

Review Paper

Analysis of Organic-Inorganic Compatibility to Synthesis Defect Free Composite Membrane: A Review

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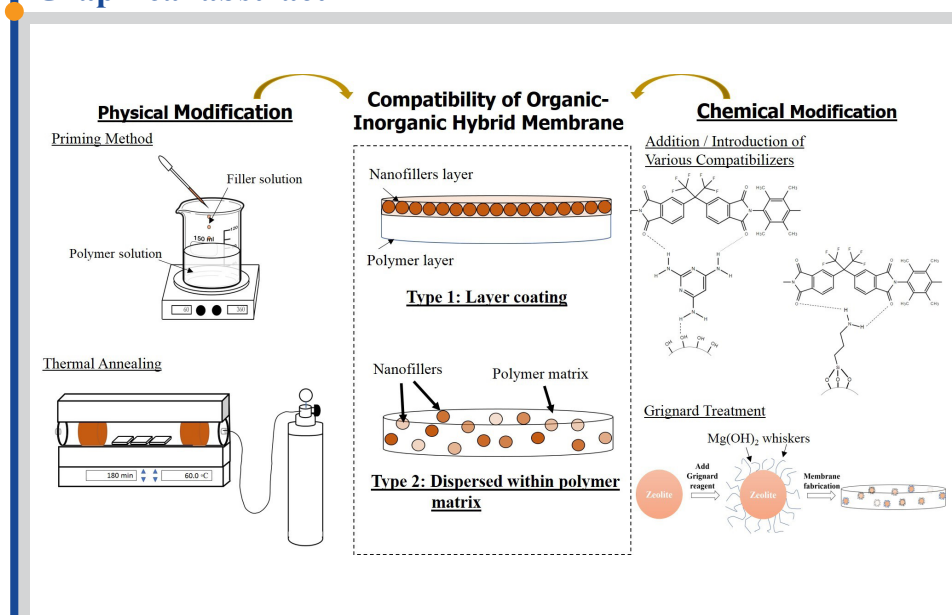
Keywords

Organic-inorganic compatibility
 Molecular dynamics simulation
 Binding energy
 Membrane

Highlights

- Compatibility between membrane and filler that affects its separation performances
- Enhancement of membrane-filler compatibility via physical and chemical modification
- Lower molecular bonding energy has indicating better membrane-filler compatibility

Graphical abstract



Abstract

Despite the excellent potential separation performance of the composite membrane, the incompatibility of organic membrane matrix with inorganic nanofiller has been remained as the major concern in producing a defect free composite membrane. Indeed, incompatibility between polymer and nanofiller caused fillers agglomeration, consequently, formed the interfacial void defect. When nanofillers are dispersed in the polymer dope, agglomeration tends to happen due to relatively large van der Waals forces of interaction. In the case of filler and polymer are not compatible, these forces will be dominant among the fillers, which caused the nanoparticles to attract to each, then induces aggregation. Such membrane defects inevitably lower the separation performances of the membrane. This review discussed the development of mixed matrix membrane, particularly on the concern of compatibility between polymer and nanofiller. Techniques to improve polymer-filler compatibility has been further discussed based on various modification and cross-linking strategies. Currently, the linker is studying experimentally to promote affinity between inorganic filler and the organic polymer. Indeed, this is time consuming and involves expensive research cost. In this review, an alternative technique using molecular dynamics (MD) simulation has also been elaborated to determine the efficiency of coupling agent to improve the matching of organic-inorganic materials, through the calculation of the molecular bonding energy. Theoretically, a multi-component system with lower energy than the total energy from its respective individual component can define as stable; hence, achieving polymer-filler compatibility.

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Contents

1. Introduction.....	30
2. Challenges of defect free mixed matrix membrane.....	30
3. Improvement of interfacial connection between organic and inorganic phase.....	30
3.1. Physical modification.....	31

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3.2. Chemical modification.....	31
3.2.1. Introduce low molecular weight material additives.....	31
3.2.2. Incorporation of room temperature ionic-liquid.....	31
3.2.3. Adding or Surface modified with silane coupling agent.....	33
3.2.4. Grignard treatment or surface roughening technique.....	33
4. Evaluation of polymer-filler compatibility through molecular dynamics (MD) simulation.....	34
5. Conclusion and future direction.....	34
Acknowledgment.....	34
References.....	34

