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Review

Advancements in Organic Solvent Nanofiltration: The Critical Role of Polyamide Membranes in Sustainable Industrial Applications

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Abstract

Organic solvent nanofiltration (OSN) has emerged as a transformative platform for molecular separation, offering energy-efficient and high-performance alternatives to conventional separation techniques across the food, petrochemical, and pharmaceutical industries. At the core of this advancement lie polyamide membranes, whose exceptional chemical resilience, tunable architecture, and compatibility with a wide range of organic solvents have positioned them as the material of choice for industrial OSN applications. Recent progress encompassing nanostructured additives, controlled interfacial polymerization, and advanced crosslinking strategies has led to significant improvements in membrane selectivity, permeability, and operational stability. As OSN continues to gain traction in sustainable chemical processing, enabling reductions in both energy consumption and environmental waste, ongoing challenges such as membrane fouling, structural degradation, and limited solvent resistance remain critical barriers to broader adoption. This review critically examines the role of polyamide membranes in OSN, emphasizing their structural versatility, physicochemical attributes, and capacity to meet the growing demands of sustainable separation technologies.

Keywords: OSN; polyamide; TIPS; electrospinning; LbL

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1. Introduction

The accelerating pace of industrialization has dramatically increased global reliance on organic solvents, particularly across chemical, pharmaceutical, petrochemical, and semiconductor sectors. These solvents are indispensable for synthesis, extraction, formulation, and purification processes. Since the mid-20th century, a sharp rise in solvent consumption has paralleled industrial growth, most notably in pharmaceutical manufacturing, where solvents are vital for active pharmaceutical ingredient (API) production. However, conventional solvent separation methods such as distillation and chromatography are highly energy-intensive and solvent-demanding, raising significant environmental and economic concerns [1–3]. Volatile organic compounds (VOCs), which constitute the majority of organic solvents, are major contributors to air and water pollution and greenhouse gas

emissions. Life cycle analyses estimate that manufacturing and using one pound of solvent can generate up to ten pounds of greenhouse gases, while pharmaceutical operations discard approximately 80–90% of utilized solvents [4]. Waste solvent volumes ranging from 25 to 100 kg per kg of product reflect a critical need for more sustainable separation solutions. With over 90% of solvents derived from non-renewable petrochemical sources [5,6], the urgency for greener alternatives is becoming paramount. Thermal separation accounts for 40–70% of total industrial energy use, with some operations, e.g., propylene/propane distillation, reaching up to 200 GJ per ton of product [7,8].

Organic solvent nanofiltration (OSN) has emerged as a game-changing separation strategy that addresses these inefficiencies by offering high separation performance without the need for phase changes. As a non-thermal, pressure-driven membrane technology, OSN selectively separates molecules within the 200–1000 Da range while operating at ambient or moderate temperatures, greatly reducing energy inputs and CO_2 emissions compared to traditional processes [9]. Hybrid OSN-distillation systems have demonstrated energy savings of 37–77% depending on feed composition, with CO_2 emissions reduced from ~320 to 150 kg per kg of product [9–11]. OSN's membranes-based modularity aligns well with both batch and continuous manufacturing, facilitating solvent exchange during crystallization steps and integrating into complex processes such as catalyst recovery [11–13]. Applications extend beyond pharmaceuticals to include edible oil purification, waste oil refining, and catalyst retention, with up to 90% energy savings and ~50% cost reduction [13]. Despite its promise, OSN faces significant material and operational challenges, especially under harsh chemical environments. Common polymeric membranes such as polyether sulfone (PES) and polybenzimidazole (PBI) suffer from pore deformation and swelling in polar aprotic solvents like DMSO and acetone [14]. While crosslinked polyimides (e.g., DuraMem^{TM}) offer enhanced solvent resistance, their long-term durability in solvents like methyl ethyl ketone (MEK) remains insufficient [15,16]. Swelling and densification under high pressures (30–60 bar) lead to reduced flux up to 30% in commercial systems like Puramem^{TM} 280, while high-temperature aging contributes to further permeability losses [17]. These issues are exacerbated by chemical incompatibilities: hydrophobic membranes (e.g., PDMS) resist non-polar solvents but degrade in polar environments like methanol [18,19], while hydrophilic systems (e.g., crosslinked P84) exhibit the opposite trend [15,18]. Glassy polymers provide better chemical resistance but pose processing challenges; rubbery polymers offer higher flux but at the cost of selectivity and solvent durability [14].

Amidst these limitations, polyamide membranes, particularly thin-film composites (TFCs), have emerged as dominant candidates for OSN due to their tunable structure, high chemical resistance, and selectivity [20]. Interfacial polymerization (IP) of diamines (e.g., MPD) and acyl chloride (e.g., TMC) allows precise control over crosslinking density and membrane morphology, tailoring transport properties [20–22]. Hyper-crosslinked structures created using multifunctional amines (e.g., tetraamines) and crosslinkers (e.g., TPC) further enhance molecular sieving capabilities. Membranes such as HDA-crosslinked PBI resist swelling in polar aprotic solvents, while mixed monomer strategies (e.g., TMC with isophthaloyl chloride) improve solvent resistance without sacrificing mechanical properties [21,23]. TFC membranes continue to dominate desalination due to their >99% salt rejection with water fluxes of 2–3 L m^{-2} h^{-1} bar^{-1} [20,24], and molecular simulations have illuminated the influence of charge distribution and hydrophobic balance on ion transport [21,22]. Advanced fabrication approaches such as sacrificial nanostrand templates and support-free casting have produced ultrathin polyamide films (<20 nm) with a tenfold increase in solvent permeability [24]. Additive manufacturing techniques like spray coating and 3D printing enable fine-tuning of film thickness (10 nm–1 μm) and

reproducibility [25,26]. High-density crosslinkers (e.g., TPC and CC) and thermal curing improve sub-nanometer pore size control and enhance long-term stability in solvents such as methanol [23]. The incorporation of functional nanomaterials, such as MOFs, GO, TNTs, and g-C_3N_4 nanosheets, further optimizes membrane performance. These additives enhance mechanical integrity, hydrophilicity, and fouling resistance while improving permeability and selectivity [24,25,27,28]. Ionic regulation during IP (e.g., NaCl, $NaHCO_3$) refines membrane homogeneity and reduces roughness by 57–62% [29,30]. Triple-layer designs integrating deep eutectic supramolecular polymers (DESPs) enable efficient separation of complex molecules such as Monascorubrin while reducing energy demands by 50% [31]. Polyamide OSN membranes are proving critical for advanced industrial separations, including methanol recovery (flux >70 L m^{-2} h^{-1} bar^{-1}), homogeneous catalyst retention (>99% Pd), and solvent exchange with <5% loss [32]. Co-polyamide membranes have even been evaluated for energy harvesting from salinity gradients, demonstrating 10.22 Wm^{-2} power density and a 36.7% reduction in energy demand [33]. Sustainability is further enhanced by bio-based monomers and green crosslinkers [23], aligned with global regulatory shifts like the U.S. RCRA. The integration of these eco-friendly materials into TFCs demonstrated the potential of OSN in advancing circular economy models. Over the last two decades, research in OSN has grown rapidly from fewer than 50 publications per year in the early 2000s to over 400 annual publications by 2023. While several reviews have been published focusing on general OSN principles or solvent-resistant membranes, they often provide broad overviews without emphasizing the unique physicochemical and structural advantages of polyamide-based systems. Notable examples include general OSN overviews by Marchetti et al. [16] and recent material-centric discussions (2020–2023). However, few comprehensive analyses exist that specifically focus on polyamide membranes' critical role in sustainable, scalable OSN deployment.

This review seeks to bridge the gap by offering an in-depth exploration of polyamide-based membrane architectures, with a focus on IP, crosslinking strategies, and emerging nanocomposite designs. It delineates key fabrication methods, material challenges, and industrial applications, positioning polyamide OSN membranes as the linchpin of future solvent recovery technologies.

2. Polyamide Membrane Fabrication

2.1. Materials Used

Polyamide 6 (PA6) membranes have recently emerged as compelling candidates for organic solvent nanofiltration (OSN) due to their intrinsic chemical stability, mechanical robustness, and adjustable permeability. An important invention is the manufacturing of hollow fiber PA6 membranes using a one-step thermally induced phase separation (TIPS) technique with non-toxic diluents such as dimethyl sulfone and sulfolane. This green methodology obviates the need for hazardous solvents and crosslinking agents, aligning with sustainable manufacturing principles. Membranes prepared using polyethylene glycol (PEG400) as the bore solution demonstrate excellent OSN performance, achieving a methanol permeance of 0.27 L m^{-2} h^{-1} bar^{-1} with 96.3% rejection of vitamin B12, while retaining mechanical integrity after prolonged solvent exposure, with only ~3.7% weight loss over four months [34]. In parallel, thin-film composite (TFC) polyamide membranes have emerged as a key component of OSN technology. These membranes are made via interfacial polymerization (IP) and consist of a selective polyamide layer on a porous polyacrylonitrile (PA) support. They provide exact control over the active layer properties [35]. The membrane performance is highly sensitive to monomer chemistry: aromatic diacids and aliphatic amines have been employed to enhance solvent resistance and selectivity. Notably, hyper-crosslinked structures formed by tetra-amines and terephthaloyl chloride

(TPC) yield dense networks with improved molecular sieving capabilities and solvent tolerance. The introduction of metal ions such as Co^{2+} as additional crosslinking agents further strengthens the polyamide matrix, improving durability without sacrificing permeability [36]. Process additives also play a crucial role in optimizing membrane architecture and performance. Surfactants like sodium dodecyl sulfate (SDS) stabilize the polymerization interface, while alkyl phosphates such as tributyl phosphate (TBP) enhance diamine solubility in the organic phase, both contributing to elevated permeance and rejection rates in complex solvent systems [37]. Recent advances have pushed OSN membrane performance to new heights, with permeate fluxes up to 109.9 bar^{-1} for solvents such as n-hexane, coupled with >99% rejection rates for various solutes [37]. Importantly, structural modifications and crosslinking strategies confer long-term stability in aggressive solvents, ensuring membrane performance remains uncompromised under industrial conditions [34,36]. Together, these innovations in PA6 hollow fiber and TFC polyamide membranes underscore a paradigm shift towards scalable, high-performance, and environmentally responsible OSN technologies. Table 1 provides a brief comparison of the advantages and disadvantages of polyamide membranes vs. other membrane materials for OSN.

Table 1. Comparison of the advantages and disadvantages of polyamide membranes compared to other membrane materials for OSN.

Membrane Material	Advantages	Disadvantages	References
Polyamide (PA)	- Highly selective and durable. - Tunable properties via interfacial polymerization. - Widely used in TFC configuration. - Good scalability and up-scaling potential.	- Susceptible to chlorine and oxidative degradation. - Hydrolytic instability in some solvents. - Environmental concerns in fabrication (toxic solvents). - Challenging to achieve defect-free ultrathin layers.	[26]
Polyimide (PI)	- Excellent chemical and thermal stability. - Good solvent resistance.	- Lower permeance for polar solvents. - Can be expensive. - May require post-treatment for selectivity.	[38]
Polydimethylsiloxane (PDMS)	- High solvent resistance. - Good flexibility. - Easy fabrication.	- Lower selectivity for small molecules. - Swelling in some solvents.	[39]
Polybenzimidazole (PBI)	- Outstanding chemical and thermal stability. - Good performance in harsh solvents.	- Lower flux compared to PA. - Difficult to process and expensive.	[40]
Polyacrylonitrile (PAN)	- Good mechanical strength. - Stable in some organic solvents.	- Good mechanical strength. - Stable in some organic solvents.	[41]
Ceramic membranes	- Excellent chemical and thermal stability. - Long lifespan. - High fouling resistance.	- High cost. - Brittle. - Lower permeance for some applications.	[42]

2.2. Fabrication Techniques

2.2.1. Phase Inversion Process

Phase inversion, shown in Figure 1, is a fundamental approach in the manufacturing of polyamide membranes for OSN, providing fine control over membrane morphology and performance. This procedure involves the transformation of a homogeneous polymer solution into a solid membrane via induced phase separation, which is commonly begun by immersing the cast polymer solution in a nonsolvent coagulation bath, a technique known as nonsolvent-induced phase separation (NIPS) [43]. The subsequent exchange

of solvent and nonsolvent precipitates the polymer, resulting in a membrane structure with a dense selective layer atop a porous substructure, which is required for efficient OSN applications. Polymer concentration, solvent–nonsolvent interactions, and phase separation kinetics all have a significant impact on the morphology and performance of the membranes that emerge. Adjusting these parameters enables the tailoring of membrane properties, including pore size distribution and permeability, to meet specific OSN requirements. Moreover, the incorporation of additives and post-treatment modifications, such as crosslinking, can enhance membrane stability and selectivity, thereby extending their applicability in harsh solvent environments [13]. Phase inversion techniques, notably thermally induced phase separation (TIPS) and evaporation-induced phase separation (EIPS), are pivotal in tailoring polyamide membranes for organic solvent nanofiltration (OSN). TIPS leverages thermal demixing by cooling a homogeneous polymer solution, reducing polymer solubility, and inducing phase separation, offering nuanced control over membrane architecture [44]. The selection of solvents significantly influences membrane morphology and performance. For instance, polyamide 66 (PA66) membranes prepared using hydrochloric acid (HCl) exhibit a denser top layer (~23 μm) compared to those fabricated with formic acid (FA) (~10 μm), resulting in lower porosity and water flux in HCl-based membranes [45]. This morphological variance underscores the critical role of solvent choice in dictating membrane characteristics. Membrane performance in OSN is further modulated by parameters such as polymer concentration, casting conditions, and coagulation bath composition. Optimizing these factors enables the fabrication of membranes with enhanced mechanical stability, selectivity, and permeability, catering to the separation of both polar and non-polar solvents. Such advancements underscore the versatility of phase inversion methods in engineering polyamide membranes tailored for efficient and durable OSN applications.

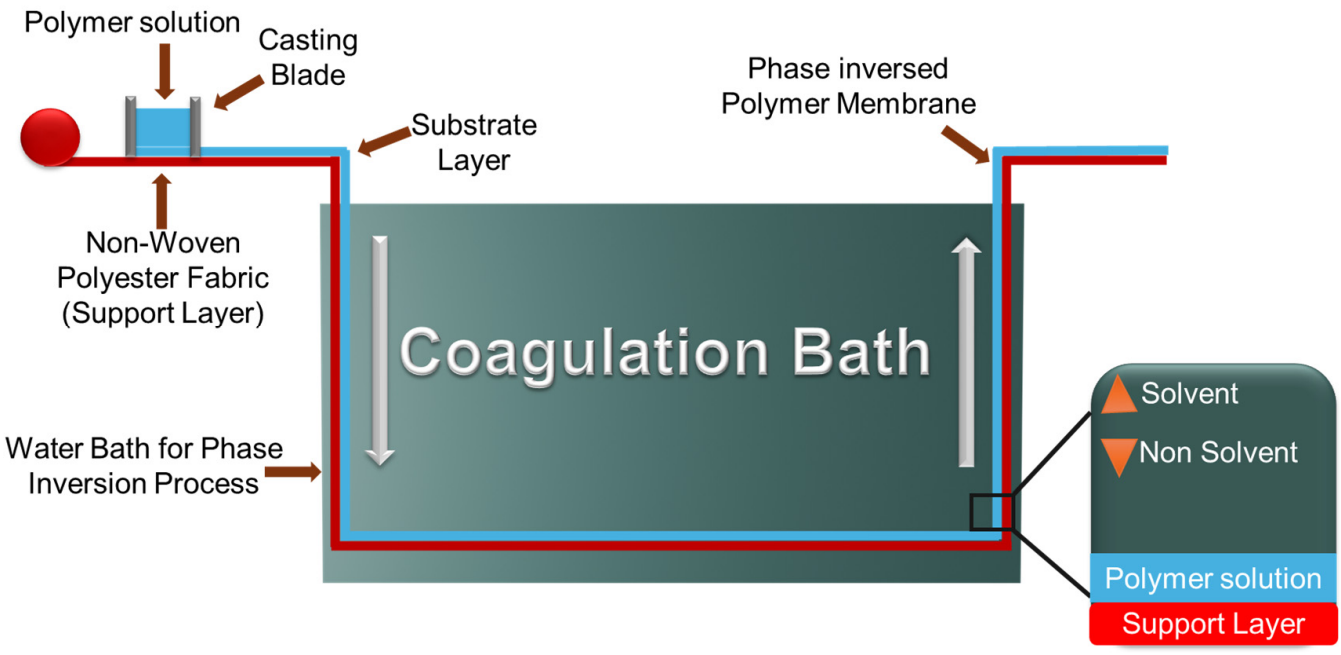


Figure 1. A diagrammatic representation of the phase inversion process.

