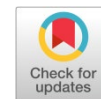


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Recent advances in synthesis and applications of mixed matrix membranes

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ABSTRACT

Researchers are currently considering membranes separation processes due to their eco-friendly, process simplicity and high efficiency. Selecting a suitable and efficient operation is the primary concern of researchers in the field of separation industries. In recent decades, polymeric and inorganic membranes in the separation industry have made significant progress. The polymeric and inorganic membranes have been challenged due to their competitiveness in permeability and selectivity factors. A combination of nanoparticle fillers within the polymer matrix is an effective method to increase polymeric and inorganic membranes' efficiency in separation processes. Mixed matrix membranes (MMMs) have been considered by the separation industry due to high mechanical and physicochemical, and transfer properties. Moreover, gas separation, oil treatment, heavy metal ions removal, water treatment and oil-water separation are common MMMs applications. Selecting suitable polymer blends and fillers is the key to the MMMs construction. The combination of rubbery and glassy polymers with close solubility parameters increases the MMMs performance. The filler type and synthesis methods also affect the morphological and transfer properties of MMMs significantly. Zeolites, graphene oxide (GO), nanosilica, carbon nanotubes (CNTs), zeolite imidazole frameworks (ZIFs) and metal-organic frameworks (MOFs) are used in the MMMs synthesis as fillers. Finally, solution mixing, polymerization in situ and sol-gel are the primary synthesising MMMs methods.

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KEYWORDS

Separation process
Mixed matrix membranes
Nanofiller
Polymer blend
Synthesis

1. Introduction

The advent of mixed matrix membranes (MMMs) has led to significant membrane performance advances [1]. The simultaneous increase in permeability, selectivity and physicochemical properties of the membrane are the main advantages of increasing the performance of MMMs compared to traditional membranes (polymeric and inorganic membranes) [2]. The advantages and disadvantages of polymeric, inorganic and mixed substrates are demonstrated in Fig. 1.

The MMMs consist of a basic phase (single or polymeric blend) and filler phases, including different nanoparticles [3]. Fig. 2 represents a schematic of the MMMs.

The MMMs application was first reported in the 1970s in the separation of CO₂ gas from CH₄ using simultaneous zeolite 5A to polydimethylsiloxane rubber polymer (PDMS) [4]. Mixed matrix membranes currently have many applications such as gas separation [5], oil treatment [6], removal of heavy metal ions [7], water treatment [8] and oil-water separation [9].

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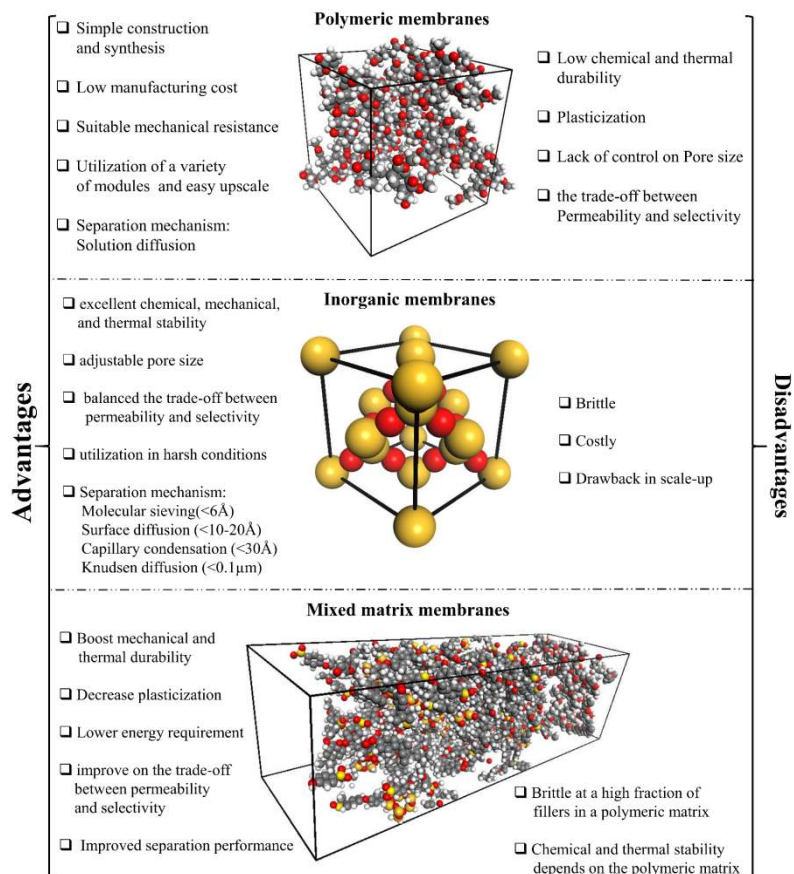


Fig. 1. Characteristics of different membranes (polymeric, inorganic and mixed matrix membranes).

The mixed matrix membranes construction has problems such as chemical structure control and surface chemistry that affect membrane performance [10]. It is usually challenging to construct ideally mixed matrix membranes due to the differences between the inorganic and

polymer properties [11]. The filler's tendency to accumulate and the low compatibility between the polymer and the filler cause these defects in the two-phase interface. These defects, which significantly affect membrane performance, include interface void or sieve-in-a-cage, hardening of the polymer layer around the particles, and particle pore blockage [12]. For example, the accumulation of filler particles around each other and the need to break them for better membrane performance and the low tendency of glass polymers to inorganic fillers due to the low mobility of polymer chains mainly cause this complexity.

Synthesis methods and the type of filler used during synthesis are the keys to an ideal mixed matrix membranes success. Different synthesis methods and solutions have been used to create flawless and high-performance MMMs [5]. For example, various stirring methods (mechanical, ultrasound) are used to prevent particles' accumulation during polymer preparation [13]. Another way to improve a mixed matrix membranes performance and prevent surface imperfections is to reduce the T_g polymer matrix by adding a softener to the membrane formulation. Blending polymers with different properties to construct a stable composition in physical and chemical properties is another way to improve mixed matrix membranes' performance. The key to this method's success is selecting polymers with close solubility parameters [14]. The type, physicochemical properties, structure, and surface chemistry of nanoparticles (fillers) significantly impact the performance of MMMs [11]. Some of the most used nanofillers are

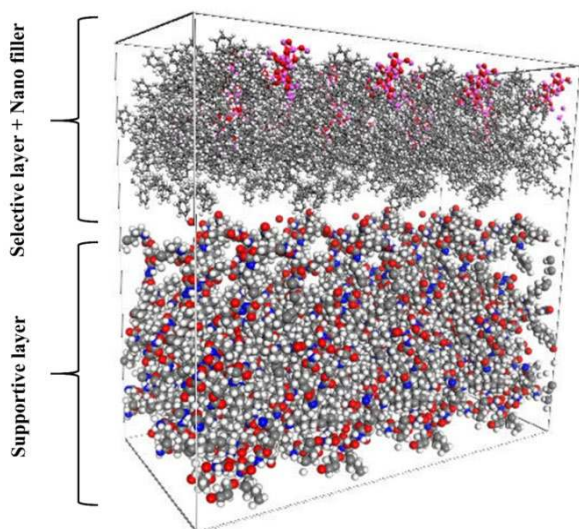


Fig. 2. Represents a schematic of the MMMs.

zeolites [15], graphene oxide (GO) [16, 17], nanosilica [18], carbon nanotubes (CNTs) [19, 20], natural clay attapulgite (ATP) [21], zeolite imidazole frameworks (ZIFs) [22], metal-organic frameworks (MOFs) [23], porous coordination polymers (PCPs) [24] and covalent organic frameworks (COFs) [25, 26]. The selection of suitable solvents, the synthesis method and surface modification of these nanofillers are of special importance in improving mixed matrix membranes' performance. The present study's authors tried to overview the various synthesis methods and their advantages and disadvantages in constructing MMMs.

2. Mixed matrix membranes application

Mixed matrix membranes have a variety of applications in the separation industry. Recently, the gas separation industry using MMMs has made significant progress compared to traditional membranes [27]. On the one hand, despite their ease of use in gas separation, polymeric membranes have been challenged due to competitive conditions between permeability and selectivity. On the other hand, inorganic membranes, although they have high separation properties, the problematic conditions of formation and high manufacturing costs have created a significant challenge in their use [28]. The use of glassy and

rubbery polymers and nanofillers simultaneously has increased mixed matrix membranes' performance under high temperature and pressure conditions in gas separation [29]. Mixed matrix membranes are widely used in the CO₂, CH₄, N₂, H₂, O₂ and H₂S gases separation. Research using mixed matrix membranes in the gas separation industry is reported in Table 1. Reverse osmosis, electrodialysis, ion exchange, chemical deposition, liquid-liquid extraction, emulsion liquid membrane, etc. are common techniques for removing heavy metals from sewage [30-33]. High energy consumption, high processing and operating costs, large production of liquid waste, and toxic sludge have created a significant challenge in using conventional methods [34]. Therefore, the mixed matrix membrane can have an actual application due to the low energy consumption process and materials with high absorption capacity and selectivity. Limited studies have been reported on removing heavy metals using mixed matrix membranes (Table 1). Production of liquid wastes due to high environmental pollution, phytoalexins release, and increased oxygen consumption are severe oil treatment problems. Significant disadvantages of traditional oil processing methods have led to the development of new techniques to improve performance in this area. Mixed matrix membranes have reduced the problems and weaknesses of conventional methods in the oil treatment industry [35].

Table 1. Mixed matrix membranes research in different application in the separation industry.

Gas separation application				
Polymer	Nanofiller	Gases	Description	Ref.
Polysulfone (PSF)	Porphyrin	<ul style="list-style-type: none"> • CO₂ • CH₄ • N₂ 	<ul style="list-style-type: none"> • Uniform distribution of nanofillers in the polymer structure • Proper thermal stability • Improving permeability and selectivity properties • Improving permeability with increasing temperature 	[36]
Polyimide 6FDA-durene	UiO-66	<ul style="list-style-type: none"> • CO₂ • CH₄ 	<ul style="list-style-type: none"> • Reducing the accumulation of nanofillers in the copolymer structure using the NH₂ functional group • Improving CO₂/CH₄ separation performance 	[37]
Polysulfone (PSF)	Iron pillared cloisite 15A (P-C15A)	<ul style="list-style-type: none"> • CO₂ • N₂ • O₂ 	<ul style="list-style-type: none"> • Proper dispersion of nanofillers in polymer matrix • Increasing the permeability by increasing the number of nanofillers • Reasonable performance of MMMs with Robson upper bond chart 	[38]
Matrimid	ZIF-68, 69 and 78	<ul style="list-style-type: none"> • CO₂ • CH₄ • N₂ 	<ul style="list-style-type: none"> • The maximum increase in CO₂ permeability using ZIF-68 • Increasing the selectivity of CO₂/N₂ and CO₂/CH₄ using 20% ZIF-68 	[39]
Polysulfone/polyethylene glycol (PSF/PEG)	Graphene hydroxyl	<ul style="list-style-type: none"> • CO₂ • CH₄ 	<ul style="list-style-type: none"> • Proper distribution of nanoparticles in the polymer matrix • Increasing the permeability of CO₂ • Improving the selectivity properties by increasing the nanoparticles 	[40]
Polyurethane	Zeolite 3A and ZSM-5	<ul style="list-style-type: none"> • CO₂ • CH₄ • N₂ • O₂ 	<ul style="list-style-type: none"> • Using central composite design for optimization • Optimization of permeability at 18 wt% nanoparticle concentration, temperature 30 °C and 0.8 MPa pressure • Optimization of selectivity at 5.8 wt% nanoparticle concentration, temperature 22.5 °C and 2.5 MPa pressure 	[41]
Pebax-1657	MIL-101 and NH ₂ -MIL-101	<ul style="list-style-type: none"> • CO₂ • N₂ 	<ul style="list-style-type: none"> • The successful synthesis of MIL-101 and NH₂-MIL-101 polymer matrix • Improving selectivity properties at -20 °C compared to ambient temperature 	[42]
Pebax 1657/PES	ZIF-8	<ul style="list-style-type: none"> • CO₂ • CH₄ 	<ul style="list-style-type: none"> • Improving CO₂ permeability and CO₂/CH₄ selectivity 	[43]

Table 1. Continued.