1. Introduction

Membrane technology has become a distinguished solution for the separation of substances between two phases in almost all engineering approaches. One of the many benefits of the membrane is operating without heating or at mild temperature. Therefore, it uses less energy and enables separations to take place that would be not possible using conventional thermal separation processes such as distillation or crystallization. Unfortunately, trade-off between the membrane selectivity and permeability has restricted their applications. Extensive efforts are devoted to adjusting the membrane's pore structure, including pore size, skin thickness, and free void volume [1]. One of a universally effective adjustive strategy is to incorporate inorganic nanomaterials into the polymer polymeric backbone to form polymer-inorganic membrane structure, or known as nanocomposite membrane. The structure, mechanical strength properties and surface chemistry of inorganic material used as a dispersed phase in the nanocomposite membrane are expected to provide a better resultant membrane property; while retaining the attractive features of the polymeric membrane [2,3]. Consequently, these architecturally engineered membranes with the benefits of inorganic particles could be more cost-effective relative to inorganic membranes [4-6]. Zeolites, carbon molecular sieve, silicas [7], metal-organic frameworks [8], and carbon nanotube [9] are some commonly selected fillers in nanocomposite membranes [10-12].

There are few reported strategies to incorporate nanofillers into a polymer matrix. The required amount of inorganic fillers/nanoparticles can be first dispersed in a suitable solvent to stir for a specific time, followed by adding the polymer [13-15]. This low viscosity fillers-solvent suspension prepared could help in preventing agglomeration caused by the high shear stress while stirring [13,16]. In another approach, the polymer will first dissolve in the solvent, then, the inorganic fillers are introduced in the same solution and continue to stir [17-19]. The main benefit of this strategy is that nanofillers can be drop-wise added to the polymer solution. Different from previous strategies, inorganic fillers and polymers can be stirred in the separate solvent, respectively. After that, the filler suspension will be poured into polymer solution and continue to stir [13,20,21]. Among these fabrication processes, the third strategy is more suitable to disperse inorganic particles because of prior preparation of a dilute inorganic suspension and well-dissolved polymer before mixing.

No matter which preparation strategy is used, the utmost important characteristic of a membrane is defect-free with excellent organic-inorganic compatibility [22-24]. Unfortunately, the property of the selected inorganic fillers and polymers are usually different from each other [25-27]; hence, affecting its compatibility and adhesion between each other during membrane fabrication. Consequently, affecting the membrane functionality. The non-compatibility between the polymer and filler is the main challenge to produce a defect free composite membrane, because of the aggregation of filler particles that formed interfacial defects [28-30]. For example, a porous organic polymer (POP) was selected by Wang and co-workers [31] as filler to synthesis nanocomposite membrane due to its good interfacial compatibility with PIM-1 matrix. No visible interfacial void has been observed, suggesting POP filler was well compatible with the polymer matrix. Thus, resulting in excellent separation performances by surpassing the upper bound Robeson curve for both CO₂/CH₄ and CO₂/N₂. This review discussed the unfavorable interfacial structures and consequences of the incompatibility towards membrane separation as well as the techniques to improve it.

2. Challenges of defect free mixed matrix membrane

Formation of interfacial voids is common scenario occurred in MMMs. It mostly related to the nature of fillers and polymers. With different thermal expansion coefficients and repulsive force of polymers and fillers, it produces weak interactions between them. This poor adhesion or filler-polymer incompatibility creates the "sieve in a cage" structure which voids created at the polymer-filler interface [13,16,32]. Owing to the least resistance

pathway provided, more of penetrants passes through the voids instead of the filler's pore, which lost the filler's functionality. This "sieve in a cage" interface configuration also known as "leaky interface" which the voids have a larger size than the penetrant molecules [16,33]. Consequently, the overall permeation flux would be increasing with the significant dropping of selectivity. For instance, in the research carried out by Liu and co-workers [34], the polyimide nanocomposite membrane possessed interfacial voids in between the nanofiller and polymer, which might be caused by the interfacial stress during the membrane phase inversion process.