2.2.2. Interfacial Polymerization

Interfacial polymerization (IP), shown in Figure 2, remains a cornerstone technique in the fabrication of polyamide thin-film composite (TFC) membranes, particularly for organic solvent nanofiltration (OSN) applications [46,47]. This method involves a rapid polycondensation reaction between amine and acyl chloride monomers at the interface

of two immiscible phases, typically aqueous and organic, resulting in the formation of a selective polyamide layer [48]. While IP has been extensively utilized in aqueous systems, its adaptation for OSN has necessitated modifications to enhance membrane performance and stability in organic solvents, such as employing green solvents like oleic acid, vapor-phase polymerization, or bio-renewable solvents like cyclopentyl methyl ether [49,50]. Recent studies have focused on refining the IP process to address challenges such as non-uniform pore distribution and structural heterogeneity within the polyamide layer, which can adversely affect membrane permeability and selectivity. One approach involves the incorporation of inorganic salts during polymerization to regulate the diffusion of amine monomers to the interface, leading to a more uniform polyamide layer. This salt-mediated IP technique has demonstrated significant improvements in membrane permeance and solute rejection rates, making it suitable for reverse osmosis and nanofiltration applications [30]. Furthermore, the strategic use of additives during IP has been shown to enhance membrane performance. For instance, the addition of tributyl phosphate (TBP) can improve the solubility of diamine monomers in the organic phase, while surfactants like sodium dodecyl sulfate (SDS) stabilize the IP interface. The synergistic effect of these additives has been reported to improve membrane permeance and rejection in solvent environments [37]. These advancements underscore the dynamic evolution of TFC polyamide membranes and reinforce their pivotal role in advancing OSN technologies. Advancements in IP techniques have significantly enhanced the performance of polyamide membranes for organic solvent nanofiltration (OSN). Anhydrous interfacial polymerization (AIP) has emerged as a promising approach to mitigate water-induced side reactions that compromise membrane integrity. By conducting polymerization under anhydrous conditions, AIP facilitates the formation of polyamide layers with precise ionic sieving capabilities, suitable for OSN applications [51]. The incorporation of sacrificial interlayers before IP has been shown to optimize support properties, resulting in smoother polyamide films with enhanced performance attributes. This strategy allows for better control over interfacial reactions, leading to membranes with increased permeability without sacrificing selectivity. The incorporation of a sacrificial interlayer before IP has been shown to optimize support properties, resulting in smoother polyamide films with enhanced performance attributes. This strategy allows for better control over interfacial reactions, leading to membranes with increased permeability without sacrificing selectivity [52]. Moreover, the use of surfactants or nanomaterials during IP can modify support layers and improve interfacial stability. These techniques aim to produce defect-free membranes with improved structural qualities, thereby enhancing OSN performance [53]. Evaluations of polyamide membranes fabricated using these advanced IP processes have reported reductions in pore size distribution and greater structural homogeneity, resulting in enhanced permeance values. Such improvements are critical for applications like OSN, where the ability to distinguish between distinct solutes is essential. Additionally, surface morphological modifications have been associated with significantly enhanced antifouling properties, crucial for maintaining long-term membrane performance [30].

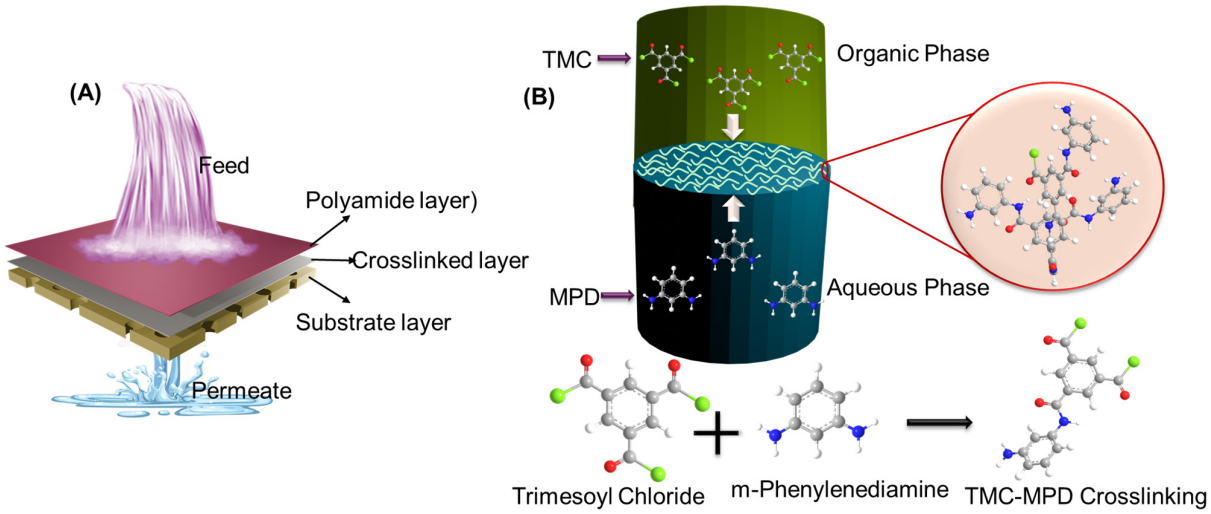


Figure 2. (**A**) Schematic illustration of TFC membrane structure. (**B**) Schematic diagram of interfacial polymerization process.

2.2.3. Other Methods

Polyamide membranes are pivotal in organic solvent nanofiltration (OSN) due to their exceptional chemical resilience and tunable selectivity. While phase inversion and interfacial polymerization are conventional fabrication methods, emerging alternative techniques offer enhanced performance and sustainability. Notably, organic–organic interfacial polymerization (OOIP) has been introduced for ultrathin polyamide TFC OSN membranes, utilizing organic solvents in both phases to achieve defect-free selective layers with superior solvent resistance and flux [46]. Additionally, vapor-phase interfacial polymerization (VIP) enables the synthesis of thin-film composite membranes without using organic solvents, presenting a greener fabrication route [49]. These innovative methods underscore the dynamic evolution of polyamide membrane fabrication, aligning with the advancing demands of OSN applications.

Stretching Method

Stretching methods in membrane production are operations that include the mechanical deformation of polymeric materials, typically through uniaxial or biaxial elongation to induce porosity, align polymer chains, and modify microstructure. These approaches are especially useful for improving mechanical strength and customizing pore architecture in membranes intended for high-pressure applications like OSN. Polyamide membranes, which are essential to OSN operations, have variable separation performance based on the fabrication methodology and solvent environment. The organic phase's physicochemical composition has a significant impact on polyamide membrane structure during IP. Solvent variables such as solubility parameters, interfacial tension, and diffusivity control monomer movement across the aqueous–organic interface, determining the thickness and crosslinking density of the resultant polyamide layer. Solvents with low polarity and interfacial tension, such as hexane, inhibit the diffusion of aqueous-phase amine monomers (e.g., m-phenylenediamine, MPD) into the organic phase, resulting in thinner, highly crosslinked polyamide films with poorer permeability. Polar or partially miscible solvents, such as toluene and ethyl acetate, enable deeper monomer penetration, resulting in thicker films with lower crosslinking and selective performance [54]. For example, polyamide 66 (PA66) membranes produced with formic acid have higher porosity and water flux than those synthesized with hydrochloric acid, owing to the production of a thinner, dense selective layer under formic acid conditions. This increased permeability is especially important

for OSN operations, where precise control of solute rejection and solvent flux is required. Furthermore, the asymmetric construction of polyamide membranes, with a dense selective surface layer above a porous support, is a distinguishing trait that influences OSN efficacy. Careful control of coagulation bath conditions and casting solution composition allows for control over dense layer thickness and porosity, which influences the flux-to-selectivity trade-off [45]. Permeability, rejection efficiency, and structural integrity under solvent exposure are all important performance indicators to consider when evaluating polyamide membranes made through stretching and other physical modifications. The optimization of polymer content, stretching parameters, and phase separation conditions has been shown to greatly improve membrane performance for a wide range of organic solvents [55].

Track-Etching Method

The track-etching technique has emerged as a precise method for fabricating polyamide membranes with well-defined pore structures, offering significant potential for OSN applications. This method involves a two-step process: initial irradiation of polymer films with high-energy heavy ions, such as uranium-235, iodine-127, or silver-107, to create linear damage tracks, followed by chemical etching to develop uniform cylindrical pores. The irradiation parameters, including ion energy and exposure time, directly influence the density and distribution of these tracks, thereby controlling the porosity of the resulting membrane [56]. Subsequent chemical etching, typically using alkaline solutions, selectively removes the damaged regions, forming pores with diameters ranging from a few micrometers. The etching conditions, such as temperature, duration, and solution concentration, are critical in determining the final pore size and geometry. The precise control over pore characteristics enables the production of membranes tailored for specific separation tasks, including the filtration of organic solvents in OSN processes [57]. Track-etched polyamide membranes exhibit several advantageous properties for OSN applications. The uniform cylindrical pores contribute to high selectivity and consistent performance. Additionally, the ability to modify surface chemistry during the etching process allows for the introduction of functional groups, enhancing solvent compatibility and selectivity. These features are particularly beneficial in OSN, where membranes must withstand harsh chemical environments while maintaining separation efficiency [58]. Despite their advantages, the production of track-etched membranes involves complex and costly procedures, including the need for specialized irradiation equipment. Moreover, the scalability of this technique for industrial OSN applications remains a challenge. Nevertheless, ongoing research focuses on optimizing fabrication processes and exploring alternative materials to enhance the practicality of track-etched membranes in organic solvent separations [59].

Electrospinning Method

Electrospinning has emerged as a versatile and widely adopted technique for fabricating polyamide membranes, particularly suitable for OSN applications. This method leverages high-voltage electric fields to draw polymer solutions into fine nanofibers, resulting in membranes characterized by high surface area, interconnected porosity, and tunable structural properties [60]. The electrospinning setup, shown in Figure 3, typically comprises a syringe pump, a high-voltage power supply, and a grounded collector. A polymer solution, such as polyamide dissolved in an appropriate solvent system, is extruded through a metallic needle under the influence of a strong electric field. This field induces the formation of a Taylor cone at the needle tip, from which a charged jet of the polymer solution is ejected. As the jet travels towards the collector, rapid solvent evaporation occurs, solidifying the polymer into nanofibers. Key parameters, including solution viscosity, polymer concentration, applied voltage, flow rate, and environmental conditions, critically

influence fiber morphology and diameter [37]. Electrospun polyamide membranes exhibit several advantageous features for OSN applications. The nanofibrous architecture provides a high surface area-to-volume ratio, facilitating efficient separation processes. The interconnected pore structure ensures adequate permeability, while the ability to fine-tune fiber diameter and pore size allows for customization to specific separation requirements. Moreover, the inherent chemical resistance of polyamide imparts solvent stability, a crucial attribute for OSN processes [60]. Recent advancements have focused on enhancing the performance and scalability of electrospun polyamide membranes. For instance, the integration of electrospun nanofibrous substrates with thin-film composite (TFC) structures has demonstrated improved mechanical strength and solvent resistance, leading to membranes capable of withstanding harsh OSN conditions [60]. Additionally, the development of bio-based electrospun polyamide membranes has shown promise in achieving high separation efficiencies while maintaining environmental sustainability [61]. Innovations in electrospinning techniques, such as needleless and wire electrospinning, have been explored to address throughput limitations and facilitate industrial-scale production. Despite these advancements, we have focused on enhancing the performance and scalability of electrospun polyamide membranes for OSN. The mechanical robustness of the nanofibrous structure under high-pressure conditions is a concern, necessitating the incorporation of reinforcing materials or post-treatment processes to enhance durability. Furthermore, the high-voltage requirements and complexity of the electrospinning setup pose safety and scalability issues that must be addressed through engineering innovations [60,61].

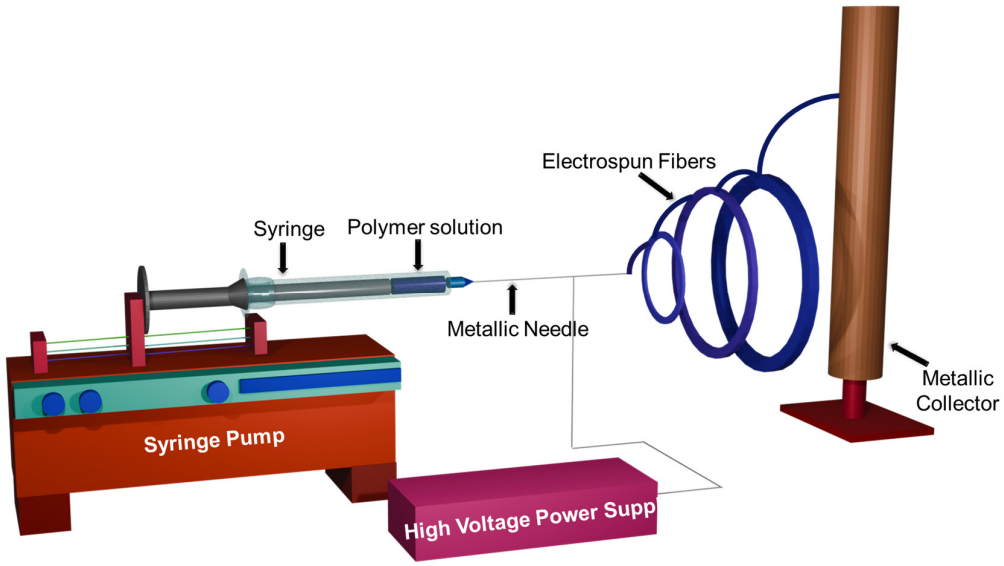


Figure 3. A schematic illustration of the electrospinning process.