Polymer	Nanofiller	Gases	Description	Ref.
Polyether block amide (PEBAX-5513)	Potassium tetrafluoroborate (KBF ₄)	<ul style="list-style-type: none"> • CO₂ 	<ul style="list-style-type: none"> • Improving CO₂ permeability 	[44]
Polyurethane	SiO ₂ , ZSM-5, and ZIF-8	<ul style="list-style-type: none"> • CO₂ • CH₄ 	<ul style="list-style-type: none"> • Best separation performance with ZIF-8 nanofillers 	[45]
Removal of heavy metal ions				
Polymer	Nanofiller	Metals ion	Description	Ref.
Polysulfone (PSF) and polyethylene glycol (PEG)	Graphene oxide (GO)	<ul style="list-style-type: none"> • Chromium trioxide, • Lead nitrate • Cadmium nitrate • Copper sulfate 	<ul style="list-style-type: none"> • Increased permeability and hydrophilicity by adding graphene oxide in the MMMs • High adsorption capacity for Pb²⁺ (79 mg/g), Cu²⁺ (75 mg/g), Cd²⁺ (68 mg/g) and Cr⁶⁺ (154 mg/g) at neutral pH, 6.7, 6.5, 6.4 and 3.5 	[34]
Polyvinylidene fluoride (PVDF) and polyvinyl pyrrolidone (PVP)	α -zirconium phosphate (α -ZrP)	<ul style="list-style-type: none"> • Cu(NO₃)₂·3H₂O, (Cu²⁺) • ZnCl₂, • NiCl₂·6H₂O, (Ni²⁺) • Pb(NO₃)₂, (Pb²⁺) • Cd (NO₃)₂·4H₂O (Cd²⁺) 	<ul style="list-style-type: none"> • 42.8% (Cd²⁺), 93.1% (Cu²⁺), 44.4% (Ni²⁺), 91.2% (Pb²⁺), and 44.2% (Zn²⁺) were removed from an aqueous solution at neutral pH during filtration using MMMs 	[7]
Polyacrylic acid (PAA) polyvinylidene fluoride (PVDF)	Immobilizing zeolitic imidazolate framework-8 (ZIF-8)	<ul style="list-style-type: none"> • Nickel nitrate • Ni(NO₃)₂ 	<ul style="list-style-type: none"> • Relatively high-water flux of 460 L·m⁻²·h⁻¹ • Nickel ion (Ni(II)) capacity (219.09 mg/g) from a synthetic high-salinity ([Na⁺] = 15000 mg/L) wastewater 	[46]
Polyethersulfone (PES)	Graphene oxide (GO)	<ul style="list-style-type: none"> • MgSO₄ • Na₂SO₄ 	<ul style="list-style-type: none"> • Reduce the contact angle between the water droplet and the surface and increase the membrane hydrophilicity • Improving the separation of heavy metals by adding graphene oxide 	[47]
Polysulfone (PSF)	Zeolite nanoparticles	<ul style="list-style-type: none"> • Lead • Nickel 	<ul style="list-style-type: none"> • Improving water absorption capacity and hydraulic permeability • Lead and nickel ions showed adsorption capacities of 682 and 122 mg/g in the membrane, respectively 	[48]
Oil treatment				
Polymer	Nanofiller	Oil	Description	Ref.
Polyethersulfones (PES) and polyvinylpyrrolidone (PVP)	Functionalized carbon nanotube (F-MWCNT)	<ul style="list-style-type: none"> • Olive oil 	<ul style="list-style-type: none"> • Optimal conditions include penetration flux 21.2 (kg/m²), flux reduction 12.6%, COD removal 72.6% and total phenol rejection 89.5% 	[35]
Polyvinylidene fluoride (PVDF)	Graphene oxide (GO) and oxidized multi-walled carbon nanotubes (OMWCNTs)	<ul style="list-style-type: none"> • Palm oil 	<ul style="list-style-type: none"> • Proper distribution of nanoparticles in the polymer matrix and successful synthesis • Improving the performance of MMMs in comparison with other membranes • Increasing anti-contamination due to nanoparticle deposition and increasing membrane humidity 	[49]
Polycarbonate	Modified halloysite nanotubes and Graphene oxide nanosheets	<ul style="list-style-type: none"> • Olive oil 	<ul style="list-style-type: none"> • Improvement of hydrophilicity and higher pure water flux due to the presence of amphiphilic sodium dodecyl sulfate surfactant in membranes containing modified halloysite nanotubes • 100% olive oil recovery efficiency 	[50]
Polysulfone (PS) and polyvinylpyrrolidone (PVP)	Aspartic acid (AA) functionalized graphene oxide (fGO)	<ul style="list-style-type: none"> • Oil 	<ul style="list-style-type: none"> • Improved membrane permeability due to reduced contact angle measurement and increased hydrophilicity • Increasing Young's modulus 	[51]
Polybenzimidazole (PBI)	Graphene oxide (GO)	<ul style="list-style-type: none"> • Oil 	<ul style="list-style-type: none"> • Improves membrane performance with high oil removal efficiency • Increasing the hydrophilic nature of the membrane and its anti-moisture properties 	[52]

3. Mixed matrix membrane synthesis and challenges

3.1. Morphological analysis

The mixed matrix membranes construction is associated with several problems, including low interaction between the nanofiller and the

polymer matrix and the heterogeneous distribution of filler particles within the continuous polymer phase. Moreover, particle size, particle pore size, dispersed phase volume percentage, and the chemical properties of polymers are other challenging factors in mixed matrix membranes synthesis [10, 53].

The type of compounds, synthesis and dispersion of the polymer matrix filler phase are essential keys to constructing a flawless mixed matrix

membrane. The polymer and the filler are bonded together by covalent and van der Waals bonds [54]. Fourier-transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) tests are the most used tests to evaluate the structure and performance of mixed matrix membranes. Determining bond type- connecting filler with continuous phase and chemical interaction between polymer and nanofiller in the mixed matrix membrane- is one FTIR test application. The absorption of infrared radiation, like other absorption processes, is a quantum process. In this way, only specific frequencies of infrared radiation are absorbed by the molecule and cause tensile and flexural vibration of covalent bonds. The energy absorbed from infrared light by chemical bonds with specific functional groups at specified wavelengths leads to a decrease in light transmission intensity, which is usually plotted as a function of the wavenumber (in cm^{-1}) [55]. Meshkat et al. used FTIR analysis to evaluate the Pebax-MIL-53 mixed matrix membranes bonds and membrane structures [56].

X-ray diffraction determines the mixed matrix membrane state in terms of crystalline and amorphous structure. Moreover, XRD is a widely used technique in investigating the characteristics of the sample and the generality of crystalline structure properties such as network constant, network geometry, qualitative determination of unidentified materials, crystal phase and size determination, the orientation of single crystals, network defects, etc. It should be noted that the membrane with the crystalline state has higher intensity peaks, while with the increasing amorphous state, the intensity of X-diffraction pattern peaks decreases. The amorphous and crystalline state of the membrane significantly affects the degree of permeability and selectivity [3, 57]. For example, Kim et al. [58] Investigated the fabrication of a mixed matrix membrane by adding TiO_2 and fly ash nanoparticles (FA) to the polymer structure for water treatment. The presence of TiO_2 nanoparticles in the polymer matrix at the peaks of FA and TiO_2 is clearly seen in the TiO_2 -FA/PU membrane. Evaluation of glass transition temperature and membrane heat resistance are respectively essential DSC and TGA tests applications [59].

Investigating the distribution of filler particles in the membrane matrix and calculating the membrane thickness are critical SEM analysis applications [1, 60]. It should be noted that the type of solvent used and the synthesis method are very useful in the morphological process of membranes [61].

Apart from the SEM test, Field Emission Scanning Electron Microscope (FESEM) and transmission electron microscopy (TEM) tests are essential and widely used methods to determine nanoparticles distribution in the polymer matrix and determine particle agglomeration phenomenon. SEM and FESEM analyses are used to see images from the sample surface. The difference is that FESEM has a higher image resolution and is used to observe the interface between particles and polymers, especially in glassy polymers. TEM analysis can show an accurate particle scattering pattern within the polymer matrix with full resolution.

3.2. Synthesis methods

In addition to selecting membrane components, synthesis methods are also crucial in constructing a mixed matrix membrane without defects.

The polymer blends with different properties are currently a crucial factor in mixed matrix membranes' success. Various factors play a significant role in the synthesis of polymers, such as the type of the polymer in terms of being rubbery and glassy, the solubility parameter, the solvent consumption and the desired temperature [62, 63]. Proper distribution of filler particles within the polymer matrix is another critical point in the fabrication of a mixed matrix membrane that directly affects the interface between the polymer and the filler. Low interaction between the filler and the polymer creates undesirable channels that allow the molecules to pass through with the least mass transfer resistance on their path and reduce membrane performance [53]. In this section, different synthesis methods related to polymeric composition and fillers are investigated.

3.2.1. Blend polymer

Scientists have considered industrial polymers synthesis to develop a new structure to improve single polymers properties. Selecting suitable polymers with close solubility parameters (polymer structure and suitable chemical properties), choosing a suitable solvent (as a reaction environment for raw polymers), appropriate reaction environment, adding stabilizers and adding a copolymer are some of the most influential parameters in the process of making a polymer blend [64]. In recent decades, many polymers with different structures have been produced and used in a variety of applications. However, the rapid advancement of technology in multiple fields has created many applications. Therefore, there is an increasing need for the production of polymers with specific properties. In this regard, researchers have used many methods, the most important of which are copolymerization and blending. The blending method has a special place among the various forms due to features such as flexibility in material selection, design properties of the final product, and economy [65, 66]. Morphological control is an essential aspect of polymer blends due to the control of rheological behavior, processability, and compounds' physical and mechanical properties. It is complicated to stabilize polymer blends' morphology to achieve the desired properties due to the lack of suitable compatibility in the molecular structure in terms of rheological thermodynamic properties [67]. The polymer blend is a mixture consisting of at least two polymers or two copolymers divided into two categories: miscible polymer blends (It is a polymer mixture that is homogeneous on the molecular scale and its free mixing energy negative ($\Delta G < 0$) and Immiscible polymer blend (Polymer blend with free mixing positive energy ($\Delta G_m > 0$)) [68, 69]. Miscibility means forming a phase of a mixture including several components in a specific range of temperature, pressure and composition. The number of miscible and immiscible polymers with glass transition temperature and their solubility parameters are reported in Table 2.

Size, shape, and distribution of one phase in another phase in immiscible polymers depend on parameters such as the percentage of the mixture, the ratio of viscosities, the ratio of elasticity, the surface tension, as well as the process conditions such as temperature, time, and mixing intensity. In general, polymer blends can be divided into two main categories: polymer blend containing a dispersed phase (such as droplets in a matrix) and co-continuous morphology [70, 71]. Mechanical blending, solution blending, reactive blending and latex blending are common methods of making polymer blends.

Table 2. Some reported miscible and immiscible polymer blend system with solubility parameter, glass transition temperature and 3D-structure.