Another possible defect occurred at the interface could be due to the uniform stresses arise in the polymer layer during membrane formation. These uniform stresses usually happen near to the filler surfaces which causing the detachment of polymer from the fillers. Consequently, forming lower polymer chain mobility around the fillers. Although the resultant membrane could have better interfacial adhesion and improved gas selectivity, it is expected to give a lower permeability in gas performance [13,16,33]. The polymer matrix has become more rigid; hence, the gas molecules face the difficulties to diffuse through the membrane. Moore and Koros [35] report that the gas permeability through the rigidified layer is only 25 to 33% of the bulk polymer. Hence, the produced membrane would tend to have lower selectivity and permeability. Besides, the incompatibility of polymer-filler was found more serious at high loading of nanofiller. For example, Ahmad and his co-researchers reported the agglomerate of UiO-66 in polyimide membrane, from 0.28 μm to 1.3 μm when the loading of UiO-66 has increased from 6 to 21 wt.% [36]. Henceforth, causing the non-selective bypass channels in between the agglomerated nanofillers and reduced gas selectivity [36].

Pore blockage of fillers is another unfavorable scenario at the interface that called as "plugged sieves" and exceptional to porous fillers. It is possible to occur when the fillers' pore sealed by the polymer chain or solvents used in membrane formation [25]. This defeat is classified as complete or partial blockage of pores, depends on the pore size of the nanofillers. For fully blocked fillers' pore, almost none gas molecules can pass through the blocked, i.e. impermeable pore [32]. These fillers become additional obstacles in the resultant membrane to minimize gas permeability. If the pore is partial inhibited, the gas permeation is mostly reported to decrease. However, the selectivity of desired gases could be either improved or reduced. It can be explained and related to the kinetic diameter of gases tested [37,38]. For example, the original pore dimension of the zeolite 4A has fall within the range of kinetic diameter for the gas pairs of N₂/O₂ and CH₄/CO₂. Even the filler pore is partially blocked, it is likely both tested gases to bypass the fillers in their penetration through the composite membrane. Thus, the selectivity will be serious decreased. Nevertheless, for fillers' pore size utilized (for example, beta zeolites) is bigger than studied gases (CO₂/CH₄ separation), the partial pore blockage may raise desired gas selectivity [39]. Briefly, blockage of fillers' pore will diminish gas permeability. Meanwhile, the selectivity performance is relying on the pore size and degree of pore blockage.

3. Improvement of interfacial connection between organic and inorganic phase

The presence of above interfacial defects in nanocomposite membrane could seriously influence the overall membrane gas performance and mechanical strength [40]. Some modifications are necessary to minimize the formation of undesirable interfacial conditions. The modifications could be carried out either chemically or physically, on polymer or nanofillers or both. Most of researches suggested that improvement in adhesion between the inorganic fillers and polymer matrix would increase the membrane separation, which have the tendency to surpass the Robeson's 2008 upper bound limit, as shown in Figure 1.

3.1. Physical modification

Physical modification to improve adhesion between polymer and fillers is relatively simple as compared to the chemical route. It does not require chemicals or involve in changing the polymer backbone or fillers' structure. Coating or thermal treatment [72,73] are among the popular techniques to modify a membrane.

Thermal annealing is a post thermal treatment process to stabilize polymers via densification of polymer chains [73]. This thermal process is implemented on a formed membrane and heated above the glass transition temperature, T_g under the vacuum. Once it reached a sufficiently high temperature, the solvent will evaporate. Then, the membrane becomes more relaxed. The reduced stress in polymer matrix leads the polymer chains to move more flexible. Subsequently, it makes the fillers and polymer matrix to adhere better to each other. Several research works had confirmed the success of this heating treatment process to enhance the compatibility of polymer-fillers [68,74,75]. However, Duval et al. [76] found a different result, where interfacial voids could not fully eliminate even though thermal annealing above T_g . Although fewer voids between the zeolite particles and the polymer phase upon annealing, however, under high-temperature treatment, the polymer matrix could also easily damaged.

Priming method is another alternative way to help in reducing the stress at fillers-polymers interface and providing better fillers dispersion. This technique performed before inorganic fillers dispersed into a bulk polymer. Without addition solvent or chemical required, an ultra-thin layer of the polymer will coat on fillers by adding a small amount of polymer solution into the filler solution. Typically, 5 to 10 wt. % of polymer solution could be sufficient to coat the surface of fillers [46,77]. As the coated surface of filler has the same nature with the polymer bulk, therefore it helps in minimizing the tendency of fillers to agglomerate for better polymer-filler adhesion [74,78,79]. Nonetheless, particles must be dispersed evenly in the solvent. Then, introducing the dope solution, to avoid agglomeration of fillers [80]. Vu et al. [81] proved that the primed CMS fillers with Matrimid had shown large increment in the selectivity of CO_2/CH_4 than that of unprimed CMS/Matrimid nanocomposite membrane. Similarly, Hillock et al. [46] also performed the priming protocol in the formation of SSZ-13/crosslinked PDMC membrane. With the addition of 10 wt. % of polymer, permeability of CO_2 and gas selectivity for CH_4/CO_2 has improved by comparing to the neat membrane. In the study, permeability result has following the Maxwell Model prediction, which implying excellent adhesion of PDMC-zeolite interface.

