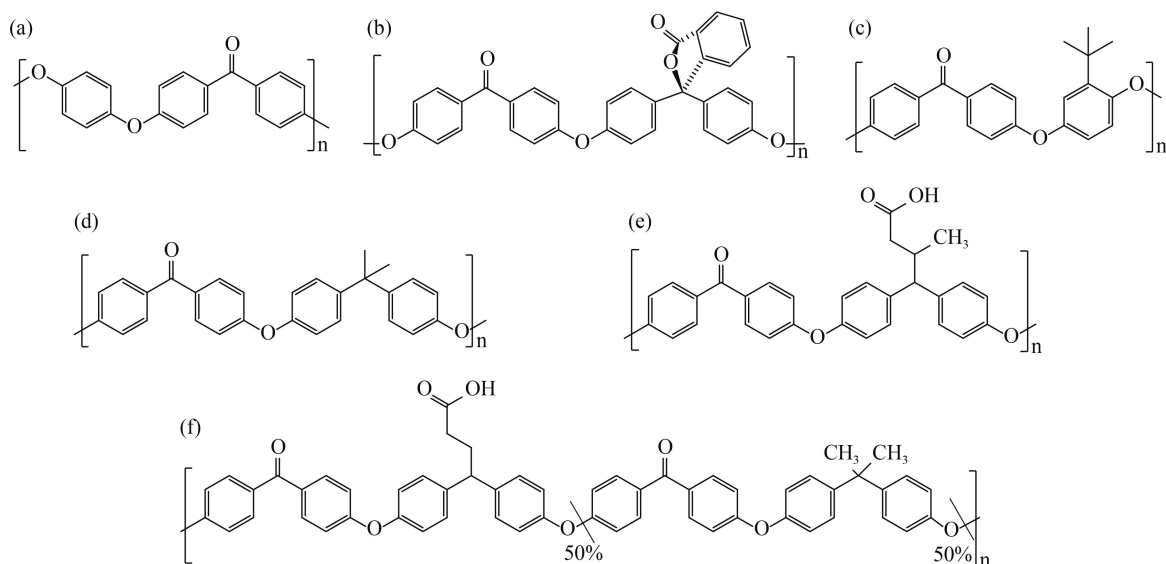


Fig. 4 Molecular structure of PEEK-based polymers in Table 2.

one-step heat treatment to prepare PEEK membranes (the mechanism has been described in Section 2.3), avoiding the problem of dissolution of semi-crystalline PEEK in membrane preparation. It was found that the obtained PEEK membrane exhibit high rejection of over 90% for BSA (66446 Da), rose Bengal sodium salt (1017 Da) and MB (799 Da), benefiting from the shrinkage of pore structure caused by heat treatment. The prepared membranes showed outstanding stability and reproducibility in various solvents even 8 mol·L⁻¹ HCl. Similarly, Zhang and coworkers [24] used the ketimine modification route to synthesize an amorphous polymer PEEKI, which was prepared into an asymmetric primary membrane as the precursor and then converted to a PEEK membrane through hydrolysis in HCl aqueous solution. DMF was used to activate the converted PEEK membrane by immersion for 30 min at room temperature. The result indicated that the separation performance of the PEEK asymmetric membrane was indeed improved through DMF activation and the optimized membrane showed an MWCO of 350 g·mol⁻¹ with a DMF permeance of 4.19 L·m⁻²·h⁻¹·bar⁻¹. In addition, the obtained PEEK membranes also possessed excellent organic solvent resistance and pressure resistance, which was very beneficial for long-term stable operation in OSN. In another study, PEEK polymer was modified first and fabricated into a porous membrane, then semi-crystalline PEEK membrane was regenerated by heterogeneous hydrolysis treatment with formic acid or HCl [66]. The semi-crystalline PEEK membrane converted from the amorphous PEEKI membrane which was immersed in water immediately after casting without THF evaporation, showed a good DMF permeability (275 L·m⁻²·h⁻¹·bar⁻¹ at 140 °C). It is meaningful that in the whole process, the PEEK membrane was obtained by the last step of hydrolysis and crystalline reconstruction without any sulfonation reaction, so it maintained the

most intrinsic high performance of pristine PEEK materials. The novel membrane fabrication method provides more possibilities for such high-performance polymeric materials which are insoluble in common solvents as PEEK and expands the application of membrane separation and purification.