Layer-by-Layer (LbL) Assembly

Layer-by-layer (LbL) assembly, shown in Figure 4, has emerged as a versatile and effective strategy for engineering polyamide membranes tailored for OSN applications. This technique facilitates the construction of multilayered architectures with precise control over thickness, surface chemistry, and functional properties [62]. The LbL process involves the sequential deposition of oppositely charged polyelectrolyte pairs, including poly (diallyl dimethylammonium chloride) (pDAC) as the polycation and poly (acrylic acid) (PAA) as the polyanion [63]. Each adsorption step is followed by a rinsing stage to remove loosely bound polyelectrolytes, ensuring the formation of uniform and stable bilayers. The number of bilayers can be tuned to achieve the desired membrane thickness and performance characteristics [64]. The driving forces for LbL assembly encompass

electrostatic interactions, hydrogen bonding, and van der Waals forces, collectively contributing to the structural integrity and functionality of the assembled membrane. This multilayer configuration imparts several advantageous properties, including enhanced mechanical strength, improved antifouling resistance, and selective permeability. The hydrophilic nature of the assembled layers mitigates fouling by reducing the adsorption of organic contaminants, while the tunable pore structure allows for precise molecular sieving [65]. In OSN applications, LbL-assembled polyamide membranes have demonstrated significant potential. For instance, the incorporation of graphene oxide (GO) nanosheets via LbL deposition, typically conducted during IP, has been demonstrated to significantly enhance membrane durability and resistance to chlorine-induced degradation, an enduring challenge in OSN. Serving as a functional interlayer on the membrane support, the GO assembly modulates monomer diffusion during IP, facilitating the formation of a more uniform and defect-resistant polyamide layer. Moreover, the intrinsic mechanical rigidity and two-dimensional structure of GO nanosheets contribute to enhanced tensile strength and structural integrity of the resulting membrane. Concurrently, the presence of GO increases surface hydrophilicity and decreases surface roughness, collectively leading to improved antifouling properties and prolonged operational stability under harsh solvent environments [66]. Moreover, the layer-by-layer (LbL) assembly technique facilitates the precise incorporation of functional nanomaterials, such as metal–organic frameworks (MOFs) and inorganic nanoparticles, into the membrane matrix. These embedded nanostructures enable fine-tuning of membrane transport properties, thereby enhancing selectivity and permeability towards targeted solute-solvent systems and enabling the efficient separation of complex organic mixtures [62]. Despite these advantages, challenges remain in scaling up the LbL process for industrial applications. The iterative nature of the assembly process can be time-consuming, and the requirement for precise control over deposition conditions necessitates careful optimization. Additionally, the long-term stability of LbL-assembled membranes in aggressive solvent environments requires further investigation to ensure consistent performance over extended operational periods [63].

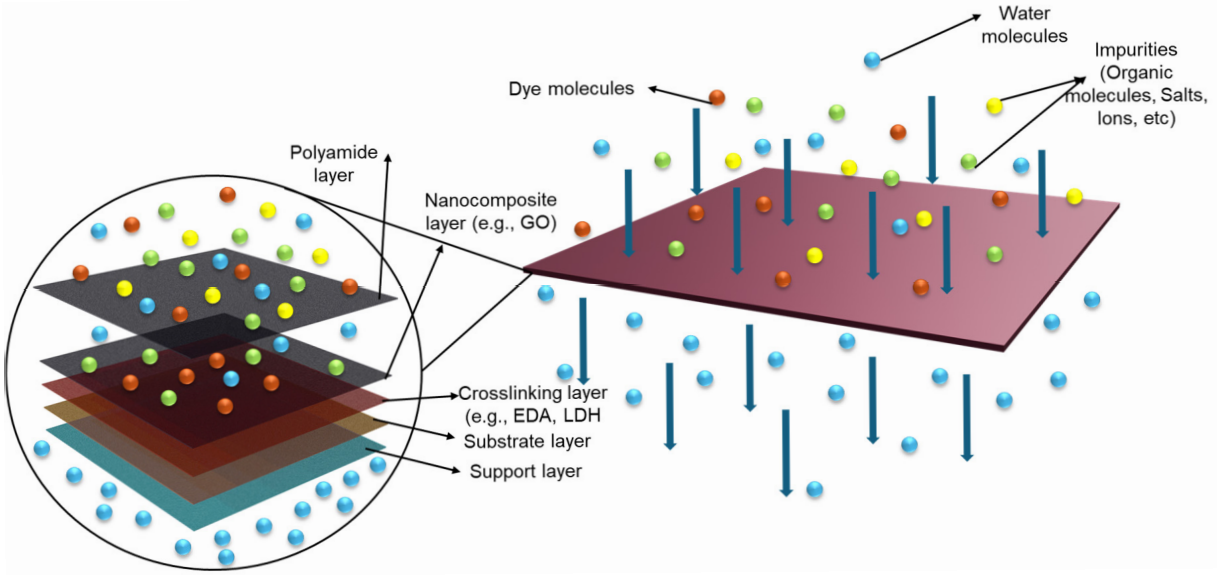


Figure 4. A schematic representation of the layer-by-layer assembly process (**top**) and the layered structure (**bottom**) of GO/LDH nacre-like hybrid coatings.

Table 2 gives a systematic summary of the separation of the pros and cons of various polyamide membrane fabrication techniques.

Table 2. A systematic summary of the pros and cons of various PA membrane fabrication techniques.

Fabrication Techniques	Pros	Cons
Phase inversion	- Morphology control. - Scalability. - Versatility.	- Solvent dependency. - Thickness limitations. - Long processing times.
Interfacial polymerization	- High selectivity. - Rapid reaction. - Tunability.	- Toxic solvents. - Permeability-selectivity trade-offs. - Substrate dependency.
Stretching method	- Enhanced porosity. - Mechanical strength.	- Material limitations. - Defect formation.
Track-etching	- Uniform pores. - Controlled pore density.	- Low porosity. - High cost.
Electrospinning	- High surface area. - Customizability.	- Slow production rates. - Mechanical weakness.
Layer-by-layer assembly	- Precise control. - Fouling resistance.	- Time-consuming. - Scalability challenges.

3. Modification Strategies for Enhanced Performance

In many applications involving filtration and separation, especially reverse osmosis (RO) procedures, polyamide membranes are indispensable. A number of modification tactics have been explored to improve their performance. Key tactics based on current study findings are outlined here.

3.1. Surface Modification Techniques

Layer-by-layer (LbL) assembly has emerged as a versatile technique for tailoring the surface properties of polyamide membranes, particularly in OSN and complex water treatment applications. This method involves the sequential deposition of oppositely charged polyelectrolytes, resulting in conformal and tunable surface coatings. For example, alternating layers of polydiallyl dimethylammonium chloride (pDAC) and polyacrylic acid (PAA) have been shown to significantly enhance the antifouling properties of polyamide membranes. In filtration tests simulating oil sands-affected water treatment, these modified membranes exhibited higher permeation fluxes and reduced fouling propensity, underscoring their suitability for harsh operating environments [20,63]. Moreover, the grafting of super-hydrophilic polymers, such as hyperbranched polyglycol (hPG), onto the surface of polyamide thin-film composite (TFC) membranes has demonstrated remarkable improvements in both hydrophilicity and water permeability. Specifically, hPG-grafted membranes achieved a 41.5% increase in water flux, alongside a substantial reduction in protein adsorption, thereby improving antifouling performance under OSN-relevant conditions. These advances highlight the effectiveness of surface functionalization strategies in overcoming traditional trade-offs between permeability and fouling resistance [67].

3.2. Incorporation of Nanoparticles

Incorporating nanoparticles into polyamide membranes has emerged as a highly effective strategy for enhancing their performance in OSN and other advanced separation processes. This approach leverages the unique physicochemical properties of nanoparticles to improve key membrane characteristics, including permeability, thermal stability, and antifouling resistance. Recent studies have demonstrated that embedding inorganic nanomaterials, such as titanium dioxide (TiO_2), graphene oxide (GO), and zeolites, within the polyamide matrix or onto its surface can significantly alter membrane morphology and surface chemistry, leading to increased solvent flux and improved resistance to fouling and degradation under harsh chemical conditions [68,69]. These membranes must

maintain selectivity and durability in the presence of aggressive solvents. The following section summarizes major strategies and insights from contemporary research into nanoparticle-enhanced polyamide membranes for OSN applications [67].

3.2.1. Types of Nanoparticles Used

Titanium dioxide (TiO_2) nanoparticles are among the most frequently incorporated nanomaterials in polyamide membranes due to their photocatalytic activity, hydrophilicity enhancement, and thermal robustness properties highly beneficial for OSN. Recent studies have reported that TiO_2-integrated thin-film nanocomposite (TFN) membranes exhibit significantly improved permeability and biofouling resistance, making them suitable for high-temperature solvent-based separation processes. Notably, a biphasic solvothermal synthesis route enabled homogeneous dispersion of TiO_2 within the polyamide matrix, resulting in membranes with superior mechanical integrity and enhanced separation efficiency under harsh OSN conditions [69,70]. In parallel, silver nanoparticles (AgNPs) have been employed for their potent antibacterial functionality. AgNP-functionalized polyamide 12 membranes demonstrated strong antimicrobial activity, making them promising candidates for applications that demand sterility and fouling resistance, including solvent-based pharmaceutical processing and biomedical separations. The incorporation was achieved via sol–gel methods, allowing precise control over nanoparticle size and distribution, as confirmed through X-ray diffraction (XRD) and UV–visible spectroscopy [71,72]. Zinc oxide (ZnO) nanoparticles have also garnered attention for their dual role in enhancing both membrane hydrophilicity and antimicrobial performance. When embedded in polyamide membranes, ZnO significantly improved antifouling characteristics. However, studies caution that excessive ZnO loading can lead to increased resistance to solvent flow, thereby reducing permeability. For instance, one study found that although ZnO addition raised surface hydrophilicity by 25%, a concurrent decline in solvent flux was observed when compared to pristine membranes. These findings underscore the importance of optimizing nanoparticle loading to balance selectivity and permeability in OSN applications [67,68].

3.2.2. Modification Techniques

Nanoparticle integration via self-assembly techniques offers a controlled and efficient route to enhance the performance of polyamide membranes, particularly for applications in OSN. In one study, titanium dioxide (TiO_2) nanoparticles were deposited onto the surface of a commercial polyamide membrane through a pressure-assisted self-assembly method [69]. This modification significantly improved surface hydrophilicity and photocatalytic activity, which are critical for mitigating fouling in complex solvent environments such as wastewater treatment. Notably, the membrane retained stable performance over multiple filtration cycles, indicating strong nanoparticle adhesion and long-term durability [72]. In addition to post-synthetic surface modification, incorporating functional nanomaterials directly into the interfacial polymerization (IP) process has proven effective in enhancing membrane functionality without compromising structural integrity. For instance, Ag@UiO-66-NH_2 metal–organic framework (MOF) nanoparticles were successfully embedded into the polyamide selective layer during IP. The resulting hybrid membranes demonstrated excellent antifouling properties, high flux recovery ratios, and enhanced performance in OSN processes. This in situ nanoparticle integration strategy capitalizes on synergistic interactions between the polymer matrix and embedded nanostructures, leading to membranes with tailored separation properties and increased resistance to solvent-induced degradation [69,72].

3.2.3. Performance Enhancements

The integration of nanoparticles into polyamide membranes has emerged as a pivotal strategy to enhance their antifouling properties, thermal stability, and overall performance in OSN applications. Nanoparticles such as titanium dioxide (TiO_2) have been shown to significantly improve membrane hydrophilicity, thereby reducing foulant adhesion and enhancing flux recovery ratios (FRRs). For instance, TiO_2-incorporated thin-film nanocomposite (TFN) membranes demonstrated FRRs exceeding 95% after exposure to foulants like humic acid, indicating superior antifouling performance [73,74]. Beyond antifouling, TiO_2 nanoparticles contribute to the thermal resilience of polyamide membranes. Studies have reported that TFN membranes with TiO_2 maintain stable water flux and salt rejection rates even at elevated temperatures (up to 65 °C), outperforming unmodified membranes that exhibit significant flux decline under similar conditions [73]. This enhancement is attributed to the nanoparticles' ability to restrict polymer chain mobility, thereby mitigating thermal compaction. However, the concentration of nanoparticles is critical; while moderate TiO_2 loading (e.g., 0.1 wt%) enhances water permeability and maintains high salt rejection (>96%), excessive loading can lead to nanoparticle aggregation, creating micro voids that compromise membrane selectivity [75]. Therefore, optimizing nanoparticle concentration is essential to balance permeability and selectivity in OSN membranes.

Table 3 gives a concise summary table comparing different nanomaterials for OSN membranes

Table 3. Comparison of nanomaterials for organic solvent nanofiltration.

Nanomaterial	Structural Characteristics	Integration Method	Permeability Impact	Selectivity Impact	Chemical Stability	Ref
MOFs (e.g., MIL-101(Cr), ZIF-8)	Tunable porosity (0.3–3.4 nm), high surface area, molecular sieving capabilities	Dispersion in the organic phase during interfacial polymerization (IP)	Permeance: MeOH: 1.5 → 3.9 $L{\cdot}m^{-2}{\cdot}h^{-1}{\cdot}bar^{-1}$; THF: 1.7 → 11.1 $L{\cdot}m^{-2}{\cdot}h^{-1}{\cdot}bar^{-1}$	>90% rejection of styrene oligomers (MW 232–295 $g{\cdot}mol^{-1}$)	Stable in harsh solvents (DMF, methanol); retains performance after prolonged immersion	[76]
Graphene Oxide (GO)	2D nanosheets with oxygen functional groups, hydrophilic	Crosslinking with boronic acid polymer (BA); ODA functionalization for dispersion in hexane	Permeance: Ethanol: 2.8 → 6.0 $L{\cdot}m^{-2}{\cdot}h^{-1}{\cdot}bar^{-1}$; Methanol: 3.94 $L{\cdot}m^{-2}{\cdot}h^{-1}{\cdot}bar^{-1}$	>95.8% rejection of acid fuchsin (AF) in methanol	BA crosslinking enhances stability in DMF/water; functionalization prevents swelling	[77]
g-C_3N_4	2D layered structure, high porosity, photocatalytic properties	Vacuum filtration; embedding as nanofiller in PA matrix	Water flux: 51.0 $L{\cdot}m^{-2}{\cdot}h^{-1}$ at 0.0100 wt% loading	High salt rejection (Na_2SO_4 > $MgSO_4$ > NaCl); dye rejection > 99%	Exceptional chlorine resistance (99% salt retention after 10,000 ppm·h chlorination)	[78]
Titanate Nanotubes	Branched 3D network, inner Ø 6 nm, outer Ø 12 nm, titanate layers	Hydrothermal growth on titanium substrates	Not explicitly quantified for OSN; high surface area benefits separation	Effective for molecular sieving in membrane separation	Thermally/chemically robust; suitable for harsh environments	[79]

3.3. Blending with Other Polymers

Incorporating additional polymers into polyamide membranes has emerged as a promising strategy to enhance their performance in OSN applications. This approach leverages the unique properties of various polymers to improve membrane permeability, selectivity, antifouling characteristics, and mechanical robustness. Recent studies have demonstrated that blending poly(amidoamine) (PAMAM) dendrimers into the polyamide matrix can significantly increase water flux while maintaining high salt rejection. For instance, Tang et al. reported that incorporating PAMAM G4 and G5 generations into the membrane structure resulted in a pure water flux improvement of 106% without com-

promising separation performance [80]. An effective modification strategy involves the deposition of a network-like interlayer composed of tannic acid (TA) and poly (sodium 4-styrenesulfonate) (PSS) onto the membrane surface. This interlayer significantly enhances hydrophilicity and provides a chemically favorable microenvironment for subsequent IP, thereby promoting the formation of more uniform and defect-free polyamide layers. However, while the introduction of such interlayers improves both permeance and salt rejection, increased interlayer thickness may impose additional resistance to water transport by extending the diffusion path and altering local porosity. Therefore, optimizing the interlayer thickness is critical to balance the trade-off between enhanced selectivity and minimized hydraulic resistance, ensuring high separation efficiency without compromising flux [81]. Additionally, the integration of amphiphilic polymers through surface modifications has been shown to improve antifouling properties. For example, a two-step surface modification using triethanolamine (TEOA) and perfluorooctyl trichlorosilane (PFTS) resulted in a membrane with enhanced resistance to fouling while maintaining desirable separation performance [82]. These polymer blending techniques offer a versatile and effective means to tailor polyamide membranes for specific OSN applications, addressing challenges related to solvent resistance, fouling, and separation efficiency. Ongoing research continues to explore novel polymer combinations and fabrication methods to further optimize membrane performance in diverse industrial contexts [83].