3.2. Chemical modification

Besides the physical modification, the compatibility between inorganic particles and polymer matrix can improve chemically (Figure 2). Chemically modified polymer chain could affect the ability of polymer in membrane separation. To retain the original polymer chain structure, most of the modification techniques are focused on modifying the surface of fillers or added a minor component. Generally, carboxyl and hydroxyl functional groups are used to reduce filler agglomeration and to promote interfacial contact between fillers and polymers. Besides, fillers or incorporated coupling agents with a good affinity towards polar gases such as silane and ionic liquid could also provide the resultant membrane with improved gas performance.

3.2.1. Introduce low molecular weight material additives

Adding of low-molecular-weight additives (LMWA) into membrane dope is a promising approach to minimize non-selective interfacial defect. LMWA is not used to modify the surface of the polymer or fillers, but it has been introduced as a compatibilizer in the nanocomposite membrane by filling the space between fillers and polymer matrix [82-86]. Their attractive functional group such as amine, nitro, carbonyl, and hydroxyl group can induce hydrogen bond with another functional group in the polymeric chain and inorganic nanoparticle, to develop membrane with defect free structure. Since LMWA is a compatibilizer in a membrane, hence its concentration should not be too high [87]. Thus, additives with a multifunctional group are preferred, which can interact with polymer and inorganic fillers. Besides, the chosen additive is required miscible with the solvent, so it could be homogeneously mixed with the membrane dope [82,88,89]. The selected LMWA also must appear in solid form at room temperature for prohibiting evaporation during membrane fabrication. Otherwise, their ability to illuminate interfacial voids will disappear. Example of LMWA includes 2,4,6-triaminopyrimidine, 4-amino-3-nitro-phenol, 2-hydroxy-5-methyl aniline and p-Nitroaniline, to promote filler-polymer compatibility. These additives comprise of polyaromatic compound and long chain aliphatic, with rigid and planar structure. Some researchers reported the incorporation of LMWAs into membrane can enhance the gas selectivity but lower gas permeation

[85,90,91]. It is because of reduced free volume when added LMWAs. LMWAs filled the interfacial voids causing an anti-plasticization effect to increase the stiffness of polymer. As a result, the gas molecules became more difficult to diffuse through the modified membrane.

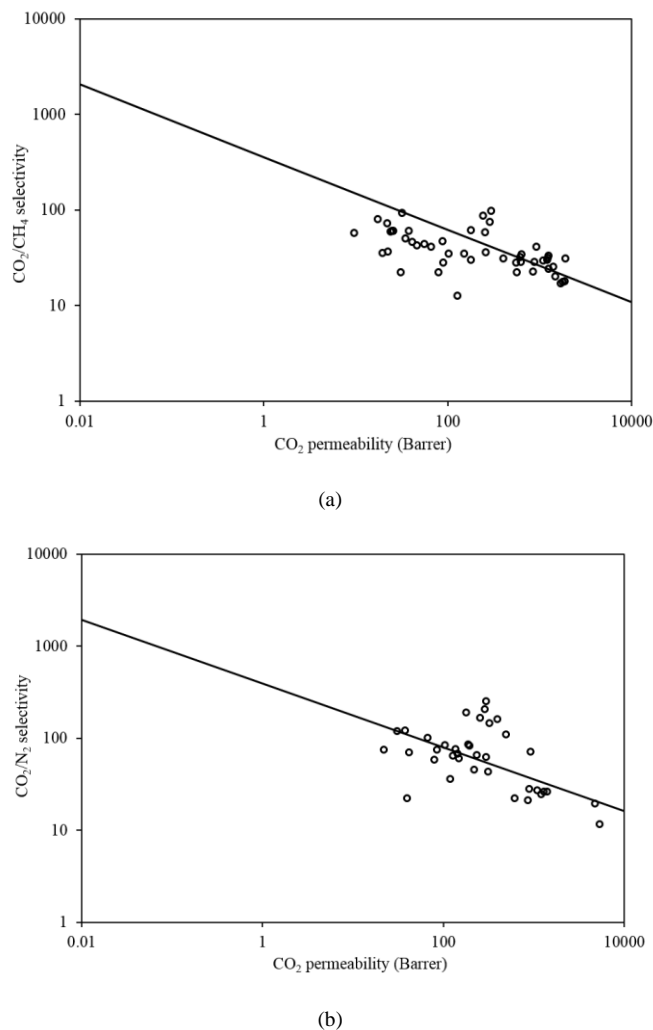


Fig. 1. Robeson's 2008 upper bound plot for CO_2/CH_4 separation. The literature data were obtained from researchers' works [41-71].