Considering the difficulty in solubility of the pristine PEEK polymer, researchers turned their attention to PEEK-based materials with different side chains. PEEKWC is a widely used modified PEEK with cardo groups that has been industrially produced [108]. As an amorphous polymer, PEEKWC can be dissolved in various common organic solvents with medium polarity, such as DMAc, chloroform, dichloromethane, DMF, while alcohols, alkanes and acid are insoluble [109]. Buonomenna et al. [106] prepared a series of integrally skinned asymmetric PEEKWC membranes with various morphology and structures by the NIPS technique using DMF, DMA, THF, chloroform, dichloromethane, 1,2-dichloroethane as solvents and water as non-solvent. PEEKWC membranes used in the NF can be obtained by dry-wet phase inversion and applied in NF or membrane contactor for the aqueous solution containing organic compounds or organic solvent treatment [110]. PEEKWC NF membrane was used in alcohol solutions and compared their performance with Desal 5 DK, a commercial SRNF osmotic (hydrophilic) membrane with an MWCO of ca. 150–300 g·mol⁻¹ [101]. It was found that the optimum PEEKWC membrane fabricated with chloroform as the solvent, 0 s evaporation time before coagulation and butanol as internal non-solvent displayed similar transport properties with the commercial NF Desal 5 DK membrane and the flux of alcohols homologues (methanol, ethanol, propanol, butanol) reduced as viscosity increased.

Standard PEEK is synthesized from monomers difluorobenzophenone and hydroquinone. By altering the

original monomers 4',4'-difluorobenzophenone or hydroquinone, the obtained modified PEEK could be selectively dissolved in some solvents, which makes it suitable to fabricate membranes via the universal phase inversion technique. Hendrix and co-workers substituted monomers tertiary-butylhydroquinone (TBHQ) and bisphenol A (BPA) for hydroquinone to synthesize a soluble PEEK referred to as TBPEEK and BPAPEEK respectively [102,103]. Both TBHQ and BPA provide enough steric hindrance and affect the stacking of the polymer chain. As hydrophobic PEEK derivatives, they can be dissolved in NMP, THF, toluene and other polar aprotic solvents to prepare membranes via phase conversion. The membrane structure was regulated from UF to NF by introducing volatile THF as co-solvents, changing evaporation time and casting thickness and altering the coagulation bath composition, achieving a desirable retention of RB and rhodamine B (RA) in isopropanol. Regrettably, after the treatment in alkaline conditions (30 wt % KOH aqueous solution), the separation performance of both TBPEEK membranes and BPAPEEK membranes decreased drastically, although their mechanical stability was maintained well. Chemical crosslinking is the combination of polymer covalent bonds, which can improve the strength, heat resistance, wear-resistance and chemical stability of materials and reduce swelling and plasticization. To improve the chemical stability of the membranes, diphenolic acid containing a valeric acid group was induced into PEEK to get a modified polymer referred to as VAPEEK. The carboxylic acid of resultant VAPEEK was activated by EDC and NHS agents in the casting solution and the cast activated polymer film was crosslinked subsequently with diamines dissolved in the water coagulation bath in advance, crosslinking and phase inversion occurred simultaneously during the process of membrane formation [104]. It should be noted that they only used THF as the solvent to dissolve VAPEEK, so the residence time in the air before immersion in the coagulation bath should be kept as short as possible to avoid full volatilization of the solvent and the solidification of the nascent film, to ensure the progress of crosslinking. The resulted VAPEEK membrane cross-linked with HDA at a concentration of 10 wt % proved to be the best, fully stable in acetone with RB retention of 90% although the permeation flux remains as low as $0.19 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$. Partly built on the previous findings, this research group developed two new modified PEEK-based polymers containing valeric acid groups and introduced free amino groups with multifunctional PAA and difunctional HDA as the crosslinkers, significantly improved the hydrophilicity of the membrane, allowing the membrane applicable for edible oil purification from acetone [105]. The two novel crosslinked polymer, namely BPAVAPEEK and TBVAPEEK, owns better mechanical properties due to higher molar mass compared to the

previously prepared VAPEEK. Sunflower oil retention in acetone increased with the enhancement of membrane hydrophilicity, which reduced the affinity between the membranes and the oil. BPAVAPEEK crosslinked with PAA membranes exhibited the best retentions of oil in acetone about 94%, almost twice of other crosslinked membranes with PAA and HAD. On the other hand, it must be mentioned that the permeability of both acetone and isopropanol was much lower than that of commercial PEBAX membranes, and further research is necessary in the future.