3.3.1. Blending with Flexible Polymers

A promising strategy to enhance the performance of polyamide membranes in OSN involves the integration of flexible polymers into the membrane matrix, thereby creating composite membranes that synergistically combine the mechanical resilience of polyamide with the permeability advantages of flexible moieties. In a recent case study, piperidine (PPR), a monoamine featuring a flexible aliphatic ring, was incorporated into the interfacial polymerization (IP) reaction between m-phenylenediamine (MPD) and trimesoyl chloride (TMC) to modify the polyamide network. This structural modification significantly enhanced the membrane's water permeance, achieving nearly a threefold increase, while maintaining a high NaCl rejection rate of 99.4%. The introduction of the flexible aliphatic rings contributed to a more open and interconnected polyamide microstructure, facilitating increased water transport channels without compromising the structural integrity of the membrane [84,85]. Moreover, this modification effectively alleviated the conventional permeability–selectivity trade-off typically associated with traditional TFC polyamide membranes. The enhanced chain mobility enabled by the flexible PPR units promoted more efficient molecular packing within the polyamide matrix, thereby maintaining high selectivity alongside increased permeability. These findings underscore the potential of flexible polymer incorporation as a design principle for next-generation OSN membranes, especially where high throughput and robust solvent resistance are required [85].

3.3.2. Incorporation of Hyperbranched Polymers

An innovative and effective strategy to enhance the hydrophilicity and antifouling properties of polyamide membranes in OSN systems involves the grafting of hyperbranched polyglycerol (hPG) onto the membrane surface. The incorporation of hPG into thin-film composite (TFC) polyamide membranes has been shown to dramatically reduce the water contact angle to approximately 16.4°, reflecting a significant increase in surface hydrophilicity. This structural modification facilitates the formation of a highly hydrated surface layer that resists protein adsorption, thereby enhancing antifouling performance under filtration conditions. In comparative studies, hPG-grafted TFC membranes demonstrated a 41.5% increase in water permeability relative to pristine TFC membranes, without

compromising selectivity [67]. The exceptional performance of hPG-modified membranes can be attributed to the three-dimensional, dendritic architecture of hPG, which not only provides abundant hydrophilic functional groups but also supports efficient solvent transport pathways. This configuration directly addresses the longstanding trade-off between permeability and fouling resistance that limits conventional polyamide membranes, offering a promising route for the development of high-performance membranes suitable for extended operation in chemically aggressive OSN environments [86,87].

3.3.3. Blending with Thermoplastic Polyurethanes

Blending polyamide with thermoplastic polyurethanes (TPUs) has emerged as a promising strategy to enhance the mechanical robustness and flexibility of membranes for OSN applications. The incorporation of TPU into polyamide matrices has been shown to significantly improve elongation at break and tensile strength, thereby enhancing operational durability under high-pressure conditions. These enhancements are critical for OSN systems, where membranes are routinely subjected to mechanical stresses during prolonged exposure to organic solvents and pressure-driven operations [67,68]. Importantly, the TPU-modified membranes retained satisfactory separation performance, indicating that mechanical reinforcement did not compromise filtration capabilities. The improved elasticity and toughness of the blended membranes provide an effective means of mitigating failure due to deformation or fatigue, positioning these materials as strong candidates for solvent-resistant OSN applications requiring high durability and structural integrity [68].

3.3.4. Challenges and Considerations

While polymer blending offers a viable strategy to enhance the performance of polyamide membranes for OSN, achieving compatibility between dissimilar polymers remains a critical challenge. Incompatibility often leads to phase separation, resulting in non-selective voids that compromise membrane selectivity and mechanical integrity. To address this, recent studies emphasize the importance of optimizing blend ratios and tailoring processing conditions to promote homogeneous dispersion and stable interfacial interactions between polymer phases [67]. The choice of fabrication technique plays a pivotal role in the success of blending strategies. Methods such as solution casting and melt blending are commonly employed; however, precise control over parameters like temperature, solvent evaporation rate, and mixing time is essential to prevent the degradation of sensitive components and to maintain membrane uniformity during fabrication. Ensuring compatibility and processing optimization is therefore central to the development of high-performance OSN membranes that combine the advantages of multiple polymeric constituents [88]. The strategic blending of polyamide membranes with complementary polymers represents a significant advancement in membrane technology, particularly for OSN applications. This approach has been shown to improve key performance metrics such as mechanical strength, permeability, selectivity, and antifouling properties. For instance, the incorporation of thermoplastic polyurethanes (TPUs) into polyamide matrices has enhanced mechanical flexibility and tensile properties without compromising filtration performance. Similarly, grafting hyperbranched polymers such as polyglycerol (hPG) has led to improved hydrophilicity and fouling resistance, contributing to increased solvent permeability and operational stability [83,89]. Moreover, rigid-flexible coupling, by integrating flexible monomers like piperidine into interfacial polymerization processes, has shown promise in overcoming the traditional permeability-selectivity trade-off, yielding membranes with enhanced transport efficiency and salt rejection. Despite these advances, challenges related to polymer compatibility and phase dispersion persist. Ongoing research continues to focus on optimizing blending strategies and processing conditions to

unlock the full potential of polyamide-based OSN membranes across diverse chemical separations [83,84].

4. Properties of Polyamide Membranes

Polyamide membranes are widely utilized in OSN due to their exceptional chemical stability, mechanical robustness, and selective permeability. These attributes make them particularly suitable for separating solutes in diverse and often harsh organic solvent environments. In the context of OSN, polyamide membranes demonstrate remarkable resistance to a variety of organic solvents, including methanol, ethanol, acetone, N-methylpyrrolidone (NMP), dimethylformamide (DMF), and tetrahydrofuran (THF) [34]. This broad solvent compatibility is attributed to the inherent chemical resilience of polyamide material, which maintains structural integrity and performance in aggressive solvent conditions. The mechanical strength of polyamide membranes ensures durability under the high-pressure conditions often required in OSN processes. This robustness is essential for maintaining membrane performance over extended operational periods, reducing the frequency of membrane replacement and thereby lowering operational costs. Selectivity permeability is another critical feature of polyamide membranes in OSN applications [90]. The ability to finely tune pore size allows for the precise separation of molecules based on size and other physicochemical properties. This selectivity is crucial for applications such as solvent recovery, purification of pharmaceutical intermediates, and removal of impurities from chemical feedstocks [91]. Recent advancements have further enhanced the performance of polyamide membranes in OSN. For instance, the development of flexible aliphatic–aromatic polyamide thin-film composite membranes has led to improved stability and selectivity in various organic solvents. These membranes exhibit high permeability and can precisely fractionate molecules with minimal differences in molar mass, demonstrating their potential for efficient molecular separations in the pharmaceutical and chemical industries [84].

4.1. Structural Characteristics

Polyamide membranes exhibit distinctive structural characteristics that critically influence their performance in OSN applications. Their architecture, encompassing parameters such as pore size, crosslinking density, and surface morphology, plays a pivotal role in determining solvent permeance, solute rejection, and long-term operational stability. A key structural feature of polyamide membranes is their dense, crosslinked network, which imparts exceptional chemical resistance and mechanical strength. This robustness enables the membranes to withstand a variety of organic solvents, including polar aprotic solvents like dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), as well as non-polar solvents such as toluene and n-hexane [84]. The crosslinked structure also facilitates the formation of sub-nanometer pores, allowing for precise molecular sieving and high selectivity in solute separation [92]. Surface morphology is another critical aspect influencing membrane performance. For instance, the incorporation of “leaf-like” nanostructures on the membrane surface has been shown to increase surface area and enhance solvent flux without compromising selectivity [93]. Additionally, the integration of flexible aliphatic chains into the polyamide matrix can modulate free volume within the membrane, thereby improving permeability while maintaining high rejection rates [84]. Recent advancements have also explored the use of inorganic supports and nanomaterials to further enhance membrane properties [93]. For example, the deposition of polyamide layers onto ceramic-supported membranes has resulted in improved solvent resistance and mechanical stability, making them suitable for harsh OSN conditions. Moreover, the application of Surfactant-Assembly Regulated Interfacial Polymerization techniques has led to the development

of membranes with highly uniform sub-nanometer pores, achieving sub-1 Å precision in molecular separation [92].

4.1.1. Pore Structure and Size Distribution

The pore architecture of polyamide membranes plays a pivotal role in determining their performance in OSN applications. Tailoring this microstructure has become increasingly feasible through advancements in fabrication strategies. Traditional IP often results in membranes characterized by heterogeneous and irregular pore distributions, which can compromise selectivity and long-term flux stability. In contrast, emerging approaches such as Surfactant-Assembly Regulated Interfacial Polymerization (SARIP) have enabled the formation of highly uniform sub-nanometer pores, greatly enhancing molecular sieving precision and solute rejection efficiency [92]. A particularly promising yet underexplored phenomenon influencing polyamide morphology is the formation of nanobubbles during IP. These nanoscopic gaseous domains, generated at the aqueous–organic interface, act as transient pore-forming templates that can locally disrupt polymer chain packing. This disruption introduces additional free volume and fosters the development of more interconnected and uniform pore networks within the selective layer. The presence of nanobubbles has been associated with an increase in porosity and a refinement in pore size distribution, thereby offering an additional degree of control over membrane structure and function. Complementing this understanding, positron annihilation lifetime spectroscopy (PALS) studies have revealed that polyamide membranes fabricated using advanced IP techniques, particularly those that incorporate nanobubble formation or surfactant-mediated structuring, exhibit more narrowly distributed free volume elements compared to conventional counterparts. Such structural precision directly correlates with improved size-exclusion capabilities, enhanced solvent permeability, and greater operational stability in chemically aggressive environments typical of OSN processes [94]. Together, these insights underscore the importance of fabrication-driven morphological control in the continued development of high-performance OSN membranes. A tabular summary of the pore structure and size distribution in polyamide membranes is in Table 4.

Table 4. A tabular summary of the pore structure and size distribution in polyamide membranes.

Membrane Type	Pore Size Distribution	Average Pore Size	Method of Fabrication	Key Findings	Reference
AIP-PA Membrane	Sub-nanometer to micrometer range	Not specified	Anhydrous interfacial polymerization (AIP)	In comparison to traditional techniques, the AIP membrane exhibited a thinner thickness and reduced pore strength, along with a smaller molecular weight cutoff (MWCO) for solutes.	[52]
TFC Membrane	Narrowly distributed free volume pores	Smaller than pristine PA layer	Inorganic salt-mediated (IP)	Improved permeance (20–435%) and solute rejection (10–170%) were the results of increased structural homogeneity.	[30]
TFC Membrane	Wide distribution due to liquid–liquid phase separation	100–1000 nm	(IP)	A dense, thin layer of the active skin layers created by gelation permits regulated permeability and selectivity.	[95]

Table 4. *Cont.*

Membrane Type	Pore Size Distribution	Average Pore Size	Method of Fabrication	Key Findings	Reference
NF Membrane	Uniform sub-nanometer pores	Sub-Angstrom scale	Surfactant-assembly regulated interfacial polymerization (SARIP)	Compared to traditional IP, accurate solute separation was achieved with a sharper pore size distribution.	[92]
Electrospun Membrane	0.55 μm to 1.14 μm	Increasing with polymer concentration	Electrospinning	A narrow pore size distribution is beneficial for filtration efficiency, and pore size increases with polymer concentration.	[61]
Nanofiltration Membrane	Heterogeneous mass transfer leading to wide distribution	Not specified	Multiple interfacial polymerization process	Both separation efficiency and antifouling performance were enhanced by a narrowing pore size distribution.	[96]

4.1.2. Layer Structure

Thin-film composite (TFC) architectures, central to the design of high-performance polyamide membranes for OSN, are constructed by depositing an ultrathin polyamide selective layer onto a porous support. This bilayered configuration synergistically enhances mechanical durability while maximizing selective transport through the active surface. Typically, the polyamide selective layer exhibits a thickness in the range of 30–40 nm, striking a balance between reduced mass transfer resistance and high solute rejection efficiency. The functional performance of OSN membranes is closely governed by the morphology and formation dynamics of this active skin layer [92]. The dense polyamide layer is generally formed via IP, where gelation at the interface gives rise to a defect-free barrier layer, while the porous substructure is shaped by liquid–liquid phase separation (LLPS) of the support polymer. The interplay between these two layers is critical; their structural integration dictates the overall permeance, rejection characteristics, and long-term stability of the membrane under exposure to harsh organic solvents. Recent investigations have underscored the importance of tuning the polymerization kinetics and phase inversion parameters to optimize interlayer adhesion and mitigate delamination under OSN operating pressures [52]. Table 5 provides a comparative summary of layer morphologies and compositions across various polyamide TFC membranes developed for OSN applications.

Table 5. A tabular summary of the layer structure in polyamide membranes.

Membrane Type	Layer Structure	Layer Thickness	Fabrication Method	Key Findings	References
TFC Membrane	Nanoscale-ordered polyamide layer on porous support	55 ± 3 nm (PIP/g-C_3N_4)	Interfacial polymerization (IP) with g-C_3N_4 nanosheets	Improved homogeneity and hollow channel configuration enhanced selectivity and penetration.	[28]
TFC Membrane	Dense polyamide layer with diffusion-limited growth	50–400 nm	In situ IP between MPD and TMC	Spatial heterogeneity characterizes layer formation; a higher density in the center provides a selection barrier.	[30]
TFN Membrane	Hollow ridge-and-valley structure with embedded nanoparticles	20–30 nm (PA layer)	Interfacial polymerization with C_3N_4 nanoparticles	Water permeance was improved by the nanoparticles' increased surface area and hydrophilicity.	[97]
AIP Membrane	Thinner selective layer with granular protrusions	~35 nm (AIP-PA) vs. ~40–50 nm (CIP-PA)	Anhydrous interfacial polymerization (AIP)	Water permeance is improved by a thinner selective layer because it lowers transport resistance.	[52]

Table 5. *Cont.*

Membrane Type	Layer Structure	Layer Thickness	Fabrication Method	Key Findings	References
TFC Membrane	Ultrathin PA selective layer over microporous support	~50–400 nm (PA) over ~140 μm (PES)	In situ IP between MPD and TMC	FTIR and XPS revealed the successful development of the PA skin layer; the preparation temperature affected the surface morphology.	[98]
Composite Membrane	Integrally skinned PA layers over PES support	5–10 nm (active layer) on PES substrate (~140 μm)	In situ IP reaction of MPD and TMC at the interface of water-organic solutions	XPS was used to check the elemental composition; the absence of support peaks signifies that the membrane formed successfully.	[95]

4.1.3. Morphological Features

The surface morphology of polyamide membranes plays a pivotal role in determining both their separation performance and fouling resistance, two critical parameters for effective OSN. High-resolution scanning electron microscopy (SEM) studies have consistently shown that many polyamide membranes exhibit relatively smooth and uniform top surfaces, which reduce the likelihood of foulant adhesion and thus enhance antifouling properties. Surface topography, including microscale roughness, also influences hydrophilicity; membranes with moderate roughness often display improved wettability, further contributing to fouling resistance in harsh solvent environments [63,99]. In electrospun polyamide membranes, prominent candidates for next-generation OSN systems, the fiber diameter and arrangement significantly influence the resulting pore size and porosity. Experimental investigations have demonstrated that increasing the polymer concentration during electrospinning yields thicker fibers and consequently larger mean pore sizes due to reduced jet stretching during fiber formation. The resultant nonwoven nanofibrous mat allows for fine-tuned control over membrane porosity, as interfiber spacing directly defines pore boundaries. Such structural versatility enables the fabrication of membranes with customized filtration profiles suitable for OSN applications, where precise control over solvent transport and solute rejection is essential [100,101]. Table 6 shows a summary of the morphological features of polyamide membranes.