3.2.2. Incorporation of room temperature ionic-liquid

Ionic-liquid (IL) is a kind of molten salt comprises of inorganic anion and organic cation. There are more than 10^6 of different ILs can be formed with multiple combination cation/anion. Hence, ILs can conclude as designer solvents. By combining different anions and cations, ILs could have excellent thermal stability, low vapor pressure, and tunable properties [42,92,93]. Hydrogen bond and ionic cluster are two mesoscale structures that affect the properties of ILs. The viscosity of ILs is mainly depended on the strength of hydrogen bonds; while their dissolution and acidity properties will influence by the ionic cluster [94]. ILs, especially imidazolium-based ILs, have higher solubility of CO_2 , making it attractively used for gas separation [41,95]. Mostly, ILs can be incorporated into the membrane through direct blending or surface modifying nanofillers to tailor the separation properties. The direct blending of ILs into polymeric membranes usually increase the permeability significantly by reducing the crystallinity of the polymer [47]. The presence of ILs will plasticize the organic polymer matrix causing the polymer chains to move more flexibly and contact with the surface of inorganic dispersed fillers. Consequently, the interaction between polymer chains and fillers is enhanced.

For example, Casado-Coterillo and co-workers [67] direct blended IL ([emim][Ac]) with chitosan (CS), followed by adding either HKUST-1 or ZIF-8 nanofillers to form the composite membrane. Although both

membranes showed good interaction between polymer-IL and IL-fillers, ZIF-8 was found more compatible with CS and IL rather than HKUST-1 particles. IL may act as a wetting agent between the particles and polymer to enhance the interface adhesion. Membrane added with ZIF-IL-CS (10 wt. %) or HKUST-IL-CS (5 wt. %) performed the highest enhancement to permeate CO₂ and to separate CO₂/N₂. Jomekian et al. [48] has proposed to modify the surface of Pebax-1657 using by using 1,3-Di-n-butyl-2-methylimidazolium chloride IL. By adding ZIF-8 particles, the membrane has formed with IL modified Pebax 1657. The resultant membrane showed improved ZIF-8/Pebax 1657 interaction, by forming C-C bondings between the Pebax 1657, DnBMCl and ZIF-8. Indeed, the modified membrane showed higher ideal selectivity to separate CH₄/CO₂, CO₂/H₂ and N₂/CO₂ than that of the pristine membrane.

Moreover, improved adhesion at filler-polymer interfacial by applying ILs modified fillers had also reported. Ban and co-workers [66] has successfully confined bmim-Tf₂N into the nanocage of ZIF-8 through ionothermal synthesis. The bmim-Tf₂N -ZIF-8 showed a reduced pore

volume, which causes the sorption amount of N₂ and CH₄ decreased but enhancing CO₂ uptake. Their modified membrane (IL-modified ZIF-8/PSf) showed a remarkable improvement in separation selectivity than that of the unmodified membrane. However, this process could cause IL excessive occupying in ZIF-8 cavities. In work carried out by Li and co-workers [49], IL ([bmim][Tf₂N]) was added onto the outer structure of ZIF-8 fillers and dispersed in Pebax 1657 dope to form nanocomposite membrane via water-washing method. IL functionalized ZIF-8 toughen the contact of ZIF-8 with polymer chain because of the hydrophobic interaction between the IL-modified filler and membrane matrix. By having 15 wt. % loading of IL modified ZIF-8, the permeability of CO₂ as well as selectivity (CO₂/N₂ and CO₂/CH₄) had boosted by 45%, 74%, and 92% respectively. Table 1 listed some results from the researches related to ILs. Although ILs can perform well in improving membrane performance and improved compatibility between organic polymer and inorganic fillers, however, this material is highly expensive [96].