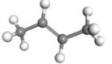
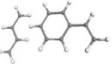
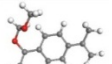
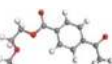
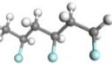
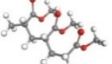

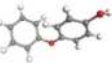
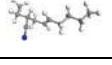
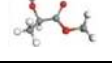
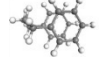
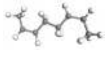
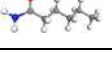
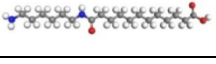
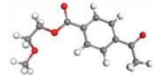
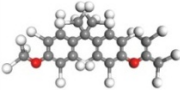
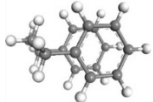
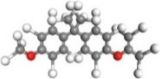
Polymer blend	Structure	Formula	Component, %	T _g value	Solubility parameter	Ref.
Miscible polymer blend						
Polybutylene		(C ₄ H ₈) _n	25	-100 °C	15.5 – 16.4 MPa ^{1/2}	[72]
Styrene-butadiene		C ₁₂ H ₁₄	75	-15 °C	17 – 19 MPa ^{1/2}	
Polybutylene terephthalate		(C ₁₀ H ₈ O ₄) _n	25	40 °C	22.4 MPa ^{1/2}	[73]
Polyethylene terephthalate		(C ₁₂ H ₁₂ O ₄) _n	75	81 °C	17.8 – 24.8 MPa ^{1/2}	
Polyvinylidene difluoride (PVDF)		-(C ₂ H ₂ F ₂) _n -	25	-40 °C	16.8 – 18.4 MPa ^{1/2}	[74]
Polymethyl acrylate (PMA)		(C ₄ H ₆ O ₂) _n	75	16 °C	18.2 – 21.3 MPa ^{1/2}	
Polystyrene (PS)		(C ₈ H ₈) _n	20	96 °C	18.3 MPa ^{1/2}	[75]
Poly (p-phenylene oxide)		(C ₈ H ₈ O) _n	80	216 °C	20.8 – 21.6 MPa ^{1/2}	
Acrylonitrile butadiene styrene (ABS)		(C ₈ H ₈ -C ₄ H ₆ -C ₃ H ₃ N) _n	30	105 °C	N/A	[76]
Poly (L-lactide) (PLLA)		(C ₃ H ₄ O ₂) _n	70	60 °C	19.2 – 21.1 MPa ^{1/2}	
Immiscible polymer blend						
Polystyrene (PS)		(C ₈ H ₈) _n	30	96 °C	18.3 MPa ^{1/2}	[77]
Polybutadiene (PB)		(CH ₂ CH=CHCH ₂) _n	70	-100 °C	17.0 MPa ^{1/2}	
Nylon 6		(C ₆ H ₁₁ NO) _n	20	54 °C	21.5 – 32.0 MPa ^{1/2}	[78]
Nylon 612		C ₁₈ H ₃₆ N ₂ O ₃	80	46 °C	21.5 – 23.3 MPa ^{1/2}	

Table 2. Continued.

Polymer blend	Structure	Formula	Component, %	T _g value	Solubility parameter	Ref.
Polyethylene terephthalate (PET)		(C ₁₂ H ₁₂ O ₄) _n	20	81 °C	17.8 – 24.8 MPa ^{1/2}	[79]
Polycarbonates (PC)		C ₁₅ H ₁₆ O ₂	80	149 °C	17.95 MPa ^{1/2}	
Polystyrene (PS)		(C ₈ H ₈) _n	20	96 °C	18.3 MPa ^{1/2}	[80]
Polycarbonates (PC)		C ₁₅ H ₁₆ O ₂	80	149 °C	17.95 MPa ^{1/2}	

3.2.1.1. Mechanical (melting) blending

The most straightforward commercial and non-contaminating techniques to produce polymer blends are using a mechanical blending process [81]. In the industrial method of mechanical blending, a single screw extruder is used, which is one of the advantages of this method: the continuous movement of the screw and production in a suitable form for further processing. The low penetration rate of polymers due to their high molecular weight slows down the mixing process and prolongs the melt mixing time due to the low thermal stability of some polymers, causing problems. Placing the raw materials in a special chamber and increasing the temperature to create a uniform mixture is one of the main steps in making a polymer composition. It should be noted that temperature, pressure and process time are determining

factors in this method. The two-screw extruder is used to increase shearing forces and improve mixing (Fig. 3). In mechanical mixing, the mixture properties are affected by the mixer's speed, the mixing temperature of the components and the mixing time [82].

3.2.1.2. Solution blending

The production of a thin film by dissolving two polymers in a common solvent and then evaporating the solvent is known as the solution blending method. If fuzzy separation occurs in the solvent presence, the two polymers become immiscible as a result of uniform mixture is not obtained. Evaporation of the solvent will also be problematic to produce thicker films. This method is used to produce polymer films and membranes that are used for commercial applications. The conventional techniques of stirring two polymers are shorn mixing,

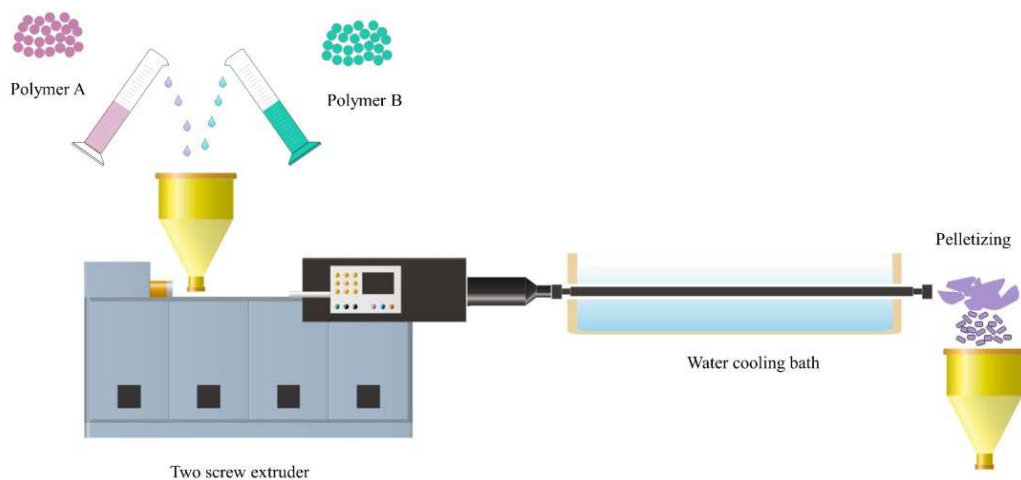


Fig. 3. The schematic of two screw extruders for mechanical blending.



Fig. 4. A general schematic of making a polymer blend using the blending solution method.

magnetic stirring and reflux methods [83]. The essential steps to perform this method are summarized as follows [84]:

- Proper selection of polymer compounds
- Select a suitable solvent for the dissolution process
- Homogeneity process in a specified time
- Add binders and compatibilizers
- Casting process

A General schematic of making a polymer blend using the blending solution method is shown in Fig. 4.

3.2.1.3. Freeze drying

Freeze-drying is one method of making polymer blending in which the polymer components are placed in a very low temperature and frozen solution. In this method, polymers are rarely agglomerated, and all frozen solvents can be collected. Sublimation is an excellent technique to remove solvents from the polymer composition. The use of symmetric solvents increases the viability / feasibility of this method [85]. The polymer blending synthesizing steps via freeze-drying are

shown in Fig. 5. According to Fig. 5, first, the polymers are dissolved in a suitable solvent, and then the solvent temperature is reduced by placing it in a cold chamber to form solvent crystals. It is then taken under severe temperature reduction to remove the solvent from the sample, and finally, a polymer aerosol is formed.

3.2.1.4. Latex blending

The latex polymer composition is another method of manufacturing and synthesizing polymer blends. Creating resistant polymer mixtures with stable dispersion (emulsion phase) of polymer particles on the microsurface in any specific aqueous medium is one of the advantages of this method. The main factor in making such blends is selecting auxiliary polymers in the form of latex or emulsion and the appropriate mixing process to create a homogeneous latex of small size and distribution of discrete phases [86, 87]. Several types of research have been reported in the synthesis of the polymeric blending with the methods mentioned are listed in Table 3.

Table 3. Summary of several research works in the field of synthesis of polymeric blending.

Polymer blend	System	Description	Ref.
Mechanical (melting) blending			
High-density polyethylene recycled polytetrafluoroethylene micronized powder (HDPE/rPTFE)	Investigation of mechanical, gel fraction, morphological and thermal properties	<ul style="list-style-type: none"> • Improves the thermal stability of the polymer composition by increasing rPTFE • Increased tensile strength • Improves adhesion between rPTFE micronized powder and HDPE matrix using electron beam irradiation • Increases storage module 	[88]
Polypropylene (PP) and thermoplastic polyurethane (TTPU)	Evaluation of performance improvement of polypropylene and thermoplastic polyurethane using compatibilizer-polypropylene grafted maleic anhydride (MA) to produce a stable and environmentally friendly polymer blend	<ul style="list-style-type: none"> • Increases thermal stability using a polymer combination of PP and TTPU • Increases thermal stability by adding MA to PP and TTPU structures • Improves interfacial compatibility and adhesion 	[89]
Polypropylene (PP) and low-density polyethylene (LDPE)	Synthesis of the polymer composition of polypropylene and low-density polyethylene to prevent degradation during the recycling process	<ul style="list-style-type: none"> • Reduction of plastic waste and production of a valuable material using PP polymer blend with low-density polyethylene mixture additive 	[90]

Table 3. Continued.

Polymer blend	System	Description	Ref.
Solution blending			
Styrene-butadiene rubber (SSBR)/ trans-1,4-polyisoprene (TPI)	Evaluation of the structural performance of polymer composition	<ul style="list-style-type: none"> Improves the performance of the polymer structure blending 	[91]
Sulfonated polysulfone (SPSf) and Tröger's base (TB) polymer	Evaluation of mechanical strength improvement and separation performance of ultrafiltration membranes	<ul style="list-style-type: none"> Increased surface area and total porosity Increasing the water contact angle by adding hydrophobic cell polymer and forming the acid crosslinking structure Increased the mechanical strength of the membrane 	[92]
Polyvinyl alcohol/ poly (N-vinyl pyrrolidone) (PVA/PVP)	Evaluation of dielectric conductivity and conductivity in the polymer blending	<ul style="list-style-type: none"> Increase in frequency-dependent dielectric constant (ϵ') with increasing concentration of reduced graphene oxide (rGO) Increased AC conductivity by increasing rGO doping concentration 	[93]
Freeze Drying			
Poly(L-lactic acid) / poly(methyl methacrylate) (PMMA)	Construction of a stable polymer blending of poly (L-lactic acid) / poly (methyl methacrylate) using selective hydrolysis degradation without any organic solvents	<ul style="list-style-type: none"> Using dry ice to prevent the accumulation of monoliths Control of porosity and pore density by increasing the weight fraction of PLLA The adjustability of mesoporous by changing the mechanical composition of mixed polymers by making integrated mesoporous polymer without organic solvent 	[94]
Carboxymethyl cellulose (CMC) and alginate (ALG)	Evaluation of a polymer composition for the practical fabrication of mucosal adhesive wafer in effective sublingual delivery and preservation of protein vaccines	<ul style="list-style-type: none"> High adhesion to sublingual mucosal tissue, extensive leaching tolerance and improved protein penetration into tissues using high CMC content wafers Improving mechanical strength, protection against a model enzyme (β-galactosidase) against lyophilization and heat challenge using wafers with high ALG content 	[95]
Poly(propylene glycol)-silane-poly(ethylene glycol) (PPG-Si-PEG) and Polyvinylidene Fluoride (PVDF)	Fabrication of gravity-driven membranes with high flux and low deposition (GDM) using amphiphilic polymer composition of poly (propylene glycol) -silane-poly (ethylene glycol) (PPG-Si-PEG) and synthesized in polyvinylidene fluoride matrix	<ul style="list-style-type: none"> Improved hydrophilicity using PEG Increased water flux of membranes Improved antifouling properties of the modified membrane 	[96]
Latex blending			
Acrylic (BA-St-AA) copolymer and Polydimethylsiloxane (PDMS) homopolymer	Assembly of a stable polymer composition using resins used in coatings to increase soil shrinkage resistance using latex method	<ul style="list-style-type: none"> Creating continuous and transparent films with low pollution pickup properties using 10–12% by weight PDMS in compounds Creating a suitable outer coating and uniformity of hydrophobic state of the composition by mixing acrylic and silicone latexes in a two-state particle size distribution 	[97]
Poly(methyl methacrylate)/ Polystyrene (PMMA/PS)	Investigation of heating effect on morphology and physical properties of PMMA/ PS shell core composite latex and polymer compounds	<ul style="list-style-type: none"> Morphological instability of polymer composition Proper compatibility of polymer composite components Suitable stability Morphology of polymer composition 	[98]
Polyurethane/ polyacrylic esters	Construction of polymer composition of polyurethane/ polyacrylic esters using hybrid polymer latex method	<ul style="list-style-type: none"> Reactivity of NCO chain with water as an extender Improving their mechanical properties with the properties of the prominent component films (latex polyurethane and acrylic) 	[99]