In addition to the integrated asymmetric membrane, PEEK-based materials can also be fabricated into composite SRNF membrane, with the SPEEK, PEEK in the sulfonated form, being the most widely used one. Cao et al. reported a PEEK-SPEEK composite NF membrane prepared by coating SPEEK on a PEEK UF membrane. They synthesized an SPEEK precursor, sulfonated poly(ether-ether ketone amine) (SPEEKt), and the PEEK-SPEEK NF membrane was obtained using SPEEKt as dipping solution followed by heat treatment of HCl solution (exhibited in Fig. 5). The optimized membrane possessed an ultra-high pure water flux of $126 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ and exhibited high rejection for Congo red (CR) as 98.8% and low retention for NaCl below 10%. As shown in Fig. 6, compared with the polyamide-based commercial NFI membrane, the PEEK-SPEEK membrane regenerated completely after multiple washing with ethanol, exhibiting outstanding organic solvent resistance, chemical stability and antifouling properties, showing great potential in the sustainable treatment of textile wastewater [11]. Wang and co-workers [111] reported a ZnO nanoneedle-modified PEEK fiber membrane to separate *n*-hexane from formamide, dimethyl sulfoxide, glycol, and DMF with different polarities. First, the PEEK felts were fabricated via a nonwoven technology [112], and then surface sulfonation by extremely dilute chlorosulfonic acid was adopted to recover partial deformation of felts caused by hot-press treatment, followed by the deposition of flower-like ZnO nanoneedles through UV/ozone cleaning and hydrothermal process. The prepared PEEK-f-Z membrane proved to own high selectivity with *n*-hexane separation efficiencies varied from 98.19% to 98.62% from the above solvents and 99.99% both from normal temperature water and hot water with a high flux of $4.63 \times 10^4 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$. Furthermore, PEEK-f-Z membrane maintained stable separation performance even after undergoing 48 h high-temperature treatment at 100 °C and 200 h immersion in dichloromethane, demonstrating outstanding solvent resistance and excellent thermal stability.

From this section, it is obvious that PEEK-based membranes prepared by various methods have been widely used in SRNF such as solvent recovery and oil-water separation owing to remarkable chemical stability, mechanical and thermal resistance. Traditional

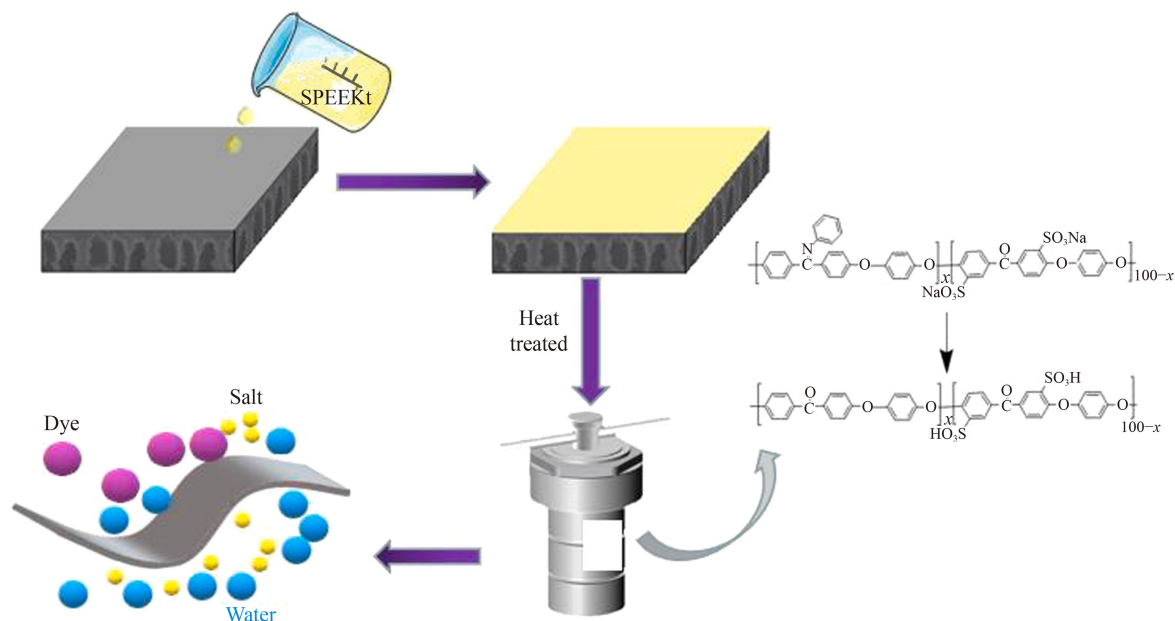


Fig. 5 Illustration for preparing the PEEK-SPEEK NF membrane. Reprinted with permission from Ref. [11], copyright 2021, Elsevier.