Table 6. A tabular summary of the morphological features of polyamide membranes.

Membrane Type	Morphological Features	Surface Roughness	Layer Thickness	Key Findings	Reference
Polyamide Membrane	Dome and dimple crumpling observed via TEM	Not specified	Not specified	Membrane synthesis and performance were impacted by quantitative morphometry, which connected morphology characteristics to monomer concentrations.	[102]
AIP-PA Membrane	Dense surface with granular protrusions observed via SEM	7.2 nm (AIP-PA) vs. 6.82 nm (CIP-PA)	Not specified	AIP membranes performed better at separation because they had a more consistent structure and a lower free volume than CIP membranes.	[52]
PIP/g-C_3N_4-PA Membrane	Nanoscale-ordered hollow structure with arched channels observed via TEM and AFM	Not specified	55 ± 3 nm (PIP/g-C_3N_4-PA) vs. 83 ± 5 nm (control)	By increasing surface area and structural homogeneity, g-C_3N_4 increased permeability characteristics.	[28]

Table 6. *Cont.*

Membrane Type	Morphological Features	Surface Roughness	Layer Thickness	Key Findings	Reference
Polyamide-6 Membrane	Isotropic to anisotropic morphology transition with increased gelation time observed via SEM	Increased with gelation time	Not specified (but noted to change)	The density of the skin layer increased with gelation time, influencing the size of pores and the way they swelled.	[102]
TFC Membrane	Ridge-and-valley structure observed via FESEM; varying surface features based on preparation temperature	Not specified (but noted to change)	Thinner PA film at lower temperatures; thicker at higher temperatures (TFC 3: ~50–400 nm)	Filtration efficiency was impacted by the considerable variations in surface shape with preparation conditions.	[98]
Bio-based Electrospun Membrane	Nonwoven fibrous structure with varying fiber diameters observed via SEM and AFM	Not specified; hydrophilicity noted	Not specified; fiber diameter influences pore size distribution	Increased microplastic filtering efficiency as a result of electrospinning's high surface area and porosity.	[61]

4.2. Chemical Composition

The widespread application of polyamide membranes in separation technologies, including OSN, is largely attributed to their distinct chemical composition, which governs key performance attributes such as solvent resistance, selective permeability, and structural stability. Recent studies have provided critical insights into the molecular architecture of polyamide membranes, revealing that their performance in OSN systems is tightly linked to the presence of amide linkages and aromatic backbones formed during interfacial polymerization. These structural motifs not only enhance membrane rigidity but also contribute to their excellent chemical resistance against a broad spectrum of organic solvents [30,103]. Advanced spectroscopic analyses, including Fourier Transform Infrared Spectroscopy (FTIR) and XPS, have confirmed that the ratio and distribution of functional groups, such as carboxyl, amine, and amide moieties, can be systematically tuned to tailor membrane–solvent interactions, thereby optimizing solute rejection and permeability. Moreover, modifications to the polyamide chemistry, including the incorporation of hydrophobic or crosslinkable monomers, have been shown to enhance solvent resistance while maintaining membrane selectivity in aggressive OSN environments [36,62].

4.2.1. Basic Chemical Structure

The primary structural motif in polyamide membranes is the amide linkage (-CONH-), formed through the condensation reaction between diamines and diacyl chlorides [104]. In the context of thin-film composite (TFC) membranes for OSN, m-phenylenediamine (MPD) and trimesoyl chloride (TMC) are among the most widely used monomer pairs [23,105]. Their IP at the aqueous–organic interface leads to the formation of a dense, crosslinked polyamide selective layer, which exhibits robust mechanical strength and excellent chemical resistance, critical attributes for OSN applications [106]. The integrity of the polymerization process is typically validated using FTIR, where the characteristic stretching vibration of the carbonyl group (C=O) around 1650 cm^{-1} is strongly observed, confirming the successful formation of amide bonds [36]. These covalent linkages play a pivotal role in ensuring membrane durability under harsh organic solvent conditions while also enabling precise molecular sieving based on solute size and solvent–membrane interactions [20].

4.2.2. Additives and Modifications

Recent advances in polyamide membrane engineering have focused on the incorporation of functional additives to enhance performance attributes critical to OSN. For instance, the integration of polydimethylsiloxane (PDMS) into polyamide matrices has been shown to significantly influence gas permeability and selectivity [107]. The inclusion of PDMS not only enhances membrane flexibility but also mitigates brittleness, thus improving mechanical durability under solvent exposure [84,108]. In another study, the introduction of graphitic carbon nitride (g-C_3N_4) into the polyamide layer resulted in notable improvements in separation efficiency. This enhancement is attributed to both chemical modifications and structural reinforcement of the membrane matrix. X-ray photoelectron spectroscopy (XPS) analysis revealed that g-C_3N_4 alters the nitrogen-to-carbon ratio within the membrane, modulating surface charge and influencing solute–membrane interactions, key factors in achieving superior OSN performance [28]. Moreover, the development of semi-aromatic polyamide, achieved by copolymerizing aromatic and aliphatic monomers, has yielded membranes that exhibit a favorable balance between permeability and selectivity. Such hybrid structures, containing rigid aromatic backbones with flexible aliphatic chains, have demonstrated enhanced salt rejection while maintaining high solvent permeance. These molecular design strategies represent a promising route to mitigate the inherent trade-off between selectivity and flux commonly observed in membrane separations [107,109].

4.2.3. Crosslinking and Density

The degree of crosslinking in polyamide membranes is a critical determinant of their mechanical integrity and chemical resistance, properties that are essential for robust performance in OSN. Recent comparative studies highlight that membrane synthesis via anhydrous interfacial polymerization (AIP) can yield significantly higher crosslinking densities than those produced by conventional interfacial polymerization (CIP). The absence of water in AIP allows for more efficient reaction kinetics between acyl chlorides and diamines, leading to tighter polymer networks and enhanced separation performance under aggressive solvent conditions [52,110]. To elucidate the chemical structure and crosslinking characteristics of polyamide membranes, advanced spectroscopic techniques such as FTIR and X-ray photoelectron spectroscopy (XPS) are frequently employed. FTIR analysis typically reveals strong absorption bands around ~1650 cm^{-1} and ~1540 cm^{-1}, corresponding to the C=O stretching (amide I) and N-H bending (amide II) vibrations, respectively, indicative of successful amide bond formation. Complementarily, XPS provides detailed elemental composition profiles, identifying the presence and relative ratios of key elements such as carbon (C), nitrogen (N), and oxygen (O). These insights are particularly valuable in assessing membrane crosslinking, surface chemistry, and functional group distribution relevant to solvent-specific separations in OSN [20,111].

4.2.4. Chemical Stability

Polyamide membranes exhibit remarkable chemical stability, enabling them to endure a wide range of solvent exchange and pH conditions, which is essential for their deployment in OSN, desalination, and advanced wastewater treatment. Empirical studies have demonstrated that polyamide membranes retain structural and functional integrity even under chemically aggressive environments, making them suitable for prolonged operational lifespans in both aqueous and organic media [34,103]. The filtration performance and separation efficiency of polyamide membranes are intrinsically linked to their chemical composition. The foundational structure, dominated by amide linkage, can be molecularly engineered through variations in crosslinking density and the incorporation of functional

additives to meet application-specific demands. For instance, increased crosslinking enhances resistance to swelling in polar solvents [112], while the incorporation of hydrophilic or charged moieties can fine-tune solute selectivity and antifouling behavior [113]. Continued research efforts are focused on chemically tailoring polyamide matrices to enhance their compatibility with diverse solvents and to expand their operational envelope. These innovations are driving the development of next-generation OSN membranes with superior permeability-selectivity trade-offs [36,114]. Based on recent research findings, Table 7 gives a summary of the different chemical compositions of polyamide membranes.

Table 7. A tabular summary of different chemical compositions in polyamide membranes.

Membrane Type	Chemical Composition	Key Monomers	Additives/Modifiers	Key Findings	References
PA-PDMS Membrane	Polyamide with PDMS groups	p-phenylenediamine (MPD), Trimesoyl Chloride (TMC)	Poly(dimethylsiloxane) (PDMS)	Membranes showed improved permeability and gas selectivity; PA-PDMS-20 demonstrated CO_2/N_2 selectivity of 41.84.	[108]
AIP-PA Membrane	Polyamide layer with amide groups	Piperazine (PIP), TMC	None specified	FTIR validated the successful synthesis, which was distinguished by its high crosslinking density and ionic sieving ability.	[52]
PA-g-C_3N_4 Membrane	Polyamide with graphite carbon nitride (g-C_3N_4) nanosheets	Piperazine (PIP), TMC	g-C_3N_4 nanoparticles	Nanoscale ordered structures improve separation performance; at pH > 3, there is a modest increase in negative charge.	[28]
TMC-MPD Membrane	Crosslinked polyamide network	MPD, TMC	None specified	Showed good rejection rates for NaCl; the performance was correlated with the synthesis's monomer ratio.	[115]
TMC-BA Membrane	Polyamide with carboxylic acid groups	3,5-diaminobenzoic acid (BA) TMC	None specified	Greater crosslink density than conventional IP membranes, which improves salt rejection and hydrophilicity.	[116]
PA Composite Membrane	Polyamide with varying degrees of crosslinking	MPD, TMC	None specified	Different levels of crosslinking impacted performance indicators, including chlorine tolerance, according to chemical structure analysis.	[117]

4.3. Mechanical Properties

Polyamide membranes are widely recognized for their exceptional mechanical robustness, a critical attribute underpinning their reliability and durability across a broad spectrum of filtration and separation processes, including OSN. Their mechanical integrity ensures resistance to deformation, compaction, and delamination under high transmembrane pressure and aggressive solvent conditions, which are characteristics of OSN operations [34]. Recent studies have provided deeper insight into the tensile strength, elastic modulus, and elongation at break of polyamide membranes, emphasizing the role of fabrication techniques, crosslinking density, and additive incorporation on mechanical behavior [52,116]. For example, membranes fabricated via anhydrous interfacial polymerization (AIP) exhibit significantly enhanced mechanical properties compared to those synthesized through conventional interfacial polymerization (CIP), owing to the formation of a more densely crosslinked network [52]. Additionally, the mechanical stability of polyamide membranes has been shown to directly influence long-term OSN performance. Membranes that combine high tensile strength with sufficient flexibility demonstrate reduced suscepti-

bility to solvent-induced swelling and mechanical fatigue, leading to prolonged operational lifetimes in high-pressure solvent environments [116].

4.3.1. Tensile Strength

Tensile strength is a key metric in evaluating a membrane's ability to withstand mechanical stress during high-pressure filtration, particularly in OSN environments. Polyamide membranes, especially those derived from polyamide 6.9 (PA 6.9), exhibit significantly superior tensile strength compared to commonly used polymeric materials such as polyvinylidene fluoride (PVDF) and polyacrylonitrile (PAN), making them ideal candidates for demanding OSN applications. Notably, electrospun PA 6.9 membranes have demonstrated enhanced mechanical integrity, attributed to their nanofibrous architecture and well-aligned molecular structure, which facilitates high stress tolerance during solvent exposure [61]. The mechanical robustness of polyamide membranes is heavily influenced by the fabrication route. Comparative studies have shown that membranes fabricated via anhydrous interfacial polymerization (AIP) possess markedly higher tensile strengths than those produced by conventional interfacial polymerization (CIP), primarily due to increased crosslinking density and reduced defect formation. For instance, AIP-derived polyamide membranes have demonstrated tensile strength values approaching 4.1 MPa, indicating a level of mechanical resilience suitable for long-term solvent-based separations under elevated pressures [52]. These findings underscore the importance of tailoring fabrication strategies to optimize mechanical performance, a critical requirement for extending membrane longevity and maintaining separation efficiency in OSN systems.

4.3.2. Elongation at Break

Elongation at break is a critical parameter that reflects a membrane material's ductility and flexibility, indicating its capacity to undergo deformation under mechanical stress before failure. In the context of OSN, where membranes are often subjected to high pressure and solvent-induced swelling, such mechanical resilience is essential for operational stability. Polyamide membranes are recognized for their favorable elongation properties, which contribute significantly to their robustness during prolonged OSN processes [118]. Recent studies have demonstrated that the elongation at break in electrospun polyamide membranes is positively correlated with fiber diameter. Specifically, membranes comprising thicker nanofibers exhibit enhanced ductility and strain tolerance, attributes that are particularly advantageous in dynamic filtration environments. This structural adaptability reduces the risk of mechanical failure and enhances membrane longevity, thereby supporting reliable performance under repeated solvent cycling and high-stress conditions [61]. These findings highlight the importance of tailoring fiber morphology during membrane fabrication to enhance mechanical flexibility, a crucial design consideration for next-generation polyamide membranes optimized for OSN applications.

4.3.3. Stiffness and Young's Modulus

Young's modulus is a fundamental metric for assessing a material's stiffness, representing its ability to resist deformation under applied stress. For polyamide membranes employed in OSN, an optimal Young's modulus is essential to maintain mechanical stability without compromising flexibility during operation. Typically, polyamide membranes exhibit moderate Young's modulus values, striking a critical balance between rigidity and mechanical compliance [119]. Experimental data suggest that an increase in membrane porosity often correlates with a reduction in stiffness due to a decrease in interfiber junctions, which compromises structural integrity under mechanical loading. This effect is particularly pronounced in electrospun polyamide architectures, where fiber packing density governs the mechanical response. Moreover, the membrane's gelation time during

fabrication significantly influences its modulus. Longer gelation times generally produce denser polymer networks, yielding membranes with higher stiffness and tensile strength but reduced elongation at break, as reported in OSN-specific membrane studies [61,120]. This interdependence implies that mechanical performance can be finely tuned by controlling fabrication parameters such as porosity and gelation time, enabling the design of OSN membranes that retain structural durability while accommodating necessary flexibility under dynamic operating conditions.