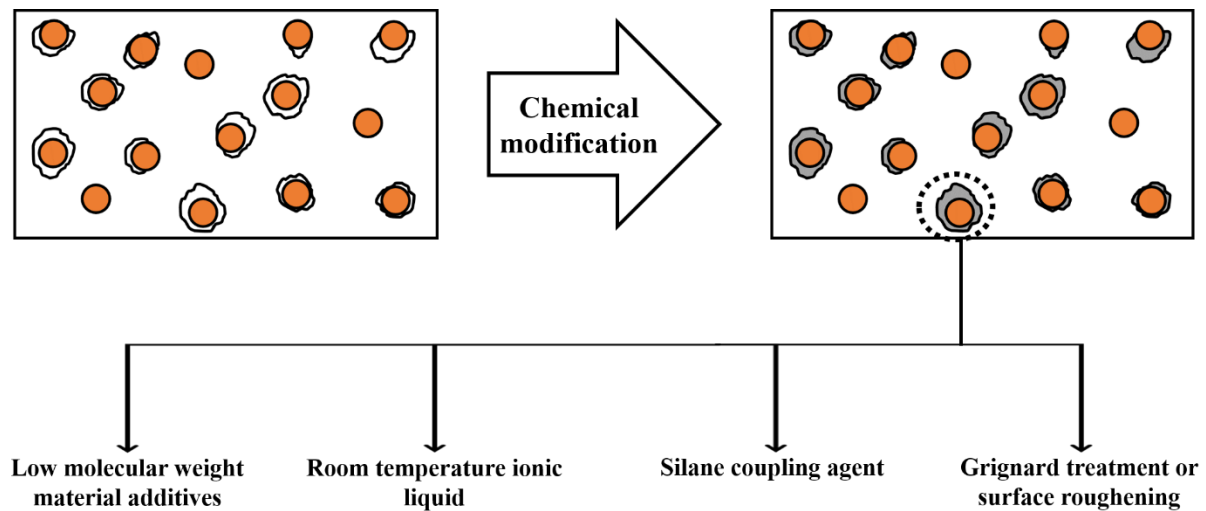


Fig. 2. Chemical modification to improve the compatibility between fillers and polymers.

Table 1

Separation performances for membranes modified using ionic liquids.

ILs and membrane combinations	Filler loading (wt.%)	Gas pair	Pristine membrane		Mixed matrix membrane		Ref.
			P _{CO2}	α^a	P _{CO2}	α^a	
Direct blending							
Ag/[bmim][BF ₄]/Pebax 1657	0.5	CO ₂ /N ₂	110 Barrer	78.6	180 Barrer	187.5	[41]
		CO ₂ /CH ₄	110 Barrer	20.8	180 Barrer	61	
SAPO-34/[emim][Tf ₂ N]/PES-Ultrason E6020	20	CO ₂ /CH ₄	24 GPU	10.5	300 GPU	62	[97]
Filler surface modification							
[emim][BF ₄]/Cu-BTC/Matrimid 5218	10	CO ₂ /N ₂	10 Barrer *	25 *	31 Barrer *	118 *	[42]
		CO ₂ /CH ₄	10 Barrer *	40 *	31 Barrer *	22 *	
[emim][OTf]/Cu-BTC/Matrimid 5218	10	CO ₂ /N ₂	10 Barrer *	25 *	38 Barrer *	120 *	[42]
		CO ₂ /CH ₄	10 Barrer *	40 *	38 Barrer *	60 *	
[emim][Tf ₂ N]/Si/Polycarbonate	3	CO ₂ /CH ₄	18 GPU	18	34.6 GPU	85.1	[98]
IL-NH ₂ @GO/Pebax 1657	0.05	CO ₂ /N ₂	92 Barrer	42	128 Barrer	64.4	[43]
		CO ₂ /CH ₄	92 Barrer	9.3	128 Barrer	12.5	

^a α = selectivity

* Results were estimated from the plotted graph

3.2.3. Adding or Surface modified with silane coupling agent

Applying silane coupling agents in the nanocomposite membrane is another common way to enhance compatibility of filler-membrane. Silane coupling agent comprises of two reactive organic and inorganic groups and known to have general formula of Z-(CH₂)_n-Si-Y₃. Particularly, the inorganic Y group (ethoxy, acetoxy or methoxy) and the organic Z group (epoxy, amino, methacryloxy) are acts as the bridge to connect inorganic fillers and organic polymers. Y group is always ready to be hydrolyzed to interact with the fillers [16,99]. By selecting suitable silane coupling agents, the surface properties of fillers such as zeolite can be changed from hydrophilic nature to hydrophobic character. By then, increased their interaction with the polymer matrix. By the coupling interactions between polymer-silane and silane-fillers, fillers can distribute uniformly with reduced non-selectivity voids. This better interfacial morphology causes an increment in gas performance. Instead of direct blending, silane can be grafted on the external structure of filler, which is known as silanation.