3.2.2. Polymer blending application

The polymer blend is a practical way to save time and money to produce materials with desirable properties. The polymer blend plays an essential role in the fabrication of MMMs in the gas separation industry. Robson upper bond showed polymer membranes weakness using a diagram in 1991 and 2008, such as competitiveness, and two critical factors; permeability and selectivity [100]. Recent studies

aimed at achieving commercialization of membranes indicate that the interaction between polymers and gases and the construction of a polymer blend with high selectivity and permeability are of particular importance. Miscible polymer blend plays an essential role in increasing the mixed matrix membranes performance due to creating a homogeneous selective layer. Table 4 reports several studies performed to improve a mixed matrix membranes performance using a polymer blend.

Table 4. Several studies performed to improve a mixed matrix membranes performance using a polymer blend.

System studied	Polymer blend	Research results	Ref.
CO ₂ gas separation	Polyethersulfone (PES)/ polyimide (PI) coated with polydimethylsiloxane	<ul style="list-style-type: none"> Construction of a high-performance polymer blend for industrial gas separation 	[101]
	Polyvinyl pyrrolidone (PVP) and polyvinyl alcohol (PVA)	<ul style="list-style-type: none"> Making low-cost and straightforward membranes with polymer composition and improving the penetration of CO₂ in the membrane shows excellent potential for membranes' industrial applications. 	[102]
	Polymers of intrinsic microporosity (PIM-1) /6FDA-DAM	<ul style="list-style-type: none"> Improving the performance of composite network membranes in CO₂ gas separation using polymer blend polymers of intrinsic microporosity (PIM-1)/ 6FDA-DAM Increasing the permeability by increasing the amount of PIM-1 in the polymer structure and increasing the d-spacing of the polymer chains 	[103]
	Polyvinyl alcohol (PVA)-modified polyether block amide (pebax®1657)	<ul style="list-style-type: none"> Improves the absorption and permeability of carbon dioxide in the membrane structure 	[104]
	Matrimid/ polyvinylidene fluoride (PVDF)	<ul style="list-style-type: none"> Improved gas permeability of membranes made using polymer composition compared to neat membranes 	[105]
	Polyvinylchloride-polyoxyethylene methacrylate (PVC-POEM)	<ul style="list-style-type: none"> Development of high-performance membranes for gas separation Improve the morphological and transition properties of the membrane 	[106]
Nano filtration	Polyethersulfone/ polyamide	<ul style="list-style-type: none"> Increased hydrophilicity of PES/ PI membranes with the modification process Improved membrane performance in NaCl separation 	[107]
	Polysulfone/ poly (1,4-phenylene ethersulfone)	<ul style="list-style-type: none"> Increase membrane mechanical strength and decrease membrane deposition Improving membrane performance in the removal of NaCl, MgCl₂, MgSO₄, K₂SO₄, KCl, CaCl₂ 	[108]
	P-amino benzoic acid/ polyisobutylene-altmaleic anhydride/ polysulfone	<ul style="list-style-type: none"> Increased membrane surface hydrophilicity Improved nanofiltration membrane performance in NaCl removal 	[109]
	Poly-diallyl dimethylammonium chloride (PDDA)/ hydrolyzed polyacrylonitrile	<ul style="list-style-type: none"> Reduce clogging and improve membrane performance 	[110]
Propylene/propane separation	Polysulfone (PSF)/ poly (polyethylene glycol) methyl ether methacrylate (PEG)	<ul style="list-style-type: none"> Uniform increase of distance between polymer chains with increasing PEG content Improved surface adhesion between ZIF-8 and the polymer by increasing the PEG content Improve mechanical strength and increase the permeability 	[111]
	4,4'-(Hexafluoroisopropylidene) diphthalic anhydride, (6FDA)/ DAM	<ul style="list-style-type: none"> Improves membrane separation performance 	[112]
Water treatment application	Polyethersulfone/sulfonated polysulfone (PES/SPSF)	<ul style="list-style-type: none"> Reduce clogging and membrane deposition Increase membrane separation performance 	[113]
Gas mixture	Polydimethylsiloxane (PDMS), polyisoprene (PI) and polyurethane (PU)	<ul style="list-style-type: none"> Improves membrane performance in gas separation 	[114]
	polyurethane and polyvinyl acetate blend	<ul style="list-style-type: none"> Increase permeability and selectivity by using a polymer blend 	[115]
Removal of toluene from water	PDMS/blended PES	<ul style="list-style-type: none"> Increase the enrichment factor by increasing the polymer concentration in the top layer Improve evaporative performance in fabricated membranes 	[116]
Removal of toluene from methanol	Polyurethane-polydimethylsiloxane (PU-PDMS) blend	<ul style="list-style-type: none"> Methanol molecules release faster than toluene Enhance membrane performance using polymer blends 	[117]
Microfiltration	Cellulose acetate-polyurethane blend	<ul style="list-style-type: none"> Improves permeability and membrane separation performance 	[118]
Humic acid removal	Polyethersulfone (PES)/ polyvinyl pyrrolidone (PVP)	<ul style="list-style-type: none"> Improved anti-fouling performance and optimal flux with the least amount of fouling resistance Increase anti-rot ability 	[119]

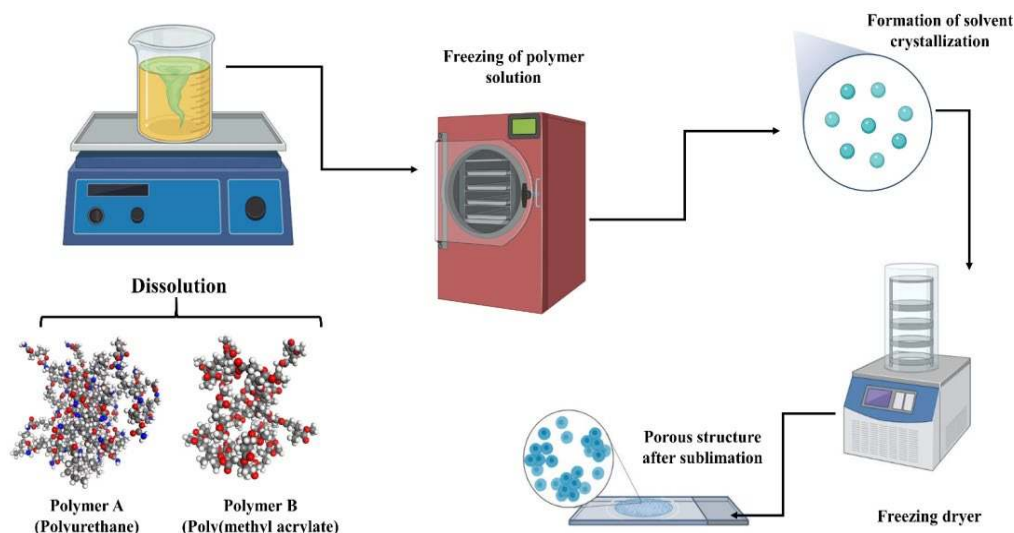


Fig. 5. A schematic of construction polymer blending using freeze-drying.

3.3. Fillers

The most important fillers applications are to prevent the accumulation of particles, void formation, blockage of pores and rigidification of the polymer in the development of MMM and improve the gas separation

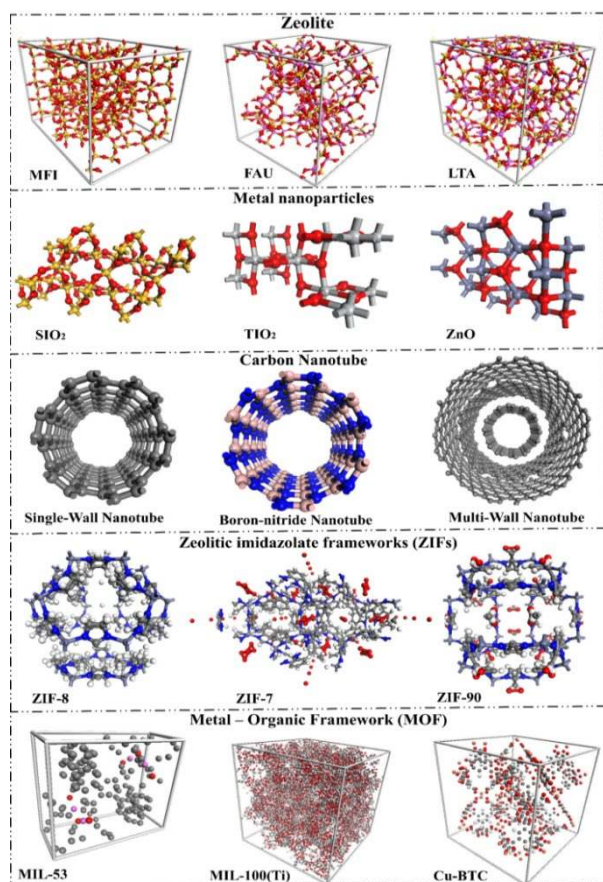


Fig. 6. Some popular fillers used in mixed matrix membranes construction.

performance. On the other hand, it may have adverse effects and reduce membrane performance based on the fillers nature [120, 121]. Improving permeability performance in mixed matrix membranes due to the presence of fillers and effects such as through membrane-penetrant interaction, molecular sieving, free volume, and polymer chain strength are other advantages of fillers [122]. In general, improving the performance of mixed matrix membranes in terms of physicochemical and transition properties of membrane structures is the main advantage of using fillers [27]. One of the main concerns in the mixed matrix membranes construction is the control of chemical structure, surface chemistry, and the type and amount of filler phase. In fact, the properties of both phases affect the morphology and membrane separation performance. It should be noted that, prevention of accumulation, proper distribution in the polymer matrix, and also low tendency of polymers to interact with fillers (especially glass polymers due to low mobility of polymer chains, compared to inorganic fillers) are among the complexities of mixed matrix membrane construction. Synthesis and surface modification methods are techniques to overcome the weaknesses of fillers to improve membranes' performance. Zeolites, graphene oxide (GO), metal nanoparticles, carbon nanotubes (CNTs), zeolite imidazole frameworks (ZIFs) and metal-organic frameworks (MOFs) are the most common fillers used in the mixed matrix membranes construction (Fig. 6). Common filler synthesis methods and their advantages and disadvantages are reported in Table 5.