4.3.4. Impact of Additives and Modification

The mechanical robustness of polyamide membranes can be significantly enhanced through polymer blending and nanoparticle incorporation, strategies increasingly adopted in the development of next-generation OSN membranes. For example, the integration of polydimethylsiloxane (PDMS) into polyamide matrices has been shown to improve both tensile strength and elongation at break, providing superior mechanical compliance under stress while maintaining structural integrity. This enhancement is attributed to the flexible siloxane chains of PDMS, which impart elasticity and reduce brittleness in the composite membrane [67,68]. In addition to polymeric additives, chemical crosslinking serves as a powerful approach to reinforce the mechanical stability of polyamide membranes. Crosslinked structures exhibit greater resistance to deformation and improved dimensional stability when subjected to the aggressive environments often encountered in OSN processes. Studies have demonstrated that crosslinked polyamide membranes not only maintain their mechanical resilience under high solvent flux but also retain separation performance over prolonged operational periods [86,88]. These advancements underscore the potential of structural modifications to tailor the mechanical behavior of polyamide membranes for high-performance OSN applications, particularly where solvent compatibility and operational durability are critical.

4.3.5. Durability and Resistance to Deformation

Polyamide membranes are widely recognized for their mechanical resilience across diverse environmental conditions, a property critical to their sustained performance in OSN systems. Thermal post-treatment has been shown to significantly enhance mechanical attributes, particularly by reducing membrane flexibility while increasing tensile strength, thereby improving their structural robustness under operational stress. This increase in tensile integrity is especially beneficial for long-term applications in solvent-rich environments, where mechanical degradation can otherwise compromise membrane efficiency [20]. Key mechanical parameters such as tensile strength, elongation at break, Young's modulus (stiffness), and fatigue resistance collectively define the functional durability of polyamide membranes in OSN. Ongoing research continues to investigate advanced fabrication strategies, including thermal annealing, interfacial polymerization tuning, and nanomaterial reinforcement, to optimize these mechanical traits. These developments aim to expand the utility of polyamide membranes across sectors, demanding chemically robust and mechanically stable filtration platforms, such as pharmaceutical solvent recovery, petrochemical separation, and fine chemical processing [52,67]. A comparative overview of mechanical properties, including tensile strength, elongation at break, stiffness, and operational durability, is summarized in Table 8 to provide insights into structure–property correlations for next-generation OSN membrane design.

Table 8. A tabular summary, based on new research findings, of the mechanical properties of polyamide membranes, such as tensile strength, elongation at break, stiffness, and durability.

Membrane Type	Tensile Strength (MPa)	Elongation at Break	Young's Modulus	Durability	Key Findings	Reference
PA 6.9 Electrospun membrane	Higher than PVDF and PAN (exact value not specified)	Increased with fiber diameter	Not specified	High durability under operational conditions	When compared to other materials, PA 6.9 membranes demonstrated excellent mechanical capabilities; stiffness rose as porosity decreased	[61]
Polyamide membrane (25% concentration)	Higher tensile strength compared to lower concentrations	Higher strain is observed in higher concentrations	Lower Young's modulus compared to others	Good chlorine tolerance and stability in varying pH ranges	Tensile strength and strain were noticeably superior to membranes with lower concentration, and mechanical characteristics improved with polymer concentration	[117]
AIP-PA membrane	Not specified but noted for high performance	Not specified	7.2 MPa (surface roughness noted)	Enhanced durability due to crosslinking density from the AIP method	Because of their special structure, AIP membranes demonstrated enhanced mechanical stability and water permeability	[52]
PA-PDMS membrane	Not specified; focused on gas separation properties	Not specified; focus on gas permeability instead	Not specified; noted for flexibility due to PDMS incorporation	Enhanced durability through blending with PDMS groups, improving flexibility, and reducing brittleness	While keeping strong mechanical qualities, the use of PDMS enhanced gas separation performance	[108]
Interfacially polymerized polyamide membrane	Up to 37 MPa (constant value for high concentrations)	Not specified	Not specified	High rupture strength correlates with permeation performance	Better permeation behavior, in line with solution–diffusion transport mechanisms, was demonstrated by membranes with greater rupture strength	[121]

4.4. Thermal Stability

Polyamide membranes are renowned for their favorable thermal stability, a critical attribute that significantly influences their performance across diverse operating conditions, particularly in OSN applications. This thermal resilience enables their widespread use in filtration and separation processes where temperature fluctuations are common [20,34]. Recent advancements have focused on enhancing the thermal stability of polyamide membranes to meet the rigorous demands of OSN. For example, the incorporation of triaminopyrimidine into the polyamide selective layer has been demonstrated to significantly enhance the crosslinking density of the resulting membrane structure. The heightened crosslinking introduces a more rigid and tightly interconnected polymeric network, which plays a critical role in improving the thermal stability of the membrane. Mechanistically, increased crosslinking limits the segmental mobility of polymer chains, thereby reducing the likelihood of chain rearrangement, relaxation, or degradation when exposed to elevated temperatures. The presence of multiple amine functionalities in triaminopyrimidine promotes extensive covalent bonding with acyl chloride groups during IP, yielding a densely crosslinked matrix that is resistant to thermal distortion. As a result, these membranes exhibit sustained permeate flux and maintain high salt rejection even at operating temperatures up to 75 °C, indicating enhanced structural integrity and separation performance under thermally challenging conditions. Such improvements are particularly advantageous

for OSN processes, where thermal robustness is a prerequisite for long-term operational reliability [122]. Furthermore, heat treatment processes have been employed to bolster the mechanical properties of polyamide membranes. Thermal annealing at controlled temperatures can lead to increased tensile strength and reduced flexibility, thereby improving the membrane's robustness for long-term applications. However, it is essential to optimize heat treatment conditions, as excessive temperatures may adversely affect membrane structure and performance [20,34,52]. In addition to chemical modifications and thermal treatments, the development of polyamide membranes with enhanced thermal stability has been achieved through the integration of inorganic components. For example, the addition of polyhedral oligomeric silsesquioxane (POSS) has been reported to improve heat resistance, with thermogravimetric analysis indicating a higher decomposition temperature compared to unmodified membranes [123]. This enhancement is attributed to the formation of a more thermally stable network structure within the membrane matrix. Overall, the thermal stability of polyamide membranes is a pivotal factor in their efficacy for OSN applications. Ongoing research and development efforts continue to explore innovative strategies to augment this property, ensuring reliable and efficient performance in high-temperature filtration processes.

4.4.1. Thermal Stability Characteristics

Thermogravimetric analysis (TGA) is a widely adopted technique for evaluating the thermal degradation behavior of polyamide membranes, offering insight into their stability under high-temperature operating conditions relevant to OSN. Studies have consistently reported that polyamide membranes exhibit high thermal resilience, with decomposition temperatures ranging from approximately 400 °C to over 500 °C, depending on their molecular architecture and the presence of functional additives. For example, the incorporation of titanium dioxide (TiO_2) nanoparticles into thin-film composite (TFC) polyamide membranes has been shown to elevate the onset degradation temperature from 430 °C to 530 °C. This enhancement is primarily attributed to the ability of TiO_2 to restrict polymer chain mobility, thereby reinforcing the membrane's structural integrity at elevated temperatures [20,34,68]. Beyond thermal resistance, TiO_2-modified membranes also demonstrate improved antifouling performance, rendering them suitable for high-temperature applications involving complex biomolecular separations. Similarly, the inclusion of polydimethylsiloxane (PDMS) moieties into the polyamide matrix has been shown to enhance both thermal flexibility and operational durability, enabling stable performance across a temperature range of 25 °C to 55 °C, conditions commonly encountered in OSN operations. These modifications underscore the potential of nanocomposite and hybrid membrane designs to push the boundaries of polyamide membrane stability and broaden their applicability in thermally demanding separation processes [67,68].

4.4.2. Thermal Response Under Operational Conditions

Polyamide membranes used in OSN are frequently subjected to variable thermal environments during operation. Elevated feed temperatures have been shown to enhance permeation flux, primarily due to increased molecular diffusion and reduced solution viscosity. For instance, thin-film composite membranes exhibit improved water permeance at temperatures up to 65 °C without compromising their structural integrity. This thermal tolerance enables more efficient separation in thermally intensive applications [20,52]. However, extended exposure to elevated temperatures can induce polymer chain mobility, leading to membrane swelling and compaction. These thermal effects may negatively impact both permeability and selectivity, as excessive swelling increases water uptake while simultaneously reducing mechanical stability over time. Compaction, in particular,

can diminish long-term performance by decreasing the membrane's effective porosity and mechanical resilience. Therefore, while moderate thermal enhancement may optimize flux in OSN systems, careful thermal management is critical to preserving membrane performance and longevity under sustained operational stress [52].

4.4.3. Comparative Studies on Fabrication Conditions

The synthesis temperature during membrane fabrication plays a pivotal role in determining the thermal stability and structural characteristics of polyamide membranes, particularly for OSN applications. Recent studies have shown that membranes synthesized at lower temperatures tend to exhibit denser and thinner polyamide layers, attributed to enhanced crosslinking efficiency under suppressed reaction kinetics. This structural refinement not only improves thermal stability but also positively influences separation performance. For example, polyamide membranes fabricated at −20 °C demonstrated superior permeability and selectivity compared to those prepared at ambient or elevated temperatures, indicating that low-temperature interfacial polymerization can yield membranes with optimized architecture for high-performance solvent-resistant filtration [20,52].

4.4.4. Long-Term Stability

Polyamide membranes exhibit robust thermal stability, maintaining performance across multiple heating cycles without significant degradation in mechanical or separation properties. This resilience is critical for applications in OSN, water treatment, and gas separation, where operating temperatures can vary substantially. Studies have demonstrated that these membranes can endure repeated thermal stress, preserving their structural integrity and functional efficacy [124]. Enhancing the thermal resistance of polyamide membranes can be achieved through the incorporation of additives such as titanium dioxide (TiO_2) and polydimethylsiloxane (PDMS). TiO_2 nanoparticles, when integrated into the polyamide matrix, have been shown to improve thermal stability by increasing the onset degradation temperature and reducing polymer chain mobility. Similarly, the addition of PDMS contributes to enhanced flexibility and thermal resistance, enabling membranes to function effectively across a broader temperature range [67,69]. Ongoing research focuses on optimizing fabrication processes and material modifications to further improve the thermal stability of polyamide membranes. Innovative approaches, such as low-temperature interfacial polymerization and the development of nanocomposite structures, aim to produce membranes with superior thermal properties suitable for advanced separation technologies [73]. Table 9 summarizes key aspects of polyamide membrane thermal stability, including thermal characteristics, response under operational conditions, comparative studies on fabrication parameters, and long-term stability, based on recent research findings.

Table 9. Tabular summary of different aspects of thermal stability in polyamide membranes.

Aspect	Description	Key Findings	Reference
Thermal stability characteristics	Decomposition temperature and thermal stability metrics	The breakdown temperatures of polyamide membranes usually range from 400 °C to more than 500 °C. The onset degradation temperature rose from 530 °C to 550 °C when TiO_2 nanoparticles were present.	[73]
Thermal response under operational conditions	Performance at elevated temperatures and swelling behavior	Because of increased molecular mobility, higher temperatures increase water flux; nevertheless, extended exposure can cause compaction and decreased performance. Membranes remained intact at temperatures as high as 5 °C.	[73]

Table 9. *Cont.*

Aspect	Description	Key Findings	Reference
Comparative studies on fabrication conditions	Impact of synthesis temperature on membrane properties	Higher temperatures created thinner, rougher PA films with better hydrophilicity and permeability, while lower temperatures produced denser, thinner films with less water permeability.	[98]
Long-term stability	Durability under thermal stress and repeated heating cycles	When used within heat constraints, polyamide membranes typically continue to function for extended periods of time. Heat treatment can improve durability and mechanical qualities without causing major deterioration.	[108]

5. Application of Polyamide Membranes in Industry

Polyamide membranes have garnered significant attention in OSN due to their exceptional selectivity, chemical robustness, and adaptability in synthesis. These attributes render them indispensable across various industries, including pharmaceuticals, petrochemicals, and fine chemical production, where precise separation of organic compounds is paramount [89,125]. Recent advancements have led to the development of thin-film composite (TFC) PA membranes with ultrathin selective layers, achieved through refined interfacial polymerization techniques. Such membranes have demonstrated enhanced permeance and selectivity, even under high solute concentrations, making them suitable for challenging OSN processes. The precise control over membrane morphology and thickness has been pivotal in achieving these performance metrics. In pharmaceutical applications, PA membranes facilitate the efficient separation of active pharmaceutical ingredients (APIs) from organic solvents, ensuring product purity and process efficiency. Their resilience against a broad spectrum of solvents underscores their suitability for rigorous OSN operations [125]. Despite these advantages, PA membranes are susceptible to degradation in the presence of chlorinated solvents, which can compromise membrane integrity and longevity. To address this, research has focused on enhancing chlorine resistance through surface modifications and the incorporation of chlorine-tolerant materials. Strategies such as grafting with zwitterionic compounds and embedding nanomaterials like graphene oxide have shown promise in mitigating chlorine-induced degradation [126]. Furthermore, the fabrication of ultrathin PA membranes has been explored to boost permeation rates, thereby reducing energy consumption in OSN processes. Techniques like in situ free interfacial polymerization have enabled the creation of defect-free, nanometer-thick selective layers, pushing the boundaries of membrane performance [127]. Ongoing research continues to optimize the balance between permeability, selectivity, and chemical stability in PA membranes, aiming to expand their applicability and efficiency in diverse OSN applications.

5.1. Pharmaceutical Industry

Polyamide (PA) membranes, particularly thin-film composite membranes (TFCMs), have become integral to OSN in the pharmaceutical industry due to their exceptional selectivity, chemical resilience, and adaptability. Their applications span from the purification of active pharmaceutical ingredients (APIs) to the concentration of antibiotics, underscoring their versatility and efficacy in pharmaceutical separation [125]. A notable advancement in this domain is the development of TFCMs utilizing novel monomers to enhance performance metrics. For instance, membranes synthesized with 4,4′,4″4‴-methanetetrayltetrakis (benzene-1,2-diamine) (MTLB) have demonstrated a selective layer thickness of approximately 27 nm, achieving a water permeance of 45.2 L m^{-2} h^{-1} bar^{-1} and a NaCl/Adriamycin selectivity ratio of 422. These characteristics indicate significant

potential for industrial-scale antibiotic purification processes [128]. Beyond antibiotic desalination, PA membranes are pivotal in API concentration operations. Their ability to facilitate the efficient separation of solvents from APIs is crucial for producing high-purity pharmaceutical formulations. The tunability of membrane properties through interfacial polymerization techniques allows for customization to meet specific pharmaceutical requirements [125]. The chemical robustness of PA membranes is particularly advantageous in pharmaceutical applications, where exposure to a diverse array of solvents is common. Studies have shown that these membranes maintain structural integrity under harsh chemical conditions, ensuring consistent performance and longevity in OSN processes. However, challenges such as membrane fouling and degradation due to chlorination persist. To address these issues, research has focused on surface modifications and the incorporation of chlorine-resistant materials. Strategies include grafting hydrophilic polymers and embedding nanomaterials like graphene oxide, which have been shown to enhance both fouling resistance and chlorine tolerance. These modifications not only improve membrane durability but also maintain or enhance separation performance [67,126]. Advancements in membrane fabrication techniques have also contributed to scalability, enabling the production of large membrane modules suitable for industrial applications without compromising performance. Innovations such as thermally induced phase separation (TIPS) and the use of non-toxic diluents have facilitated the creation of robust PA membranes with high chemical resistance, further supporting their integration into pharmaceutical manufacturing processes.