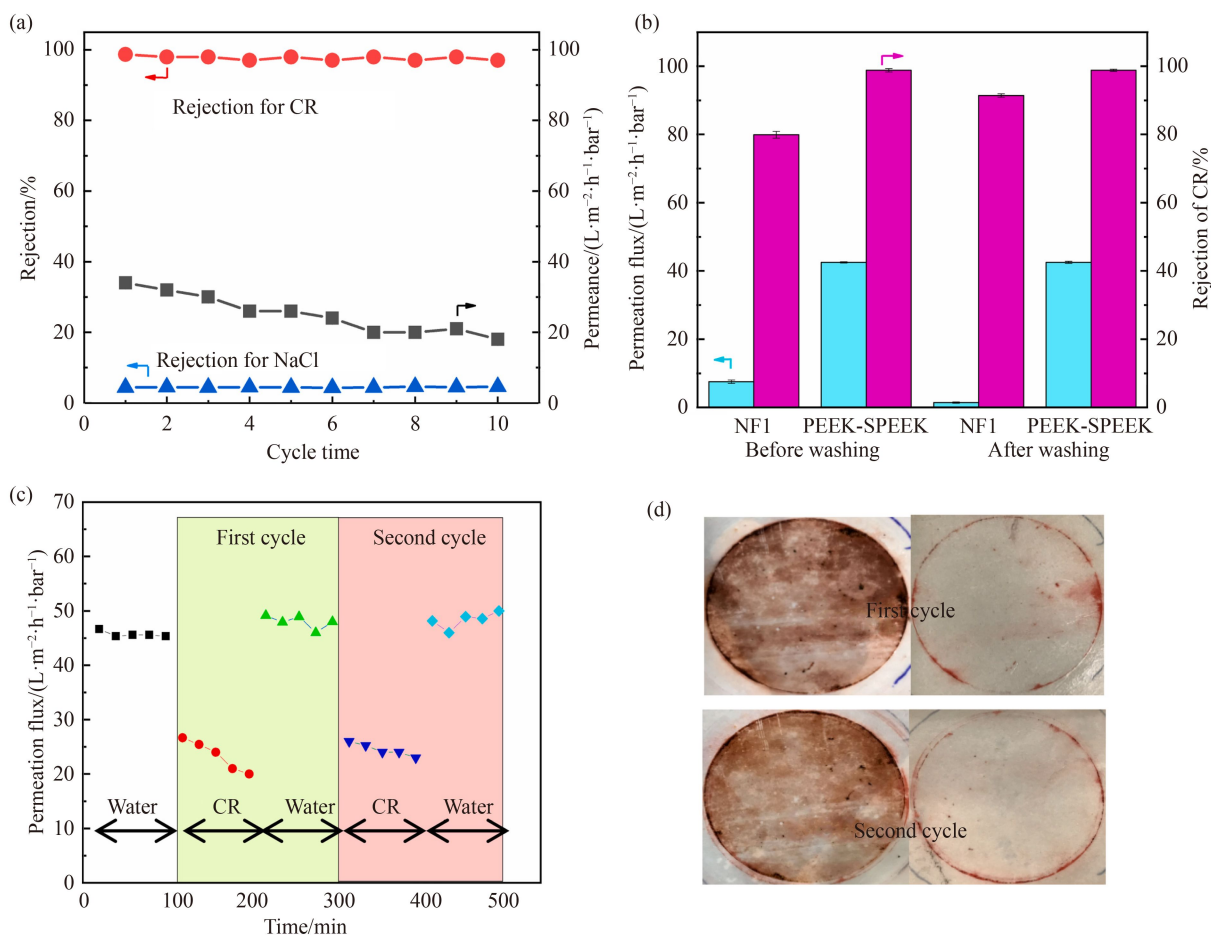


Fig. 6 (a) Long-term operation stability of membrane for CR/NaCl mixtures solution; (b) CR rejection and pure water flux variations of PEEK-SPEEK membrane and NF1 after washing with ethanol in one cycle; (c) recycling properties of PEEK-SPEEK (3 wt %) membrane during CR ($15 \text{ mg} \cdot \text{L}^{-1}$) filtration; (d) digital images of membranes before (left) and after (right) cleaning during the continuous operation. The test pressure was 3 bar. Reprinted with permission from Ref. [11], copyright 2021, Elsevier.

NIPS method using strong acid as solvent and novel CIC method are suitable for the preparation of pristine PEEK membranes with controllable morphology and distinguished stability performance to filtrate elevated temperature or/and strong acid/base/organic solutions. To enhance the separation performance and expand the application of PEEK-based membranes, it is an effective, feasible and promising method to prepare membranes via phase inversion by modified PEEK or composite membranes by dip-coating or blending with other polymer and/or organic nano-scaled fillers.