3.3.1. Zeolites

Zeolites are a group of crystalline, porous, and hydrated aluminosilicates with exchangeable cations of alkaline and alkaline earth metals that are used as adsorbents in various industries [123]. Zeolites are known as suitable fillers for utilization in mixed matrix membranes due to channels and cavities of different sizes with unique physicochemical properties with high thermal and chemical stability [124]. Achieving a high-performance zeolite-filled mixed matrix membrane is entirely influenced by the proper choice of zeolite type. According to previous studies, zeolites used with a pore size of 4 to 10 Å have an excellent performance in improving the mixed matrix membrane properties [125].

Table 5. Standard filler synthesis methods and their advantages and disadvantages.

Method	Advantages	Disadvantages
<p>Hydrothermal [151]</p> <ul style="list-style-type: none"> Hydrothermal is a method based on crystals formation and growth due to chemical reactions and changes in the solubility of materials in an aqueous solution under appropriate temperature and pressure. In this method, the reactants are dissolved in the appropriate solvent first. Ultrasonic waves are used if needed to dissolve or distribute the pre-material better in the solution. Then the solution of raw materials is poured into the Autoclave. The autoclave containing the reactive solution is heated to the appropriate temperature. As a result of this heating, the pressure inside the autoclave is increased, and suitable conditions for the premedications reaction are provided. After enough time to perform a chemical reaction inside the autoclave, the heating is stopped; the products come out of it and heat if needed for drying and calcination. The synthesis gel is heated in an autoclave at a specified temperature (induction period) The reaction of the mineralizing agent (sodium hydroxide or fluoride ion) with the chemicals in the synthesis gel (silicon and aluminum) (nucleation) Growth of nuclei and conversion of amorphous material to zeolite (crystal growth) 	<ul style="list-style-type: none"> Proper controllability of process parameters Ability to create crystalline phases that are not stable at the melting point. Grow materials that have high vapor pressure near their melting points 	<ul style="list-style-type: none"> High temperature ~ 90 °C to 200 °C Costly process Impossibility of observing crystals during growth
<p>Microwave [152]</p> <ul style="list-style-type: none"> The initial heating rate (reaching the desired temperature of the solution to start the reaction) is increased by using the microwave, and the synthesis process is accelerated. Therefore, by reducing chemical reactions from a few hours to a few minutes, energy efficiency will also increase. Factors affecting microwave-synthesized nanomaterials final properties include solvent type, reactive chemical composition, coating agents, temperature, pressure, and wave's frequency. 	<ul style="list-style-type: none"> Reduce synthesis time Significant enhancement of reaction rates High selectivity Improve penetration characteristics by controlling membrane morphology, orientation, composition Perform chemical reactions at very high temperatures "Hot spots" yielded result in a "super-heating" effect No direct contact between energy source and solution High efficiency, environmentally friendly and economical 	<ul style="list-style-type: none"> Heterogeneous reaction mixture the restricted penetration depth of microwave irradiation into absorbing materials Microwave vial explosion due to increased pressure of heating reactions far away from the boiling point of the solvent
<p>Sol-Gel [153]</p> <ul style="list-style-type: none"> Production of amorphous gel from the interaction of aluminate and silicate or silica sol or metal alkoxides additional hydrothermal treatment to get crystalline phase nucleation and quick dissolution of the gel 	<ul style="list-style-type: none"> Increase the crystallization rate in a short time, Resulting in small particle size with the narrow particle size distribution No need for expensive equipment Manufacture of high purity products The high degree of homogeneity due to reaction in the liquid phase Ability to control the percentage of porosity (by changing the temperature and time) 	<ul style="list-style-type: none"> The high cost of precursors such as metal alkoxides Time-consuming reaction steps, especially the action step Fractures on the surface of the layers created and fragmentation of the specimen
<p>Sedimentation processes</p> <ul style="list-style-type: none"> In this method, the raw materials are first dissolved in a standard solvent, and then the precipitating agent is added. The precipitating agent can be a complex, reducing or oxidizing agent. The reaction was then stabilized after nanoparticles' formation by spatial, electrostatic, or a combination of methods. 	<ul style="list-style-type: none"> The simplicity of the process No need for advanced equipment 	<ul style="list-style-type: none"> Time-consuming Requires high accuracy

Table 5. Continued.

Method	Advantages	Disadvantages
<p>Chemical vapor deposition, CVD</p> <ul style="list-style-type: none"> • Reaction gases (precursors) enter the reaction chamber at a suitable and controlled temperature • Formation of a solid layer of silicon carbide (SiC) due to the collision of these gases with the hot substrate • Trapping of exhaust gas (HCl) by NaOH and condensation by nitrogen (N₂) 	<ul style="list-style-type: none"> • Fabrication of various nanostructures • Fabrication of various nanostructures due to high reaction speed • Use of various precursors due to the high reaction temperature • Lack of by-products • Control the structure, shape and composition of the desired products by changing the reaction medium 	<ul style="list-style-type: none"> • High energy consumption • high temperature • Inadequate quality of produced films
<p>Physical vapor deposition, PVD [154]</p> <ul style="list-style-type: none"> • Stages of nanomaterial formation • Adsorption of atoms or molecules on the surface of the substrate • Horizontal penetration of adsorbed material on the surface • Forming bonds with each other as well as with substrate atoms • Atomization and compaction of atoms • Creating developed crystal structures and forming microstructures 	<ul style="list-style-type: none"> • Produce thin films with a thickness of less than 100 nm • Process safety • Use on any inorganic substance 	<ul style="list-style-type: none"> • Create a uniform film on a smooth bed surface • Formation of large nuclei in case of improper bonding of film atoms with substrate atoms and reduction of final film density • High production costs • The process requires sophisticated machines and skilled operators
<p>Reverse micelle and microemulsion</p> <ul style="list-style-type: none"> • Coprecipitation: Coprecipitation is commonly used to manufacture metal sulfides, oxides, and carbonates of metals and silver halides. In this method, two inverse micelles containing cationic and anionic ions are mixed. Because each action takes place in a nanometer water pool, the products will be nanoscale. • Resuscitation: By dissolving the metal salts in the reverse micelles, the salts in the water pool are separated into the micelles and then reduced. As a result, sediments form inside the water cavities and prevent them from clotting. This method uses strong reductants such as N₂H₄, NaBH₄ and H₂. • Hydrolysis: The hydrolysis reaction is used to make metal oxide nanomaterials. In this method, metal alkoxides are dissolved in the oil phase and react with water in the micelles. 	<ul style="list-style-type: none"> • Construction of nanomaterials with efficiency • Production of intelligent nanoparticles in the pharmaceutical industry • Manufacture of single spray nanomaterials of different sizes • Easy oxygen removal in oxygen-sensitive nanomaterials due to the use of organic matter • High stability • Nanomaterial surface modifiability 	<ul style="list-style-type: none"> • System complexity • Identify and select the appropriate surfactant • Expensive surfactant
<p>Electrochemical process</p> <ul style="list-style-type: none"> • Using this method, nanomaterials with zero-dimensional structure (nanoparticles), one-dimensional and two-dimensional, can be prepared. Two-dimensional nanomaterials are prepared by electrochemical deposition of materials on a suitable substrate. Different molds such as alumina or copolymer molds can also be used to prepare one-dimensional nanomaterials (nanowires and nanorods). These molds are also used to make nanoparticles, with the difference that the pores' length is very short. 	<ul style="list-style-type: none"> • Low cost • Suitable temperature for testing • Low energy consumption • Use inexpensive solutions • Low pollution and environmental friendliness • Controllability of test conditions • The density of composed nanomaterials 	<ul style="list-style-type: none"> • The need to use the primary sublayer • The need to remove the substrate (thinning) and thus increase the reaction steps • Lack of access to spherical morphologies in cases where the substrate is used • Toxicity of the electrolytes used • Difficulty coordinating regenerative potential in the fabrication of alloys or binary metals
<p>Thermal decomposition (thermolysis)</p> <ul style="list-style-type: none"> • Thermal degradation is a chemical reaction in which chemicals are converted to at least two other chemicals under the influence of heat. The precursor is converted to a stable compound under appropriate thermal conditions, and the waste material is evaporated removed. • This reaction is usually exothermic because heat is needed to break the chemical bonds of the substance. • Organic-metal compounds or metal complexes are used as a metal source in hot surfactant solution in this method. 	<ul style="list-style-type: none"> • High purity of reaction products • High controllability of the reaction process • The wide variety of reaction precursors 	<ul style="list-style-type: none"> • high temperature • Wide particle size distribution • Increase the adhesion of particles to each other

The most widely-used zeolites in the mixed matrix membranes construction are TS-1, ETS-10, SAPO-34, AIPO, MCM-41, COK-12, MFI, BEA, GIS, FAU, NaA, NaX, NaY, ZSM-5 and LTA [126]. The creation of "cage sieve" morphology and non-selective cavities due to inappropriate adhesion at the zeolite-polymer interface, production at high operating temperatures and costly process are disadvantages of using zeolites in the fabrication of mixed matrix membranes [127]. Surface modification using silanes, diluted solution coating of highly permeable silicone rubber on the membrane, coupling agent, the anti-plasticization process of the polymer matrix, low molecular weight additive and long aliphatic, polyaromatic compounds containing polar atoms are common methods of overcoming zeolitic weaknesses and improving the performance of mixed matrix membranes [125]. In general, zeolite is synthesized at temperatures between 90 and 200 °C over several hours to several weeks. The use of primary amorphous cell is the most effective and widely used method among the various techniques of making zeolite nanocrystals. The use of clear primary solutions and colloidal suspensions is one of the most influential and greatly applied forms of synthesis of zeolite nanocrystals. These suspensions are stable colloids, and the distributed zeolites in them do not cause sedimentation for a long time. Colloidal crystals give the production structures a unique purity and improve their performance by increasing zeolites' contact surface. The formation of smaller zeolite crystals is an important feature of zeolite synthesis in the finite space method in the absence of organic conducting agents [128, 129]

3.3.2. Metal nanoparticles

In recent decades, metal nanoparticles in the mixed matrix membranes construction have received much attention from researchers owing to their potential applications for the membrane-based separation process, preventing the formation of non-selective cavities in the nanoparticle/polymer matrix interface, improving the mechanical and physicochemical properties [125]. Factors such as chemical composition, size, shape, structure, and synthesis method determine metal nanoparticles' properties and applications. Physical and chemical processes are used as the primary method of synthesizing metal nanoparticles. Solid evaporation and its conversion to supersaturated vapor to form homogeneous germination of nanoparticles are the basis of physical methods in constructing nanoparticles [130]. In physical processes, the resulting crystals' size is controlled by temporarily deactivating the evaporation source or slowing it down by entering gas molecules into the particle-containing colloid. The growth of nanocrystals in this method is usually high-speed. Therefore, the synthesis of nanocrystals in this method requires precise control over process parameters. Inert gas condensation, arc discharge, ion sputtering, laser ablation and pyrolysis are standard physical methods of making metal nanoparticles. Chemical methods are of particular importance in synthesizing various metal nanoparticles and are usually performed under mild conditions. The basis of chemical techniques is the preparation of separate nanocrystals dispersed in a solvent (sol). It is possible to produce cells in both aquatic and organic environments [131, 132]. Some common chemical methods include reduction, solvothermal synthesis, photochemical synthesis, electrochemical synthesis, and thermolysis methods. Several factors that affect the

construction of synthesized metal nanoparticles, such as impurities in the reaction medium (even in tiny amounts) will significantly affect the nanocrystal's final shape. For example, contaminants such as Fe^{3+} , Fe^{+2} and Cl^- ions (in ppm) in the synthesis of silver nanocrystals change the morphology of the synthesized nanocrystals. Superior control over the chemical composition of the reaction system is necessary for the accurate synthesis of nanoparticles. Besides, trimmer clusters in an aqueous solution containing silver nitrate greatly affect the kinetics of the reduction process and the reaction path, resulting in nanoparticles' final deformities.