5.2. Chemical Industry

Polyamide (PA) membranes, particularly in thin-film composite (TFC) configurations, have garnered significant attention in the chemical industry for their exceptional separation performance, chemical resilience, and adaptability. Their applications span various processes, including solvent recovery, wastewater treatment, and OSN, underscoring their pivotal role in advancing sustainable chemical manufacturing [83,125]. In chemical manufacturing, PA membranes are extensively employed in reverse osmosis (RO) and nanofiltration (NF) processes to separate solvents from solutes. Their high selectivity and permeability enable efficient separation of water from organic compounds and salts, facilitating the production of high-purity chemicals. Recent studies have demonstrated that TFC PA membranes can achieve substantial water flux while maintaining high rejection rates for various contaminants, making them ideal for applications such as brine concentration and solvent recovery [129,130]. Wastewater treatment is another critical area where PA membranes contribute significantly. Their application in microfiltration and ultrafiltration processes aids in the removal of organic materials, suspended particles, and other impurities from industrial effluents. Research indicates that PA membranes effectively reduce chemical oxygen demand (COD) levels in wastewater, enhancing the overall quality of treated water. The membranes' adaptability allows for modifications that improve fouling resistance and operational longevity, essential factors for continuous industrial operations [131]. In the realm of resource recovery, techniques such as membrane distillation and pervaporation leverage the selective permeability of PA membranes to extract valuable compounds from waste streams. These methods are particularly effective in concentrating volatile organic compounds (VOCs) from aqueous solutions, thereby improving resource recovery and reducing waste generation. Such applications are especially pertinent in industries where solvent recycling is economically advantageous [132]. Despite their numerous advantages, PA membranes are susceptible to degradation by chlorine-based disinfectants commonly used in chemical processing. Chlorine attacks the PA layer, compromising membrane integrity and performance [133]. To address this

challenge, recent developments have focused on enhancing chlorine resistance through various modification strategies. For instance, incorporating nitrogen-doped graphene oxide quantum dots (NGOQDs) into the membrane structure has been shown to improve chlorine resistance without sacrificing functionality [133,134]. Advancements in membrane fabrication techniques, such as electrospinning and phase inversion, often promise avenues for enhancing PA membrane performance. These methods allow for precise control over membrane morphology and pore structure, leading to improved separation efficiency. Additionally, the incorporation of nanoparticles into PA membranes is being explored to further enhance selectivity and resistance to fouling [68].

5.3. Food and Beverage Industry

Polyamide (PA) membranes, particularly thin-film composite (TFC) variants, have become integral to the food and beverage industry due to their exceptional separation capabilities, chemical resilience, and compliance with stringent food safety standards. Their applications span water purification, juice clarification, dairy processing, beverage de-alcoholizing, and wastewater treatment [135]. In water purification, PA membranes are widely employed in reverse osmosis (RO) systems to desalinate brackish and seawater, effectively removing dissolved salts and impurities. This application is increasingly pertinent for decentralized water treatment systems, addressing the growing demand for clean drinking water [129]. For juice processing, PA membranes facilitate ultrafiltration (UF) and nanofiltration (NF) to remove undesirable components such as proteins, pectin, and starches, enhancing juice clarity and quality while preserving flavor integrity. NF technology, in particular, has proven effective in concentrating juices without significant loss of beneficial compounds, offering a superior alternative to traditional distillation or freezing methods [136]. In the dairy sector, PA membranes are crucial for concentrating whey proteins and milk solids. Toray's RO membranes, for instance, utilize crosslinked aromatic polyamide composites to maximize the retention of valuable milk components while ensuring high permeate quality. These membranes are designed to meet strict sanitary standards, making them ideal for food-grade applications [137]. PA membranes also play a role in the de-alcoholization of beverages like beer. By employing NF technology, manufacturers can effectively reduce alcohol content while maintaining the original flavor profile, offering a more palatable alternative to conventional non-alcoholic beer production methods. In terms of wastewater treatment, PA TFC membranes have demonstrated efficacy in treating oily effluents from food processing industries. Studies have shown that integrating activated carbon pretreatment with RO membrane filtration can achieve up to 99% removal of chemical oxygen demand (COD) and significantly improve permeate flux, enhancing the efficiency of wastewater management processes [138].

5.4. Semiconductor Industry

Solvent recovery is an important procedure in the semiconductor industry since high-purity organic solvents are widely used for cleaning, photolithography, and other manufacturing steps. Traditional recovery procedures, such as distillation, are energy-consuming and frequently insufficient to achieve the industry's rigorous purity standards. Polyamide (PA) membranes, particularly in thin-film composite (TFC) designs, have emerged as a potential technology for efficient and selective solvent recovery, with advantages in energy savings, process intensification, and environmental sustainability [139]. Polyamide membranes are preferred for their great selectivity and chemical resilience, making them ideal for separating solvents from complex combinations in semiconductor processes. They also offer customizable features. IP enables unique membrane designs that target specific solvent systems and scalability. It has been applied in industrial-scale water treatment and

is increasingly being adopted for OSN and reverse osmosis [139,140]. Solvents used in semiconductor production include isopropanol (IPA), acetone, and N-methyl-2-pyrrolidone (NMP). PA membranes may effectively recover and purify these solvents, even from weak or azeotropic combinations that are difficult to distill. For example, membrane-based pervaporative dehydration and OSN procedures allow for the reclamation of IPA and acetone from rinse and cleaning streams, lowering hazardous waste and solvent expenses. The semiconductor sector must comply with stringent waste minimization rules. PA membranes offer a non-thermal, energy-efficient alternative to distillation, which reduces the carbon footprint and hazardous waste associated with solvent disposal. Their great selectivity guarantees that recovered solvents fulfill the purity standards necessary for reuse in sensitive industrial stages. PA membranes are compatible with a variety of process configurations, including independent modules for solvent reclamation from waste streams. Hybrid systems use distillation and adsorption to improve separation and purity. On-site recycling enables closed-loop solvent management within semiconductor fabs, which is crucial for both cost and environmental compliance. Thin-film composite (TFC) PA membranes are made by IP, which results in a dense, selective PA layer above a porous support. Recent breakthroughs include the use of acetone-assisted polymerization to build 3D honeycomb-like structures, which significantly increase surface area and solvent permeance while retaining selectivity. Surface modification techniques like Fe^{3+} / tannic acid coating or chitosan/glutaraldehyde treatment improve membrane polarity and fix surface flaws, resulting in better separation efficiency for polar/non-polar solvent combinations found in semiconductor waste streams [77]. Modified TFC-PA membranes have achieved methanol permeance up to 7.0 L m^{-2} h^{-1} bar^{-1}, with over 94% rejection of model solutes and separation factors over 80 for difficult mixtures such as methanol/toluene. Studies indicate long-term stability in severe organic environments and the viability of scaling up membrane production for industrial deployment [141]. Membrane processes for IPA reclamation in semiconductor fabs have been tested and shown to be significantly cheaper and more environmentally friendly than existing approaches. PA membranes have been evaluated for solvent recovery from photolithography and cleaning waste, displaying good contamination rejection and efficient solvent reuse. The SOLVER project (EU-FP7) emphasized the role of nano-selective PA membranes in minimizing solvent waste and boosting sustainability in electronics and microelectronics manufacturing. Both organic and inorganic foulants in semiconductor waste streams can degrade membrane performance. Current research focuses on antifouling coatings and cleaning techniques. While PA membranes are resistant to many solvents, strong chemicals or extended exposure may necessitate additional material improvements. Machine learning and advanced modeling are utilized to build next-generation PA membranes with optimized characteristics for specific solvent systems [139].

6. Challenges and Limitations

Polyamide (PA) membranes, particularly thin-film composite (TFC) variants, are integral to OSN due to their high selectivity and chemical resilience. However, their broader application is hindered by fabrication challenges, notably the formation of defect-free selective layers. A significant obstacle in TFC membrane fabrication is the emergence of non-selective voids and pinholes within the polyamide layer. These defects can compromise membrane performance by allowing undesired solute passage, thereby reducing separation efficiency. The substrate's geometry plays a pivotal role in this context. Specifically, the "funnel effect," where water traverses tortuous pathways due to low substrate porosity, can exacerbate these issues by increasing hydraulic resistance and promoting defect formation [128]. To mitigate these challenges, recent studies have explored innovative fabrication

techniques. One such approach is the in situ free interfacial polymerization (IFIP), which allows the formation of ultrathin polyamide layers (~3–4 nm) at a free oil–water interface, subsequently assembling onto the substrate without manual transfer [127]. This method has demonstrated potential in producing defect-free membranes with enhanced performance metrics. Additionally, substrate modification strategies have been investigated to address the funnel effect. For instance, employing substrates with higher surface porosity and smaller pore sizes can facilitate more uniform polyamide layer formation, reducing the likelihood of defects. However, it is essential to balance these modifications, as overly small pores can impede solvent flow, affecting overall membrane permeability [142]. While PA TFC membranes hold promise for OSN applications, addressing fabrication-induced defects through advanced polymerization techniques and substrate engineering is crucial for optimizing their performance and expanding their industrial applicability.

6.1. Membrane Fouling

Polyamide (PA) membranes, especially thin-film composite (TFC) types, are central to OSN and RO due to their high selectivity and solvent resistance. However, membrane fouling remains a critical limitation, negatively impacting performance, shortening lifespan, and increasing operational costs. Recent studies reveal that fouling behavior is influenced by multiple factors, including membrane surface characteristics and operational conditions. Interestingly, smoother membranes may exhibit greater fouling due to uneven flux distributions and localized concentration polarization, known as the funnel effect [143]. To address these issues, researchers have implemented surface modification strategies such as grafting hydrophilic and antifouling agents (e.g., dimethylamine) [144], and coating with polydopamine, which enhances both hydrophilicity and chlorine resistance. The incorporation of nanomaterials like graphene oxide further boosts antifouling properties by increasing hydrophilicity and creating steric hindrance against foulants [133]. Nonetheless, scaling and industrial translation remain hindered by concerns over long-term stability, cost, and reproducibility [145,146]. Developing standardized testing protocols is vital for broader adoption. Fouling in PA membranes includes particulate, organic, and biological fouling. Particulate fouling results from suspended solids clogging membrane pores, reducing flux and increasing pressure requirements [131]. Organic fouling is caused by molecules such as proteins and polysaccharides adhering to the membrane surface, especially problematic in OSN due to solvent–membrane interactions [67]. Biofouling involves microbial colonization, leading to biofilm formation, permeate quality degradation, and possible membrane damage through acidic metabolic byproducts [126]. Mitigation approaches focus on surface engineering, antifouling additives, and operational optimization [68]. Even minor fouling can significantly decrease membrane permeability, increasing the frequency of cleaning and energy consumption [147]. Performance losses lead to higher operational costs, with fouling-related expenses accounting for up to 24% of RO plant operations [148]. Hence, maintaining membrane performance in OSN demands strategies like material modification, advanced cleaning protocols, and fouling-resistant designs [149]. Fouling behavior is closely tied to surface hydrophilicity, roughness, charge density, and morphology. Hydrophilic and smoother surfaces tend to resist fouling more effectively [150]. Surface charge governs electrostatic interactions with solutes, while solution conditions—pH, ionic strength, and solute composition—further influence fouling. Concentration polarization exacerbates fouling by increasing osmotic pressure and promoting gel layer formation [151]. These dynamics emphasize the need for tailored surface properties and process optimization [130]. Layer-by-layer (LbL) assembly using polyelectrolytes like PDADMAC and PAA improves antifouling behavior by enhancing surface hydrophilicity and smoothness [152]. Additionally, embedding TiO_2 nanoparticles into the PA matrix increases thermal sta-

bility and fouling resistance, and imparts photocatalytic self-cleaning ability under UV light [69]. These synergistic modifications improve flux recovery, reduce fouling, and extend membrane life, especially under harsh OSN conditions [67]. While current strategies offer improvements, complete fouling resistance remains elusive. Future research must focus on novel surface chemistries, a deeper understanding of fouling mechanisms, and application-specific membrane designs. For example, amphiphilic surface modifications combining hydrophilic and hydrophobic domains can create hydration layers that prevent foulant adhesion while preserving performance [82]. Incorporating graphene oxide (GO) has also shown promise in improving antifouling and antimicrobial properties, though ensuring modification stability under OSN conditions remains a challenge [153].

Polyamide (PA) membranes, particularly thin-film composite (TFC) variants, are widely used in OSN and RO due to their excellent selectivity and solvent resistance; however, fouling remains a persistent issue that compromises membrane performance, reduces lifespan, and increases operational costs. Contrary to earlier beliefs, smoother membranes may be more prone to fouling due to uneven flux distribution and localized concentration polarization, known as the funnel effect [143]. To overcome this, various surface modification strategies—such as grafting hydrophilic or antifouling agents like dimethylamine [144], applying polydopamine coatings, or incorporating nanomaterials like graphene oxide [133]—have been explored to enhance hydrophilicity, chlorine resistance, and steric hindrance. Despite the promising results, challenges related to long-term stability, cost, and scalability limit industrial adoption [146]. Fouling can be classified into particulate, organic, and biological types, each contributing to reduced flux and increased maintenance needs [67,126,131]. Effective fouling control requires a combination of material innovation, surface engineering, and optimized operating conditions [68,149]. Factors such as surface hydrophilicity, charge, morphology, and feed solution properties significantly influence fouling tendencies [150,151]. Techniques like layer-by-layer (LbL) assembly using PDADMAC and PAA [152], and embedding TiO_2 nanoparticles [69], have been shown to improve antifouling performance, thermal stability, and self-cleaning capability under UV light. Still, total fouling resistance remains elusive, and future research must focus on developing stable, scalable, and application-specific antifouling solutions—such as amphiphilic modifications and graphene oxide integration—that are robust under real OSN operating conditions [82,153].

6.2. Chemical Stability

Polyamide (PA) membranes are widely used in reverse osmosis (RO) and organic solvent nanofiltration (OSN) systems due to their high separation efficiency. However, their application is often limited by poor chemical stability, particularly under oxidative and hydrolytic conditions. Chlorine-based disinfectants, commonly used in water treatment, can degrade PA membranes through reactions such as N-chlorination and aromatic ring chlorination, leading to hydrolysis and irreversible damage [146,154,155]. This results in reduced salt rejection, water permeability, and overall membrane integrity. Even low chlorine levels have been found to cause significant degradation [155]. In OSN environments, the challenge is compounded by exposure to aggressive organic solvents that can cause polymer swelling, plasticization, and even dissolution. These conditions, especially at elevated temperatures and humidity, accelerate hydrolysis, breaking amide bonds and diminishing mechanical strength [126,154]. Understanding these degradation mechanisms—oxidative chain scission and hydrolytic bond cleavage—is essential for improving membrane durability [126,156]. To mitigate chemical degradation, researchers have explored new monomers, crosslinking agents, and protective coatings to enhance chlorine and solvent resistance without compromising selectivity [67,126]. For instance, using monoamines like piperidine

(PPR) in interfacial polymerization can improve membrane structure and overcome the permeability–selectivity trade-off, while diamines like piperazine (PIP) may induce phase separation and reduce salt rejection [157]. Nanocomposite strategies, such as embedding TiO_2 nanoparticles, offer benefits including enhanced thermal stability and antifouling properties. However, challenges in achieving uniform dispersion and avoiding defect formation remain [73]. Moreover, fabrication conditions, like ambient temperature during interfacial polymerization, play a critical role in determining membrane morphology and performance [158]. Long-term stability remains a concern, as membranes may gradually degrade even under mild operational conditions. Oxidative and hydrolytic processes reduce tensile strength and increase permeability, complicating lifespan predictions and limiting performance in demanding OSN applications [154,156]. Continued research into chemically resilient materials and optimized fabrication techniques is essential for developing PA membranes with improved durability and operational consistency across both RO and OSN platforms [69,126].