3.3 Membrane contactor

As a new type of separation technology originating from the 1980s, the membrane contactor is a hybrid technique combining the advantages of high selectivity in gas–liquid absorption or liquid–liquid extraction with membrane separation which is famous for modularization and miniaturization. Membrane contactor technology has attracted increasing attention and has been applied widely in industries due to many excellent characteristics such as lower capital costs, high mass transfer coefficient and separation efficiency, avoidance of flooding, foaming, gully flow and entrainment of foam, especially can be combined with other systems (especially desorption systems) to be further extended and easily amplified linearly [113,114]. A membrane contactor is able to provide more than 500 times the effective surface area than the traditional contact equipment in terms of liquid–liquid contact, when compared to conventional gas absorption process, the membrane contactor can provide about 30 times the effective contact area [115]. Membrane contactor is a quite extensive membrane process, including membrane distillation [116,117], membrane extraction [118], membrane absorption [119], membrane crystallization [120,121], membrane stripping [122], etc., in which the membrane is used as a tool for interphase mass transfer operations and does not act as a

selective barrier. A typical schematic diagram of the membrane contactor (combination of membrane extraction and membrane stripping process) is shown in Fig. 7. In comparison to the other frequently-used membrane processes, e.g., UF, reverse osmosis, pervaporation, the membranes used for contactor is generally not selective, and their main functions could be summarized into three aspects: combining the surface tension effect with the pressure difference and immobilizing the gas–liquid or liquid–liquid interface on membrane surfaces; increasing contact area so that mass transfer efficiency could be increased to compact equipment; providing a barrier to prevent the two phases contacting with each other directly. For a specialized membrane contactor, an ideal barrier material should be porous moderately to allow free transport of the separated component but blocking the mutual penetration between the feed and the extraction phases, and sufficient in mechanical stability, solvent tolerance, and also resistant to the organic extraction solvents. PEEK is the material with excellent performance around all these aspects, which has ultra-high thermal stability, wear-resistance and chemical corrosion resistance, making it an excellent candidate material for membrane contactor.

As one type of membrane contactors, membrane stripping is the inverse process of membrane extraction, which refers to extracting certain substances from the organic solvents with water or other polar solvents [123]. Huang et al. [56] fabricated an asymmetric PEEK membrane via immersion precipitation with MSA/SA mixture solvent and used the membrane for lithium stripping by a liquid–liquid membrane contactor with harsh conditions containing $7 \text{ mol} \cdot \text{L}^{-1}$ HCl and tributyl phosphate/kerosene for the first time. Continuous and uninterrupted dynamic long-term membrane stripping experiments of 504 h and weight change of PEEK membrane after soaking in different solvents for 1320 h further confirmed the durability of the PEEK membrane (Fig. 8). In the report, on one hand, the PEEK membrane

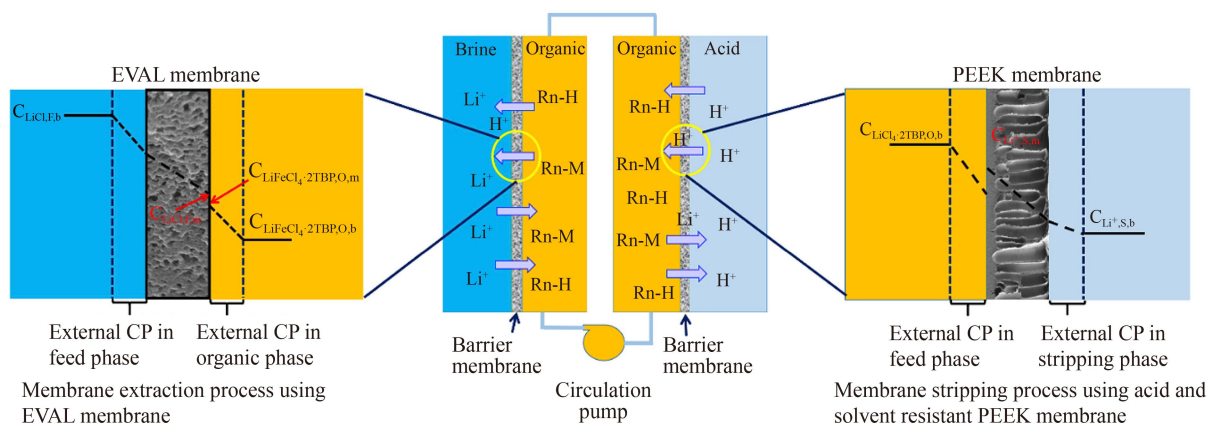


Fig. 7 Process diagram of membrane contactor: the left side is the membrane extraction section, and the right side is the membrane stripping section. Reprinted with permission from Ref. [56], copyright 2019, Elsevier.