In the current state, there are a lot of reports on using silane coupling agents to improve filler-polymer compatibility. For example, Kim and co-workers [100] modified the surface of silica with 3-mercaptopropyltrimethoxysilane (MrPS) to form a PDMS/silica nanocomposite membrane on polysulfone support. The silane-modified silica showed to be dispersed uniformly and have better adhesion within PDMS. However, in terms of the membrane separation performances, an only slight improvement was observed from 7.3 to 8.5 and 36 to 42 GPU for CH₄/N₂ selectivity and CH₄ permeability, respectively. In work carried out by Ismail et al. [15], silane (dynasylan ameo) was used to modify zeolite 4A and incorporated into polyethersulfone hollow fiber membrane. Results showed better compatibility between polyethersulfone and DA modified zeolite 4A. Membrane produced with the loading of 20 wt. % zeolite 4A and treated by 20 wt. % silane had demonstrated higher selectivity to separate N₂/O₂ and CO₂/CH₄. This scenario occurred because unselective voids have successfully lessened after modification.

Amino-organosilane which silane with an amino-functional group such as 3-aminopropyltrimethoxysilane (APTMS), 3-aminopropyltriethoxysilane (APTES), 3-aminopropylmethyldiethoxysilane (APMDES) and aminopropyl dimethylethoxysilane (APDMES) are the most common silane coupling agents applied in nanocomposite membrane. With highly affinity toward acid gases property, the amino-organosilane could help the membrane in CO₂ uptake [101,102]. Solvents polarity is one of the factors that affect the grafting of amino-organosilane onto inorganic filler [96,103]. Nik et al. [103]

used APMDES, APDMES, and APTES to graft on the surface of zeolite FAU/EMT in different solvents (hexane, toluene, ethanol, and isopropanol). Results showed a higher concentration of grafted amine groups have deposited onto zeolite in non-polar solvents (hexane and toluene). Unfortunately, the formation of amine clusters had blocked the surface pores of zeolite, hence, causing decreased surface area of zeolite and CO₂ adsorption. On the contrary, polar solvents resulted in oppositely. There are few pieces of research selected APMDES as coupling agent instead of APDMES and APTES. Comparing to APTES, the lower number of alkoxy groups of APMDES reduces the chance of pore blockage of fillers [104-106]. Despite many types of research showing improved polymer-filler compatibility, the uses of silane coupling agents have limited to a specific pair of fillers-polymer due to the polymer's and filler's chemical structure. Table 2 summarized some examples of membrane separation performances related to amino-organosilane functionalized fillers, and their separation performances when compared to the pristine membrane.

3.2.4. Grignard treatment or surface roughening technique

Generally, Grignard treatment contains a two-step reaction. First, nanocrystal seeds will form on the surface during the dealumination step. Then, the addition of Grignard reagent causes magnesium hydroxide, nano-whisker to deposit on the outer layer of fillers [108-110]. The precipitated nano-whisker makes the filler's surface rough. Consequently, help to attach to the polymer chains, which rendered to better entanglement and omitting those nonselective voids.

Shu and co-workers [110] had implemented two-step reactions to obtain this organic whisker onto zeolite 4A. Zeolite 4A was first treated using thionyl chloride, then reacted with methylmagnesium bromide. Selectivity of O₂/N₂ and CO₂/CH₄ had shown drastically increment when the treated zeolite had incorporated in Ultem. The physical interlocking mechanism provided by the whiskers was believed to stabilize the connection between fillers and polymer, hence, enhancing the gas selectivity pair. In another work carried out by Pakizeh and Hokmabadi [111], zeolite 4A was modified through precipitation. In their work, they had added a diluted ammonium hydroxide (NH₄OH) solution to MgCl₂ solution containing zeolite 4A. Reaction between the NH₄OH and MgCl₂ forms Mg(OH)₂ nano-whiskers onto zeolite 4A, rendered to better adhesion onto polysulfone polymer with reduced nonselective voids. By applying 30 wt% loading of treated zeolite 4A in the membrane, CO₂/CH₄ selectivity has raised significantly from 1.44 to 31.

Table 2
Separation performances of membrane produced using fillers grafted by amino-organosilane.