Polyamide (PA) membranes are extensively employed in reverse osmosis (RO) and organic solvent nanofiltration (OSN) due to their excellent separation efficiency, yet their chemical stability under oxidative and hydrolytic conditions remains a critical limitation. Chlorine-based disinfectants can react with the PA structure, causing N-chlorination and aromatic ring attacks that lead to hydrolysis and compromise membrane integrity, even at low chlorine levels [146,154,155]. In OSN systems, exposure to harsh solvents further accelerates degradation, especially under high temperature and humidity, by promoting polymer swelling, plasticization, and bond cleavage [126,154]. These degradation pathways, including oxidative chain scission and hydrolysis, significantly reduce membrane performance and mechanical strength [126,156]. To counter these effects, researchers are developing modified membranes using novel monomers, crosslinkers, and surface coatings that enhance resistance without sacrificing selectivity [67,126]. Additives like piperidine (PPR) improve structure and performance, whereas piperazine (PIP) can introduce defects [157]. Nanoparticle incorporation, such as TiO_2, offers thermal and antifouling advantages but faces dispersion and processing challenges [73]. Additionally, fabrication conditions, especially temperature, play a crucial role in determining membrane properties [158]. Despite advances, long-term operational stability is still a concern, and further innovation is needed to ensure reliable, chemically robust PA membranes for demanding RO and OSN applications [69,126].

6.3. Cost of Production

The production of polyamide (PA) membranes for OSN applications is hindered by multiple cost-related and scalability challenges that affect their commercial viability. A major factor is the volatility of raw material prices, particularly petroleum-derived monomers like MPD and TMC, whose costs have fluctuated significantly, with polyamide prices rising by 22% between Q1 2021 and Q2 2022 due to crude oil trends and post-pandemic recovery [159,160]. Additionally, supply chain disruptions and regional environmental regulations, particularly in China, have created material shortages and price surges, with a 28% year-over-year increase as of Q1 2024 [159]. High energy prices and logistical delays further elevate manufacturing expenses. The inclusion of performance-enhancing additives like TiO_2 improves membrane quality but increases both material and operational costs, particularly when UV activation is required [161]. Moreover, the interfacial polymerization (IP) process is complex, requiring expensive equipment, controlled environments, and skilled labor. Capital investments for batch casting facilities can exceed USD 14,895, with payout periods extending up to 7.5 years [162]. Scaling up from lab to industrial production introduces new technical and economic hurdles, including defect control and

performance consistency [83,130]. Market competition exerts additional pricing pressure, pushing manufacturers to reduce costs while maintaining membrane performance, especially for high-performance variants with nanomaterial incorporation [83]. Regulatory compliance costs also play a significant role, especially due to the use of hazardous solvents like NMP and DMF. These generate large volumes of wastewater—up to 500 L/m^2 of membrane, which requires specialized treatment and increases production costs [163]. Violations of environmental standards can result in fines or facility shutdowns, further impacting economic feasibility [164]. To overcome these barriers, current efforts focus on adopting greener solvents, improving waste management, and developing sustainable fabrication methods, which are essential for achieving economically viable and scalable PA membrane production for OSN [163].

The commercial scalability of polyamide (PA) membranes for OSN applications is significantly limited by high production costs and logistical complexities. Price volatility of petroleum-based monomers like MPD and TMC, driven by fluctuating oil markets and post-pandemic demand, has led to sharp increases in raw material costs—up to 22% between Q1 2021 and Q2 2022 [159,160]. Compounding this, environmental regulations and supply chain disruptions, particularly in China, have caused further shortages and price spikes, with polyamide prices rising 28% year-over-year by Q1 2024 [159]. The incorporation of additives like TiO_2 can enhance membrane performance but also raises material and operational costs, especially when UV activation is needed [161]. Additionally, the interfacial polymerization (IP) process used in PA membrane fabrication is technically demanding and capital-intensive, requiring controlled environments, specialized equipment, and trained personnel, pushing initial setup costs beyond USD 14,895 with long investment recovery periods [162]. Scaling up from lab-scale to commercial production introduces challenges in maintaining membrane integrity and performance consistency [83,130]. The competitive market landscape further pressures manufacturers to reduce costs without sacrificing membrane quality [83]. Regulatory compliance adds another layer of financial burden, particularly due to the use of toxic solvents like NMP and DMF, which generate large volumes of hazardous wastewater—up to 500 L/m^2—that require costly treatment [163]. Non-compliance can lead to fines or shutdowns, severely impacting profitability [164]. To address these challenges, ongoing research emphasizes green solvents, better waste management, and simplified, sustainable manufacturing approaches to ensure cost-effective and scalable PA membrane production for OSN applications [163].

7. Future Perspectives

Polyamide (PA) membranes are poised for significant advancements in OSN applications, driven by ongoing research aimed at enhancing their performance, sustainability, and scalability. Recent developments focus on the creation of ultrathin PA membranes with crumpled morphologies and interlayer structures [128]. These designs aim to improve permeability and selectivity while maintaining structural integrity, addressing the trade-off between membrane thickness and performance. Such innovations are crucial for expanding the applicability of OSN membranes in various industries, including pharmaceuticals and petrochemicals. The shift towards eco-friendly fabrication methods is gaining momentum. Utilizing non-toxic diluents and green solvents in membrane production not only reduces environmental impact but also aligns with global sustainability goals. For instance, the adoption of biodegradable solvents like methyl lactate has shown promise in producing effective OSN membranes without compromising performance [165]. Addressing the challenges of membrane fouling and degradation is essential for long-term OSN applications. Strategies such as surface modification with hydrophilic polymers and the incorporation of chlorine-resistant materials have been explored to enhance membrane

durability. These approaches aim to extend membrane lifespan and reduce maintenance costs, thereby improving overall process efficiency. The integration of advanced materials, sustainable manufacturing processes, and improved membrane designs positions PA membranes as a vital component in the future of OSN technologies. Continued interdisciplinary research and collaboration between academia and industry will be pivotal in overcoming existing challenges and unlocking new applications for PA membranes in organic solvent separations.

Polyamide (PA) membranes are at the forefront of innovation in organic solvent nanofiltration (OSN), with current research emphasizing improvements in performance, environmental sustainability, and large-scale applicability. A significant focus is placed on engineering ultrathin PA membranes with crumpled surface morphologies or embedded interlayers, which enhance permeability and selectivity while preserving structural robustness. These structural innovations address the critical thickness–performance trade-off, expanding the utility of PA membranes in sectors like pharmaceuticals and petrochemicals. In parallel, there is growing interest in adopting environmentally responsible membrane fabrication processes. The use of non-toxic and biodegradable solvents—such as methyl lactate—has demonstrated promise in minimizing ecological impact without sacrificing separation efficiency. Additionally, targeted strategies to mitigate membrane fouling and degradation are gaining traction. Surface modification using hydrophilic polymers and the inclusion of chlorine-resistant components have shown potential in extending membrane lifespan and improving process economics.

7.1. Advancements in Ultrathin Membranes

Ultrathin polyamide (PA) membranes have garnered significant attention for their potential to enhance water permeation rates, leading to substantial energy savings in applications such as wastewater treatment and desalination. Recent advancements in fabrication techniques, particularly interfacial polymerization (IP), have enabled the production of defect-free PA layers with thickness approaching the sub-10 nm scale, thereby improving permeability without compromising selectivity. However, the realization of these benefits is often hindered by the "funnel effect," wherein the geometry of the porous substrate influences the formation and performance of the ultrathin selective layer [128]. This effect can lead to non-uniform film formation and diminished separation efficiency. To address these challenges, innovative fabrication methods have been developed. One such approach is in situ free interfacial polymerization (IFIP), which involves forming the PA layer at a free-standing oil–water interface above the substrate. This technique allows for the spontaneous assembly of ultrathin PA nanofilms onto the substrate, resulting in membranes with thicknesses as low as 3–4 nm [127]. These membranes exhibit enhanced water permeance and salt rejection capabilities [128]. Another promising strategy involves heterogeneous surface-regulated IP, where the incorporation of nanoparticles like UiO-66-NH_2 onto a hydrophobic substrate creates a nano-wrinkled morphology in the PA layer [166]. This structure not only increases the surface area but also improves water flux and salt rejection, making it suitable for environmental desalination applications [167]. These advancements in ultrathin PA membrane fabrication hold significant promise for enhancing the efficiency and sustainability of water treatment processes. Continued research in this area is essential to overcome existing limitations and fully realize the potential of these membranes in various separations.

Ultrathin PA membranes are particularly attractive due to their potential to dramatically improve water flux and reduce energy consumption in filtration applications. Advances in IP techniques have allowed for the formation of sub-10 nm thick defect-free films. Nevertheless, the funnel effect, wherein the geometry of the underlying substrate

affects films uniformly, and performance remains a challenge. To address this, novel fabrication methods such as in situ free interfacial polymerization (IFIP) have been proposed. IFIP enables the formation of PA films at a freestanding oil–water interface, achieving selective layers as thin as 3–4 nm. Additionally, surface-regulated IP utilized nanoparticle-modified substrates (e.g., UiO-66-NH_2) has been employed to create nano-wrinkled morphologies that improve both flux and salt rejection. These breakthroughs pave the way for more efficient membrane designs tailored to specific separation needs.

7.2. Enhanced Antifouling Properties

Recent advancements in membrane fabrication techniques have significantly enhanced the antifouling properties of polyamide (PA) membranes, particularly in challenging applications such as OSN. One notable approach involves the layer-by-layer (LbL) assembly method, where alternating layers of hydrophilic polyelectrolytes are deposited onto the membrane surface. For instance, the sequential coating of poly (diallyl dimethylammonium chloride) (pDAC) and polyacrylic acid (PAA) onto polyamide-imide membranes has been shown to improve surface hydrophilicity, leading to enhanced fouling resistance. In the context of oil sands produced water treatment, membranes modified with four bilayers exhibited a flux decline of 50.2% and a flux recovery ratio of 100%, compared to a 75.9% flux decline and 97.8% recovery for unmodified membranes [62]. Incorporating titanium dioxide (TiO_2) nanoparticles into PA membranes has also proven effective in enhancing antifouling and thermal stability. These nanocomposite membranes benefit from the hydrophilic nature and photocatalytic activity of TiO_2, which reduce organic fouling and inhibit microbial growth. For example, TiO_2-modified membranes demonstrated a 24% increase in permeability and improved resistance to fouling by organic matter, sumac acid, and tannic acids [74]. Furthermore, the integration of TiO_2 nanoparticles has been associated with enhanced thermal stability, making these membranes suitable for high-temperature OSN applications. These advancements underscore the potential of LbL assembly and nanoparticle incorporation strategies in developing PA membranes with superior antifouling properties, thereby extending their applicability in OSN and other demanding separation processes.

Enhancing membrane antifouling characteristics remains a priority for long-term OSN use. The application of layer-by-layer (LbL) deposition, involving the alternating addition of charged polyelectrolytes such as pDAC and PAA, has effectively improved hydrophilicity and resistance to fouling. For example, in oil-contaminated water treatment, LbL-modified membranes demonstrated significantly lower flux decline and better recovery compared to unmodified membranes. Similarly, embedding TiO_2 nanoparticles into PA membranes has improved both antifouling behavior and thermal resistance. These nanocomposite membranes benefit from TiO_2's photocatalytic activity and hydrophilic nature, which reduces organic buildup and microbial contamination while enhancing overall permeability and longevity in high-temperature environments.

7.3. Sustainability and Environmental Impact

As sustainability becomes increasingly central to materials science, research into polyamide (PA) membranes for OSN is focusing on enhancing recyclability and integrating renewable energy applications. One promising avenue involves developing PA membranes from bio-based or recyclable polymers. For instance, keratin–polyamide blend nanofibrous membranes have demonstrated improved filtration for dye removal, highlighting the potential of sustainable materials in membrane technology [168]. In the realm of resource recovery, PA nanofiltration membranes have shown efficacy in lithium extraction from brines. These membranes can efficiently separate lithium ions, offering a more sustainable ap-

proach to lithium recovery. Furthermore, PA membranes are being explored for renewable energy applications, such as hydrogen production and carbon capture [169]. Membrane-based electrolysis, utilizing PA membranes, presents a promising method for hydrogen generation with reduced carbon emissions [170]. Additionally, advancements in membrane technologies are contributing to more efficient CO_2 capture processes, aiding in efforts to mitigate climate change [171]. These developments underscore the multifaceted role of PA membranes in advancing sustainability across various sectors. Continued research and innovation are essential to fully realize their potential in promoting environmental stewardship and energy efficiency.

In response to global sustainability goals, recent work has emphasized the use of renewable and recyclable materials in PA membrane fabrication. Blending polyamide with bio-derived polymers such as keratin has yielded membranes with effective dye removal properties. Furthermore, PA membranes have demonstrated utility in critical resource recovery processes, such as lithium extraction from brines. They are also being investigated for roles in renewable energy systems, including hydrogen production via membrane-based electrolysis and carbon dioxide capture, positioning them as tools for climate change mitigation. These initiatives reflect a broader movement to align membrane technology with principles of green chemistry and circular economy.

7.4. Broader Application Spectrum

Polyamide (PA) membranes, traditionally utilized in water purification, are increasingly being explored for diverse applications across various industries, including chemical manufacturing, food processing, and pharmaceuticals. Their adaptability is particularly evident in OSN, where specialized PA membranes have been developed to meet the industry's demand for efficient solvent recovery and recycling processes. Advancements in membrane fabrication techniques have led to the development of ultrathin PA membranes with enhanced performance characteristics. These membranes exhibit improved antifouling properties, increased chemical durability against chlorine degradation, and a focus on sustainability. Such innovations are crucial for extending the lifespan and efficiency of membranes in harsh operational environments [128]. The future trajectory of PA membranes is poised to be defined by continued research into novel fabrication methods and material modifications. These efforts aim to broaden the applicability of PA membranes, making them integral components in addressing global challenges such as water scarcity, energy efficiency, and environmental sustainability.

While PA membranes have been widely used for water purification, their versatility has led to their deployment across diverse industries, ranging from chemical processing and food production to pharmaceutical manufacturing. In OSN applications, specially engineered PA membranes have shown superior solvent recovery capabilities and durability under harsh operating conditions. Innovations such as chlorine-resistant coatings, ultrathin selective layers, and sustainable manufacturing methods are enhancing the membranes' service life and performance. Looking ahead, continued material innovation and cross-disciplinary collaboration will be essential for unlocking new applications and addressing pressing global challenges like water scarcity, energy conservation, and environmental sustainability.

8. Conclusions

Polyamide membranes have become essential in OSN, offering outstanding chemical resistance, selectivity, and mechanical stability. This review focuses on the advancements made in polyamide membrane manufacturing methods, such as interfacial polymerization, electrospinning, and phase inversion, which have significantly enhanced membrane perfor-

mance. Furthermore, recent innovations, including the incorporation of nanoparticles and polymer blending, have improved permeability, antifouling characteristics, and thermal stability. Nevertheless, challenges persist, particularly in addressing membrane fouling, chemical degradation, and high production costs. Polyamide membranes are used in various sectors, including pharmaceuticals, chemical processing, and food production, demonstrating their versatility and industrial significance. Ongoing research into sustainable production methods and enhanced membrane longevity will be crucial for advancing the next generation of high-performance OSN membranes. With continuous technological advancements, polyamide membranes are poised to play a vital role in energy-efficient and sustainable separation processes.

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