Moreover, gaseous species in the air, such as oxygen, nitrogen, carbon mono, and water vapor as by-products produced during the reaction, affect crystal plates' growth rate. For example, the morphology of platinum nanocrystals changes in the presence of oxygen gases and carbon monoxide. It should be noted that when the synthesis process is carried out in an aqueous medium, H^+ and OH^- species are produced, the presence of which causes changes in the shape of various nanocrystals such as gold, silver, palladium and platinum [133, 134]. SiO_2 , TiO_2 and Al_2O_3 have been known as nanoparticles in the construction of mixed matrix membranes.

3.3.3. Carbon nanotubes (CNTs)

Hollow cylinders made of graphite sheets are known as carbon nanotubes (CNT) which can have single-walled (SWNT) and multi-walled (MWNT) form. The unique physical and chemical properties of carbon nanotubes have led to significant research advances in recent years [135]. CNTs are an ideal material for reinforcing composites due to the presence of carbon-carbon bonds in graphite layers. Moreover, CNTs improve excellent magnetic, electrical and mechanical properties in membranes [136]. The use of carbon nanotubes as fillers in the construction of mixed matrix membranes improves the transitional (permeability and selectivity) and morphological (physicochemical) properties. CNT loading has a significant effect on the reinforcement and surface adhesion between nanotubes and polymers interfaces in mixed matrix membranes. Production of impurities during synthesis, lack of proper distribution in polymer matrices and organic solvents, and poor adhesion between CNTs and polymer matrix interface are some of the major problems of using nanotubes in mixed matrix membranes construction. Coating of the non-covalent surface with surfactants, attachment of polar groups to CNT sidewalls, surface functionalization, direct suspension of CNTs in polymer solution by ultrasound, surface oxidation and placement of hydrophilic functional groups on CNT surface have been commonly used to overcome the problems resulted from using nano-tubes in mixed matrix membranes construction. The tendency of CNTs to accumulate has made it challenging to distribute CNTs in the polymer matrix adequately due to the strong van der Waal attraction among the tubes [137]. Mechanical methods (ultrasonication, ball milling, extrusion, calendring, and highly-shearing/ highly-shorn mixing) and chemical processes (noncovalent and covalent methods) are common techniques for properly distributing nano-tubes in the polymer matrix [138, 139]. Chemical vapor deposition (CVD), arc discharge, laser ablation and high-pressure carbon monoxide are standard methods for constructing carbon nanotubes [140].

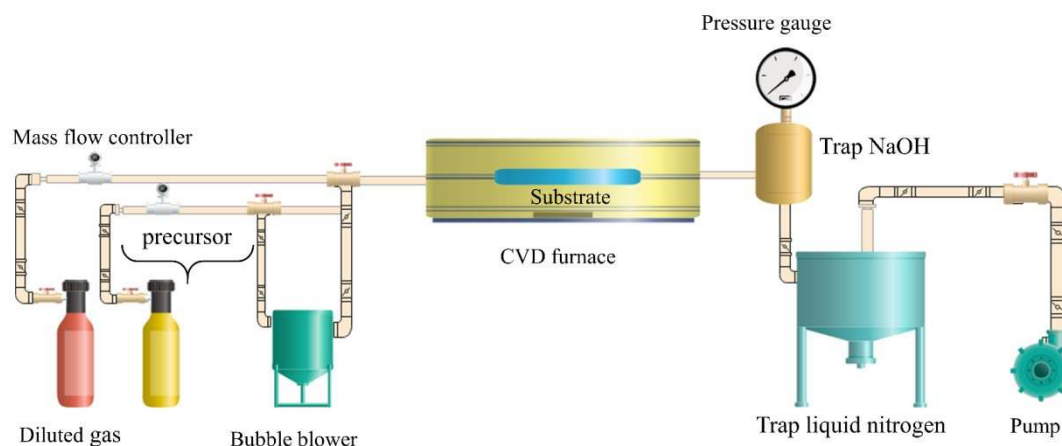


Fig. 7. Overview of the CVD process.

A chemical vapor deposition (CVD) method consists of a stream of gas or gases containing a chamber's precursor chemical compound. The chamber includes one or more hot surfaces. When chemical reactions occur near or on these hot surfaces, a deposit of the desired coating settles on them. Then, the layer is formed as a thin film on the hot surface. After the chemical reaction is completed, some by-product is formed next to the coating. These by-products are removed from the chamber and the raw gases that have not been consumed during the reaction remain. The CVD method is usually performed at temperatures above 1000 °C. Fig. 7 depicts an overview of the CVD process. As described in Fig. 7, the reacting gases (precursors) enter the reaction chamber at the appropriate and controlled temperature. A solid layer of silicon carbide (SiC) is then formed by the reaction between the precursor and the hot substratum due to these gases' contact with the hot substratum. In the CVD method, a neutral gas such as argon (Ar) is usually used as the diluent. Sedimentation temperature and pressure are two limiting factors in this method. At the end of the process, the exhaust gas (HCl) is trapped by NaOH and condensed by nitrogen gas (N₂) before leaving.

Uniformity of coatings; Possibility of depositing a wide range of materials; Very high purity of layers; No need for high vacuum and proper control of crystal structure, surface morphology and stoichiometry are the advantages of using the CVD method in making nano-tubes. Low safety, the toxicity of some of the compounds used, and the high cost of producing coatings with very high purity are some of this method's limitations.

3.3.4. Graphene oxide (GO)

Graphene is a two-dimensional (2D) sheet of carbon atoms in a hexagonal (honeycomb) configuration. The carbon atoms in graphene bond together with an SP² hybrid. Graphene is the newest member of the multidimensional graphite carbon family of materials [141]. High yang modulus (about 1100 GPa), high resistance to breakdown (125 GPa), suitable thermal conductivity (approximately 5000 W/mK), high electrical conductivity (200,000 Vs/cm²), high specific surface area (2630 m²/g), and fantastic transition phenomena such as the Hall quantum effect are reported as prominent features of graphene [142]. In recent years, graphene oxide (GO) has been highly regarded by

researchers in mixed matrix membranes production due to its outstanding properties such as high thermal and mechanical properties and high aspect ratio (>1000) [143]. Graphene oxide has been widely used to improve mixed matrix membranes performance in oil-water separation, gas separation, water treatment, and energy storage. In recent years, extensive research has been conducted to develop different methods of producing graphene. Chemical exfoliation, chemical vapor deposition (CVD), chemical synthesis, mechanical cleaving (exfoliation) are used as graphene synthesis methods [144]. Synthesis, high-quality production and large scale pure graphene are significant challenges to constructing this material. Given scientists' attention to graphene and hope for its various applications in the near future, much research effort has been devoted to producing and understanding graphene's structure and properties [145].

Exfoliation of dispersed solution graphite by placing large alkaline ions between graphite layers is the basis of graphene oxide production method based on chemical exfoliation method. High quality and purity, low simplicity and complexity, suitable for laboratory research are the advantages of this method. However, limitations such as being unsuitable for industrial production, low performance and lack of access to high purity graphene synthesis have challenged this method [146].

3.3.5. Metal-organic frameworks (MOFs)

Metal-organic Frameworks (MOFs) is a new category of nanoporous materials widely used in the storage and separation of gases due to their large size cavities, high specific surface area, and small selectable absorption molecules and optical or magnetic responses in the presence of guest molecules. Metal-organic frameworks are formed by accumulating metal ions (intermediate group metals) and clusters as coordination centers and organic ligands (Halides: Br, Cl, F) as binders [147]. The specific surface area is one of the most critical factors in assessing cavity capacity. In recent years, the available specific surface area has increased from 500 m²/g, related to zeolites, to large amounts of 4500-5900 m²/g in MOFs. These values are much larger than the ideal values for carbon compounds (2630, m²/g). In principle, the narrower the walls of the cavities the higher specific surface area. In mineral zeolites, the cavity walls are made of many O, Si and Al atoms,

while the MOFs have narrow walls. Synthesis of metal-organic frameworks is usually performed in the temperature range of ~25-225 °C, pressures ~0-20 atm and pH ~1-10.

The cavities formed in this group of nanoporous materials have a specific size and shape distribution and are different from other porous materials. Therefore, it is possible to classify metal-organic frameworks according to the cavities' size [148]. In recent years, the use of metal-organic frameworks for gas storage and separation has expanded significantly. Nanoporous metal-organic frameworks have good electrical and catalytic properties and can be used as biological carriers in drug delivery applications. In general, metal-organic frameworks have specific physical and chemical properties and are structurally controllable. The final structure and properties of metal-organic frameworks are highly dependent on both the raw material parameters and the synthesis process. The raw materials influencing these frameworks' properties are ions or metal clusters and organic binders (also called secondary building blocks). Different physical, chemical properties and cavity sizes can be achieved by changing the ligands or the central metal. The design capability of these structures has turned them into targeted compounds. The synthesis of these materials for specific purposes is one of the plans that has made a considerable investment. MMMs-based MOFs have unique performance due to their high adsorption capacity and high chemical and thermal properties. Increasing the wetting properties between the two phases with strong interaction with the polymer matrix is one of

the basic features of the organic part of MOFs. Zirconium, zinc, aluminum, and copper-based MOFs are widely used as filler in MMMs for CO₂ separation from the gas mixture and discuss MOF fillers' influence in gas transport. Solvothermal, ball milling, microwave and ultrasonic are common methods of synthesizing metal-organic frameworks.

3.3.6. Zeolite imidazole frameworks (ZIFs)

Zeolite imidazole frameworks (ZIFs) are new class of porous materials that are a subset of MOFs. These materials have a topology similar to zeolites and have a set of characteristics of both zeolite and MOF groups, including diversity in the network and cavities structure, modifiable structure, high specific surface area, high thermal and chemical stability, etc. [149]. Therefore, various applications such as gas storage and separation, catalysts, chemical sensors, and nanotechnology equipment applications can be used. Usually, the cations of divalent metals such as Zn and Co and the nitrogen atoms of the imidazole anions of the linkers form ZIFs. Metal bonding imidazole metal is made with a bonding angle of 145 °. These imidazole binders in ZIFs increase their hydrophobicity and provide better surface properties between the filler and the polymer matrix [150-154]. In general, ZIFs are suitable filler in MMMs for gas separation due to their large cavities with narrow pores. Common fillers used in the synthesis of mixed matrix membranes are listed in Table 6.

Table 6. Common fillers used in the synthesis of mixed matrix membranes.

Filler type	System studied	Outcome resulted	Ref.
Zeolite			
ZSM-5	Gas separation	<ul style="list-style-type: none"> Used in the fabrication of composite lattice membranes with matrimid® polymer Increase H₂/N₂ selectivity Establish a good bond between nanoparticles and polymers 	[155]
	Ethanol/water separation: preparation	<ul style="list-style-type: none"> Fabrication of composite network membrane with PDMS polymer Effective etching process to remove organic impurities in zeolite Increased hydrophobicity and roughness of ZSM-5 surface Increase tensile strength and swelling resistance by increasing the concentration of HF solution Increase the amount of absorption Increased surface adhesion of zeolite-PDMS 	[156]
	Pervaporation process	<ul style="list-style-type: none"> Fabrication of polyether block amide (PEBA) three component mixture matrix membranes with a combination of ZSM-5 zeolite nanoparticles and ionic liquid [Hmim] [PF6] Use of ZSM-5 nanoparticles to improve membrane performance Significant improvement of membrane separation performance with simultaneous loading of ZSM-5 and [Hmim] [PF6] in PEBA matrix 	[157]
		<ul style="list-style-type: none"> Fabrication of ZSM-5/ polyether block amide (PEBA)/ polyester sulfone (PES) bilayer mixed matrix membranes (MMM) for separation of diffusion (PV) of ethyl acetate (EAc) from aqueous solutions Synthesis of ZSM-5 zeolite nanoparticles by hydrothermal method Increase diffusion flux and improve separation performance 	[158]
Zeolite 13X	Gas separation	<ul style="list-style-type: none"> Investigation of gas separation properties of polyether block amide (PEBA) composite mesh membrane combined with 13X nanoporous zeolite on a polysulfone (PSF)/ PE layer using the molecular dynamics method Improved membrane separation performance with 13X zeolite loading 	[159]
	Pos-combustion carbon capture	<ul style="list-style-type: none"> Fabrication of 13X / PEBAX composite network membranes for carbon dioxide separation Improved gas penetration properties at Zeolite 13X to 15 W% filler load in PEBAX 	[160]

Table 6. Continued.