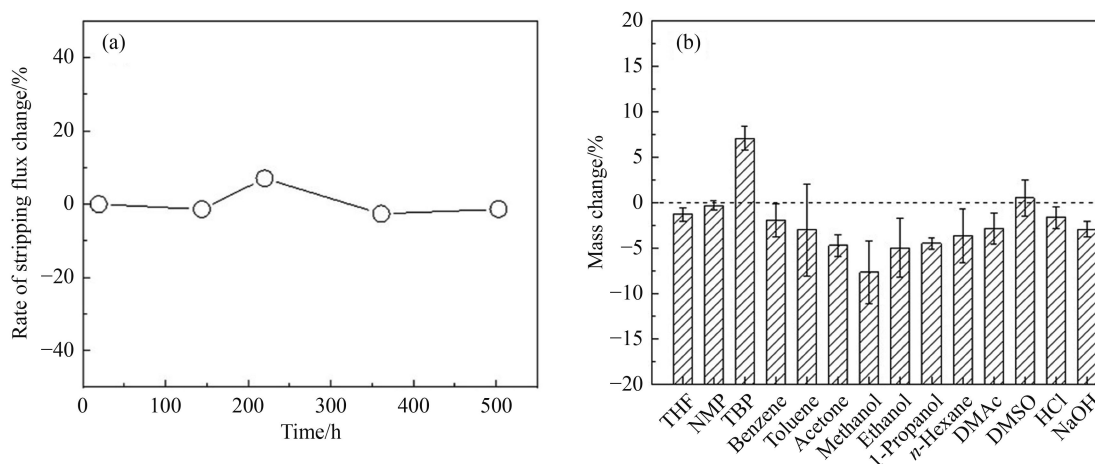


Fig. 8 Tests of organic resistance of PEEK membrane. (a) Li^+ stripping flux change of PEEK membrane in a dynamic test of 504 h; (b) weight change of PEEK membrane in different solvents, soak time: 1320 h. Reprinted with permission from Ref. [56], copyright 2019, Elsevier.

possesses excellent solvent resistance, but on the other hand, its membrane separation efficiency does not have significant advantages. A blend membrane of SPEEK and PEEK was designed to reduce the ion diffusion resistance across the membrane and improve the extraction efficiency of lithium ions [17]. The presence of amorphous SPEEK disrupted the crystalline formation in PEEK and reduced the pore tortuosity of the blend membrane, thus reducing the ion transfer resistance. Actually, the sulfate group in the SPEEK molecular structure did not contribute to the increase in lithium-ion diffusion across the blend membrane. Results showed that the membrane exhibited maximum lithium diffusion, extraction and stripping fluxes at a 50%/50% PEEK/SPEEK mixing ratio. Nearly two times stripping flux and five times lithium extraction flux were obtained as compared to the pure PEEK membrane.

Membrane extraction was proposed as an environmentally friendly sustainable process compared to conventional liquid–liquid extraction, in which the organic extractant is confined inside the membrane and no extractant leaks to the feed solution. As a modified branch material of PEEK, hydrophilic amorphous PEEKWC was diluted in a low toxic solvent gamma-butyrolactone to fabricate hollow fiber membranes with PVP K-17 as pore former agent via dry/wet phase inversion. The produced membranes were applied to extract Cr(VI) from an aqueous phase containing $\text{K}_2\text{Cr}_2\text{O}_7$ with a concentration in the range of 15 to 100 ppm (10^{-6}) using Aliquat-336 dissolved in kerosene as organic extractant via a liquid–liquid membrane contactor [124]. An extraction ratio up to 99% was obtained through the produced PEEKWC membrane at the optimal pH of 4.5 with the Aliquat-336 content of 30% (v/v). In comparison with the commercial polypropylene (PP) membrane, the hydrophilic PEEKWC membrane exhibited a good Cr(VI) extraction effect and exceeded the PP membrane after running for more than

400 min. A quite high swelling (226 ± 5) of hydrophobic PP membrane by the organic phase promoted the Cr(VI) transport across the membrane to be removed by the organic extractant, meanwhile resulting in leakage of organic phase into the aqueous feed phase, leading to a very short service life of the membrane-self, especially in long-term applications. In contrast, the hydrophilicity of the PEEKWC-based membrane with a sponge-like structure was able to resist the contamination of aqueous feed phase by the organic extractant, exhibiting promising potential in long-term operation membrane contactor.