Filler type	System studied	Outcome resulted	Ref.
Zeolite 4A	Gas separation	<ul style="list-style-type: none"> Preparation of mixed matrix membranes from PVAc as a polymer and zeolite 4A as filler via soluble casting method using dichloromethane solvent Better adhesion of MMMs prepared from calcined zeolite 4A, compared to 4A zeolite particles to PVAc Improving the stability of MMMs formulated from calcined zeolite 4A Improving the performance of CO₂, O₂, N₂ and H₂ diffusion properties 	[161]
Zeolite 4A	Pervaporation separation of water isopropanol mixtures	<ul style="list-style-type: none"> Preparation of mixed matrix membranes using 4A zeolite compound in matrimid 5218 polyamide using the solution casting method Improved adhesion between zeolite and polymer phases at annealing temperature above 250 °C Increase the diffusion flux by increasing the zeolite content in the membranes 	[162]
Zeolite NaX	Gas separation	<ul style="list-style-type: none"> Synthesis of matrix membranes of polymer/liquid/ solid three phase mixtures (PEBA/PEG/X nanoslit) Increasing the permeability coefficient and selectivity of CO₂ in membranes by increasing the pressure and PEG loading Synthesis of mixed matrix membranes (MMM) by combining NaX nano-zeolite to polyether-block-amide (pebax-1657) as an active layer on polyethersulfone pol membrane (PES) as a backing layer Synthesis of MMMs using a hydrothermal method using microwave heating Reduce the permeability coefficient for all tested gases Increase the ideal choice for CO₂/N₂ and O₂/N₂ 	[163] [164]
MFI-type zeolite	Gas separation	<ul style="list-style-type: none"> Investigation of structural properties-transport of matrix membranes of polyamide block amide (PEBA)- zeolite (MFI) MMMs by molecular simulation (MS) and Monte Carlo technique (MC) Increase the penetration coefficient of CO₂, CH₄ and N₂ by increasing the MFI load from 10 to 20% by weight Improving the performance of morphological properties of membranes 	[165]
	Remove organic structure-directing agents (OSDA)	<ul style="list-style-type: none"> Synthesis of multilayer MFI zeolite composite membrane for removal of organic structure-guiding agents Synthesis by soluble casting using MFI zeolite nanoparticles with open pores as filler and PDMS as the continuous phase Improves membrane separation performance 	[166]
SAPO-34	CO ₂ removal	<ul style="list-style-type: none"> Solve the problem of poor compatibility between polymer matrix and inorganic filler in mixed matrix membrane (MMM) using (SAPO)-34 Increased CO₂/N₂ selectivity after treatment with 1-butyl-3-methylimidazolium ([Bmim] [BF4]) ion solution in methanol 	[167]
	CO ₂ /CH ₄ and CO ₂ /N ₂ separation	<ul style="list-style-type: none"> Decrease the permeability coefficient and increase the selectivity Best performance of composite mesh membrane separation containing 20% by weight of SAPO-34 	[168]
Metal nanoparticles			
	CO ₂ separation	<ul style="list-style-type: none"> Synthesis of MMMs for CO₂ separation using polyethylene glycol (PEG) based polyethylene glycol (UTFC-MMM) containing functional SiO₂ nanoparticles (SFSNPs) Enhance the improvement of CO₂ separation performance using SiO₂ particles in polymer matrices Synthesis of polyether-block-amide/ silica (PEBA/SiO₂) MMMs for carbon dioxide separation Modification of nanoparticle surface with cis-9-octadecenoic acid for proper distribution in the polymer structure Improve the performance of separation properties 	[169] [170]
SiO ₂	Gas separation	<ul style="list-style-type: none"> Synthesis of composite mesh membrane of polyurethane mixture filled with different silica nanoparticles to evaluate the transport performance of carbon dioxide (CO₂) and methane (CH₄) Improving the proper distribution of silica nanoparticles in MMMs by modifying the filler surface of silica with long hydrophobic chains Degradation of polymer chains and improvement of carbon dioxide penetration due to the increase in free volume Improve separation performance by modifying the surface of silica nanoparticles 	[171]
	Oil/water separation	<ul style="list-style-type: none"> Synthesis of polysulfone composite mesh membrane filled with silica for separation oil/water separation Improving separation performance by adding graphene oxide and nanosilica particles to the polymer structure Increase the contact angle by adding silica nanoparticles to the structure Increase the yang modulus of the membrane by increasing the silica nanoparticles to the structure Improving the performance of polyester sulfone (PES) membranes using graphene oxide (GO) and silica (SiO₂) nanoparticle fillers in the treatment of oily wastewater Increases membrane performance in removing oil from water 	[172] [173]

Table 6. Continued.

Filler type	System studied	Outcome resulted	Ref.
TiO ₂	Desalination processes	<ul style="list-style-type: none"> • Synthesis of polyacrylonitrile (PAN) - TiO₂ MMMs using solvent-induced phase separation (NIPS) in desalination process • Improvement of membrane thermal properties and proper interaction of TiO₂ nanoparticles with polymer matrix 	[174]
	CO ₂ /N ₂ separation performance	<ul style="list-style-type: none"> • Preparation of mixed matrix membranes (MMMs) using synthesized titanium dioxide (TiO₂) nanoparticles in polyether block amide matrix (PEBA) for CO₂/N₂ separation • Improve CO₂ penetration performance by adding TiO₂ to the polymer structure • Modification of TiO₂ with dopamine (DA) and polyethyleneimine (PEI) • Improved performance of synthesized membranes compared to upper bond Robeson 2008 using modifying TiO₂ levels with dopamine (DA) and polyethyleneimine (PEI) 	[175]
	Humic acid adsorption	<ul style="list-style-type: none"> • Synthesis of PVDF- TiO₂ (MMMs) to investigate membrane adsorption behavior for humic acid (HA) removal • Improves HA absorption at low pH 	[176]
Al ₂ O ₃	CO ₂ /CH ₄ separation	<ul style="list-style-type: none"> • MMMs preparation of polyether block amide/Al₂O₃ to investigate the transfer properties of CO₂ and CH₄ • Improved performance of separation properties of MMMs compared to neat membranes 	[177]
Carbon nanotubes (CNTs)			
Carbon nanotubes (CNTs)	Nanofiltration application	<ul style="list-style-type: none"> • Application of the phase inversion method in mixed matrix membranes based on polyethersulfone/carbon nanotubes (PES/CNT) in the application of nanofiltration (NF) • Improve MMM performance using CNT in NF process 	[178]
	Pervaporation separation of water-isopropanol mixtures	<ul style="list-style-type: none"> • Synthesis of polyvinyl alcohol (PVA)/ modified carbon nanotubes MMMs to study pervaporation separation of water-isopropanol mixtures • Improving the performance of MMMs filled with poly styrene sulfonate modified carbon nanotubes • Good compatibility and interactions between fillers and polymer matrix 	[179]
Single-walled carbon nanotube (SWNT)	Water purification	<ul style="list-style-type: none"> • Synthesis of an efficient polyethersulfone membrane filled with modified particles of single carbon wall carbon nanotubes (DexDTM-g-SCNT) for the preparation of ultrafiltration membranes • Improve the hydrophilic properties of membranes • Excellent membrane performance improvement in water treatment and other separation fields 	[180]
		<ul style="list-style-type: none"> • Synthesis of a thin film (TFN) polyvinyl alcohol (PVA) nanocomposite membrane filled with single-walled aluminosilicate (SWNT) nanotubes for the nanofiltration process • Increase the hydrophilicity of the membrane surface by reducing the membrane roughness and reducing the contact angles • Increase the hydrophilicity of the membrane surface by decreasing the membrane roughness and reducing the contact angles • Increasing the diffusion flux using single-walled aluminosilicate nanotubes in the polymer matrix 	[181]
Multi-walled carbon nanotubes (MWNTs)	Water treatment	<ul style="list-style-type: none"> • Synthesis of polysulfone hollow fiber membranes (PSUs) filled with oxidized multi-wall carbon nanotubes (MWNTs) using polyvinyl pyrrolidone (PVP) solvent • Increase the net water flux by adding nanotubes to the polymer structure • Improve sediment resistance • Increase membrane hydrophilicity by decreasing contact angle 	[182]
	CO ₂ separation	<ul style="list-style-type: none"> • Membrane synthesis of new PFs based on fluorine biphenyl (cardo-PIM-1) filled with functionalized multi-walled carbon nanotubes (f-MWCNTs) • Increased absorption of CO₂ compared to N₂ • Increase the performance of CO₂ separation performance 	[183]
Boron nitride nanosheets	Humic acid removal	<ul style="list-style-type: none"> • Preparation of polysulfone based mixed matrix membranes with ultrafiltration (MMM) with two-dimensional boron nitride sheet (BNNS) • Increase water permeability and remove humic acid 	[184]
Graphene oxide (GO)	Water treatment	<ul style="list-style-type: none"> • Fabrication of graphene oxide-polysulfone (GO-PSF) mixture matrix membranes using a wet phase inversion method • Increased diffusion flux with increasing GO in the polymer matrix • Increased diffusion flux with increasing GO in the polymer matrix • Improves membrane performance in salinity removal 	[185]

Table 6. Continued.