More than 130 countries and organizations around the world have made net-zero commitments and strive to achieve carbon neutrality by the middle of the 21st century to address the problem of global warming [125,126]. CO_2 capture and storage is one of the key approaches to reducing CO_2 emissions and mitigating change of the global climate. The amine absorption process is the most well-known technology and widely commercially used for CO_2 capture from flue gas owing to high CO_2 removal efficiency and stable operation [127]. However, there exist some significant limitations within amine absorbents such as large equipment size, excessive energy to regenerate the absorbent, equipment corrosion, solvent loss and so on [128]. Gas membrane separation was reported as a technically and economically alternative for post-combustion CO_2 capture. Yet in practical applications, multiple membrane stages are always required to produce more than 95% pure CO_2 product from flue gases [119]. Combining the advantages of solvent absorption and membrane processes, the membrane contactor has attracted attention as a cost-effective technology for CO_2 capture from flue gases, in which the membrane is required to be sufficiently stable and permeable for CO_2 . PEEK is a carbocyclic polymer endowed with excellent chemical, thermal and mechanical stability, which can be used as an excellent candidate membrane material applied in membrane

Over 90% CO₂ removal and stable permeation were obtained in a single-stage membrane contactor after contact with the activated methyldiethanolamine solvent for more than 9 months, establishing the feasibility of membrane contactor combining PEEK membrane with chemical solvents to capture CO₂ from flue gases

Based on the reviewed literature above, a summary can be drawn that membrane contactor with PEEK-based membranes can be applied in ion separation by liquid–liquid extraction and CO₂ capture by liquid–gas absorption successfully. It has been demonstrated that PEEK-based membranes with different morphological structures can resist the swelling and corrosion of organic extractant or strong acid as a barrier between the feed phase and organic phase. As an emerging membrane separation derivative technology, membrane contactor will be widely developed in the future, and PEEK is one of the potential candidates for the long-term operation of membrane contactor.

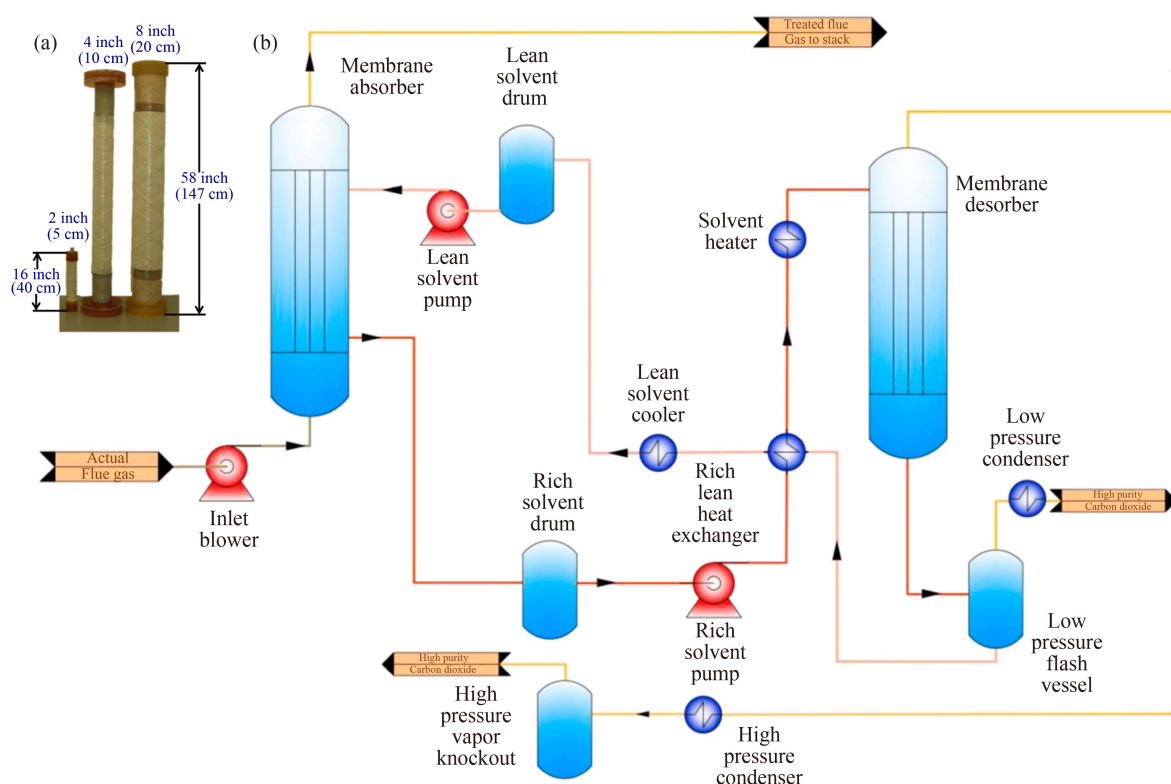


Fig. 9 (a) Scale-up of membrane cartridge; (b) process flow diagram of the membrane contactor system used in field testing. Reprinted with permission from Ref. [130], copyright 2017, Elsevier.