Filler type	System studied	Outcome resulted	Ref.
Graphene oxide (GO)	Removal of heavy metal from aqueous	<ul style="list-style-type: none"> • Synthesis of polyvinyl chloride (PVC) nanocomposite membranes of graphene oxide (GO) nanofilms • Improves membrane flux performance, chromium removal and deposition resistance • Improves the performance of tensile strength and elongation of membranes 	[186]
	CO ₂ /CH ₄ gas separation	<ul style="list-style-type: none"> • Synthesis of polysulfone (PSF) hollow fiber mixture (HFMMMs) matrix membranes filled with GO nanofibers • Improved CO₂/CH₄ gas separation performance 	[187]
Metal-organic frameworks (MOFs)			
UiO-66	Hydrogen purification	<ul style="list-style-type: none"> • Preparation of mixed membrane-matrix (MMM) based on polyethylene matrix (PEI) with UiO-66-NH₂ organic framework filler (MOF) • Improved membrane separation performance using UiO-66-NH₂ particles in membrane structure 	[188]
	dehydration of C1-C3 alcohols via pervaporation	<ul style="list-style-type: none"> • Mixed matrix membranes (MMMs) synthesis consisting of porous nanoparticles UiO-66-NH₂ and 6FDA-HAB / DABA • Improving the superior separation performance of UMO-66-NH₂-based MMMs due to the presence of hydrophilic groups (amino groups) 	[189]
MIL-53	CO ₂ /CH ₄ gas separation	<ul style="list-style-type: none"> • Construction of cellulose acetate membrane filled with NH₂-MIL 53 (Al) particles to separate CO₂ from CH₄ • Decrease in CO₂/CH₄ separation factor by increasing the temperature from 30 to 50 °C • Increase of CO₂/CH₄ separation factor by increasing the pressure from 3 to 15 bar 	[190]
	Sulfonylurea herbicides in aqueous environments	<ul style="list-style-type: none"> • Synthesis of new mixed matrix membranes (MMM) from metal-organic framework (MOF) (MIL-53) and poly vinylidene fluoride (PVDF) frameworks • It was improved the performance of hybrid network membranes and a promising prospect for sulfonylurea enrichment of aquatic environments. 	[191]
MIL-68	CO ₂ /CH ₄ separation	<ul style="list-style-type: none"> • Synthesis of matrimid-based MMM filled with MIL-68 (Al) for CO₂ / CH₄ mixture separation • Increased CO₂ permeability and CO₂/CH₄ greening • High impact on MIL-68(Al)/Matrimid MMM separation performance 	[192]
MIL-101(Cr)	Gas separation	<ul style="list-style-type: none"> • Synthesis of mixed matrix membranes (MMMs) from intrinsic microporosity PIM-1 polymer filled with MIL-101 to investigate the separation properties of He, H₂, O₂, N₂, CH₄ and CO₂ • Increase gases permeability by adding MIL-101 • High CO₂ uptake and penetration 	[193]
MIL-125(Ti)	CO ₂ separation from CH ₄ and N ₂	<ul style="list-style-type: none"> • Preparation of mixed matrix membranes (MMMs) by adding MIL-125 (Ti) to matrimid® polyimide polymer matrix • Improves good adhesion and dispersion of fillers in the polymer matrix • Significant improvement in CO₂ penetration and adsorption 	[194]
Zeolite imidazole frameworks (ZIFs)			
ZIF-7	CO ₂ /N ₂ separation	<ul style="list-style-type: none"> • Fabrication of pebax® 2533 membrane filled with ZIF-7 particles to separate CO₂ from flue gas (N₂) • Functionalization of ZIF-7 with three NH₂-, OH- and CH₃OH- binders • Improved CO₂/N₂ separation performance using functionalized ZIF-7 particles 	[195]
ZIF-8	Gas separation	<ul style="list-style-type: none"> • Synthesis of MMMs MWCNTs - ZIF-8 membranes embedded in pebax polymer matrix • Increase the improvement of CO₂ permeability and increase the free volume of membranes by adding ZIF-8 particles • Adding MWCNT inside ZIF-8 particles increases CO₂ uptake and improves CO₂/N₂ selectivity 	[196]
ZIF-11	Gas separation	<ul style="list-style-type: none"> • Development of Pebax® 2533 mixed matrix membranes filled with ZIF-11 crystals • Excellent adhesion between ZIF-11 and polymer matrix • Improve carbon dioxide permeability by adding ZIF-11 to pebax® 2533 polymer 	[197]
ZIF-67	Propylene/propane selectivity	<ul style="list-style-type: none"> • Construction of 6FDA-DAM MMMs membrane filled with ZIF-67 particles to form C₃H₆/C₃H₈ • Increased C₃H₆ permeability improvement • Very high resistance of MMM against plasticization 	[198]
ZIF-90	Gas separation	<ul style="list-style-type: none"> • Construction of mixed matrix membranes (MMMs) based on polyamide and (ZIF-90) • Proper distribution of particles within the polymer matrix • Improved permeability and gas absorption by MMMs 	[199]

3.4. Mixed matrix membranes synthesis method

3.4.1. Solution mixing

Solution mixing is one of the simplest methods for preparing mixed bed membranes. In this method, the polymer is dissolved in a suitable solvent and forms a uniform solution. The filler is then added to the solution and dispersed, stirring together. Finally, the mixed matrix membranes are cast by a blade, and its solvent evaporates in the medium at a specific temperature. This method is straightforward and is suitable for all types of inorganic fillers. The concentration of polymer and filler phases is also easily controlled. But the main problem of this method is the accumulation of fillers in the membrane structure. It should

be noted that the techniques of homogenizing the solution, such as placing the solution under ultrasound to separate the agglomerated particles from each other, should be done well to prevent the aggregates from clumping. This method is one of the most effective methods to avoid lumps inside the membrane matrix. This method can be used in three ways (Fig. 8). A) Dispersion of the particles in the solvent and stirring sufficiently, and finally adding the polymer to the solution (Fig. 8A) [200]. B) Dissolving the polymer in the solvent and mixing for a sufficient time, and finally adding the filler particles to the solution (Fig. 8B) [54]. C) Dissolving the particles and polymers separately in different solvents and then dispersing in a suitable solvent (Fig. 8C) [201].

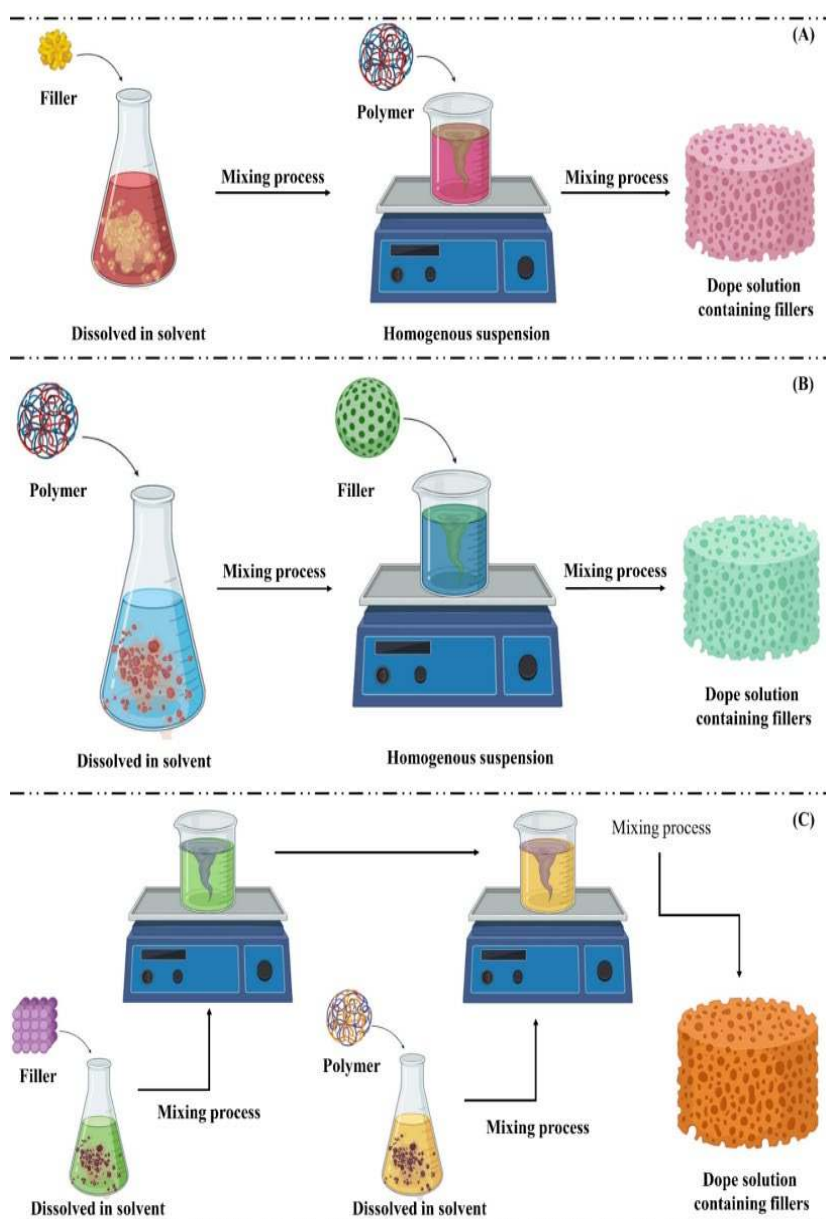


Fig. 8. Different methods of solution mixing method for mixed matrix membranes construction.

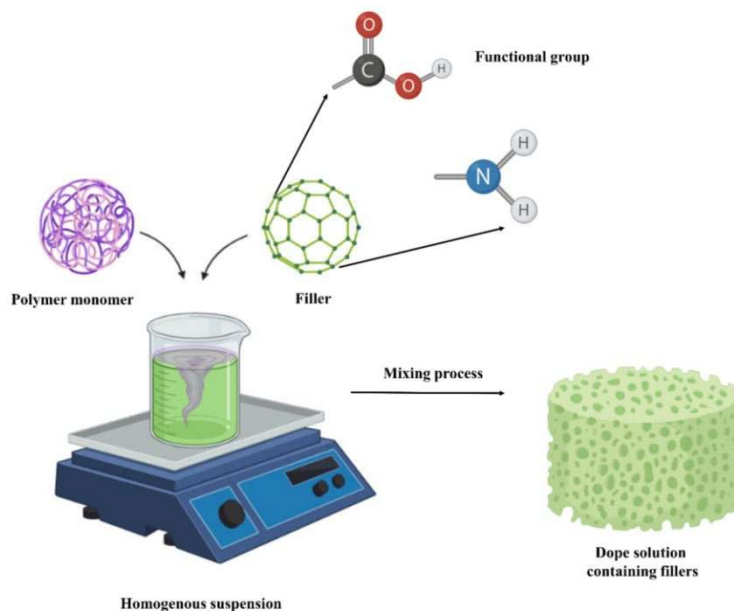


Fig. 9. The Polymerization in situ steps for constructing a mixed matrix membrane.

3.4.2. Polymerization in situ

In this method, the filler nanoparticles are mixed well with organic monomers, and then the monomers are polymerized. In this method, some functional groups such as hydroxyl and carboxyl groups on the surface of the filler particles can create free radicals, cations or anions under high radiation energy, plasma, or other methods to initiate the polymerization reaction of monomers on different surfaces. In the polymerization method, filler nanoparticles with functional groups can bind and bond with the covalent bonds' polymer chain. However, it is challenging to prevent filler nanoparticles' accumulation in membranes formation [54]. The Polymerization in situ steps for constructing a mixed matrix membrane is shown in Fig. 9.

3.4.3. Sol-gel

In this method, organic monomers or polymers and the precursor of inorganic nanoparticles are combined in solution. Then the inorganic precursor is hydrolyzed, and the nanoparticles are well-dispersed in the polymer matrix. This method's advantage is the mild reaction conditions (usually room temperature and ambient pressure) and easy control of organic and inorganic components' concentration in the solution. In addition, these particles disperse at the molecular or nanometer level in the membrane and form a homogeneous membrane. The sol-gel steps for constructing a mixed matrix membrane are depicted in Fig. 10.



Fig. 10. The Sol-gel steps for constructing a mixed matrix membrane.

4. Conclusion

Proper adhesion and uniform distribution to improve performance are significant challenges in the mixed matrix membranes synthesis. There have been repeated efforts and research, and chemistry and materials have been used to resolve this defect in this context. Although these methods have been somewhat effective, more investigations are still needed in this area. Typically, glassy polymers have good selectivity properties, and rubbery polymers have high permeability properties. Synthesis of polymeric blends with distinct properties is a practical method to increase mixed matrix membranes performance improvement. The preparation of a membrane with homogeneous dispersion of particles is of particular importance. Although chemically compatible with the polymer matrix, particle aggregation is a significant challenge for these membranes, directly affecting the performance of mixed matrix membranes performance. Metal-organic frameworks (MOFs) and zeolites imidazolate frameworks (ZIFs) are efficient nanofillers for mixed matrix membranes synthesis. Cost is another major challenge in the synthesis of combined network membranes. In fact, several network-mixed membranes have been able to cross the Robson exchange line, but the number of economically cost-effective ones is deficient.

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