4 Conclusions and perspectives

This review has comprehensively summarized the preparation of polymeric membranes based on PEEK and their applications in complex and harsh environments. The common polymeric materials used in membrane separation always exhibit extraordinary inferior stability due to relatively poor mechanical, thermal and chemical resistance, which greatly limits the application of these membranes under severe conditions. As the tip of the pyramid plastic industry, rigid benzene rings, compliant ether bonds and carbonyl groups in the molecular chain endow PEEK with desirable properties such as high-heat resistant grade, excellent physicochemical stability, and outstanding mechanical property, which make it an ideal candidate polymer used in extreme circumstances such as superhigh-temperature, corrosive and organic solvent system. The application of PEEK-based membranes in special UF and MF, SRNF and membrane contactor was discussed in this review. In addition, the pristine PEEK could be utilized in the preparation of both asymmetrical and homogeneous membranes with porous structures in the forms of flat sheet and hollow fibers via TIPS, NIPS and CIC techniques. The modification of PEEK with various functional groups expands the solvent selection for membrane fabrication, to obtain membranes with different pore structures and morphology.

In MF and UF membrane fabrication, the PEEK-based materials can be used to prepare both hydrophilic and hydrophobic porous membranes with adjustable homogeneous or asymmetrical structures by TIPS and NIPS methods. In particular, PEEKWC hollow fiber UF membrane has been successfully applied in the clarification of juice processing with a steady-state permeate flux of about $26 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ and a nearly complete restoration of the initial hydraulic permeability after a chemical cleaning treatment. The anti-fouling properties and permeability of MF and UF membrane can be significantly improved via UV modification by grafting different hydrophilic functional groups, among which the neutral monomers have the best effect on the BSA pollution resistance and greatly promote the water permeability simultaneously.

In the case of SRNF membranes, PEEK-based membranes with controllable morphology prepared by traditional NIPS and novel CIC method can be widely used in different situations rich in strong acid/base/organic solutions such as solvent recovery, solvent purification and oil–water separation, owing to their remarkable chemical durability, mechanical stability and thermal resistance. To enhance the membrane separation performance and expand the applications of PEEK-based membranes, composite membranes by dip-coating or blending with other polymers and/or organic nanofillers are effective, feasible and promising methods.

In membrane contactor with liquid–liquid extraction or liquid–gas absorption, PEEK-based membranes with different structures and morphology are applied to separate the feed phase and extractant phase as a barrier. Membrane contactor technique with the configuration of flat sheet or hollow fibers shows large application potential in ion extraction from complex system or CO_2 capture from the elevated temperature flue gas. Accordingly, PEEK-based membrane is one of the potential candidates for long-term operation membrane contactor due to its remarkable chemical resistance, thermal stability and brilliant mechanical property as well as tunable membrane pore structure which makes it a perfect separator to organic phase leakage or corrosion and allows the separated substances to pass through efficiently.

In conclusion, high-performance PEEK materials are widely used in membrane separation. Its significance is to provide strong stability membrane materials for substance separation under extreme environmental conditions. Although the membrane separation performance is not always the best, based on its excellent material intrinsic properties, the continuous optimization and modification are expected to realize a sustained improvement of performance. On one hand, further investigations and research are needed on membrane formation and structure regulation of pure PEEK which owns the best stability in all aspects. In the novel CIC method, designing more suitable groups easy to be removed by hydrolysis can solve the current drawbacks and expand its applications in the membrane fabrication of solvent-resistant materials. IP of covalent organic frameworks layer on PEEK UF membrane may be an ingenious methodology to fabricate high-performance NF membrane utilized in high temperature and/or organic/strong acid/base solutions. In addition, the modified PEEK with various functional groups can be selectively dissolved in some solvents and have tolerance to other solvents, which has a certain significance for further study. The focus is to study the effect of functional groups on the properties of materials, among which charged groups with crosslinking function may be a choice with research value. Besides, PEEK-based composite membranes by dip-coating or blending with other polymers and/or organic nanofillers are also worth digging deeper into, which is expected to improve the performance and broaden the application to fields such as gas separation, pervaporation and proton exchange membranes.

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