Polymer	Filler (% loading)	Amino-silane agents	Solvent	Outcomes	Ref
6FDA/DAM:DABA modified using 1,3-propane diol	SSZ-13 zeolites (15 wt% loading)	APDMES	Isopropanol	Permeability of CO ₂ has increased from 66 to 88.6, but, decrement of CO ₂ /CH ₄ selectivity from 51 to 41.9.	[46]
6FDA-durene	SAPO-34 zeolites (5 wt% optimum loading)	APTES	Toluene	Improved compatibility between SAPO-34 and 6FDA-durene. CO ₂ /CH ₄ ideal selectivity was increased but gases permeability were dropped.	[107]
Pebax 1657	TiO ₂ (3 wt% loading)	APMDES	Ethanol	Better adhesion at polymer-filler interface with enhanced thermal stability. Significantly increment to permeate CO ₂ and to separate CO ₂ /N ₂ .	[69]
6FDA-ODA	Low silica FAU/EMT intergrowth zeolites (25wt% loading)	APMDES	Isopropanol	Defect free membrane has formed with APMDES functionalized FAU/EMT. Permeability of CO ₂ decreased but selectivity was increased, largely due to the nonselective voids were sealed.	[50]
Matrimid 5218	NaY zeolite (15wt% optimum loading)	APMDES	Ethanol	Low degree of particle agglomerations. CO ₂ permeability reduced but CO ₂ /CH ₄ selectivity increased.	[44]
Polyethersulfone (PES)	MCM-41 mesoporous silica (20wt% optimum loading)	APTMS	Ethanol	An improved interaction between N-H group in the modified MCM-41 and PES polymer chain. Membrane showed to have higher thermal and mechanical strength. Improvement of CO ₂ permeability (250%) and selectivity of CO ₂ /CH ₄ (40%).	[25]

However, Grignard treatment is complex, as well as the solvents used are sensitive. Thus, leading the development of solvothermal treatment [112]. Lee and co-workers [112] had carried out a study to investigate the differences between solvothermal and two steps Grignard treatment in improving the compatibility between organic polymer and an inorganic filler. They treated MFI zeolite with sodium chloride and methylmagnesium bromide using two-step Grignard treatment, meanwhile, performed solvothermal treatment with the reaction of ethylenediamine and magnesium sulfate heptahydrate ($MgSO_4$) aqueous solution at $160^\circ C$. Results showed that the modified MFI through solvothermal having higher surface roughness than the other one. Furthermore, the more roughened surface of solvothermal treated MFI also shown to have lesser interfacial voids when mixed with poly(vinyl acetate) to form a nanocomposite membrane. Similarly, Bae et al. [113] also compared general Grignard treatment and solvothermal modification on MFI zeolite and LTA zeolite. In their study, LTA zeolite and mixture of diethylenetriamine (DETA) with $MgSO_4$ powder has undergone solvothermal reaction at $180^\circ C$. The Utem-treated LTA nanocomposite membrane was shown to have better interfacial morphology due to the better LTA dispersion within the membrane. The resultant membrane demonstrated increment for CO_2 permeation and CO_2/CH_4 selectivity.

Although the solvothermal method can enhance interactions of membrane with fillers, this process is not environmentally friendly due to a large amount of corrosive EDA or DETA used in the process. Alternately, ion exchange with extra-framework of cation aluminosilicate zeolite has proposed [45,114]. Lydon et al. [114] performed this method by ion-exchanged Na-LTA (zeolite 4A or Na-A zeolite) zeolite with $MgCl_2$ in water. The hydrate Mg-containing zeolite was then be activated by $NaNO_3$ solution prior integrated into Matrimid matrix. Comparing to bare zeolite with Matrimid nanocomposite membrane, ion-exchanged zeolite/Matrimid membrane provided enhanced interaction strength at the interface due to a higher surface roughness of zeolite. Hence, improving the CO_2/CH_4 selectivity. In another work, Gong and co-workers [45] further exchanged the residual extra-framework cations of zeolite with Ca^{2+} in calcium nitrate to form a modified 5A zeolite. The surface roughness of ion-exchanged zeolite 5A was successfully improved. Nanocomposite membrane that comprises of Matrimid and ion-exchanged zeolite 5A had demonstrated greater mechanical strength. Consequently, the gas transport performance increased as well. In short, the success deposition of $Mg(OH)_2$ nano-whiskers onto zeolites implied an effective defect-free membrane formation. However, the process is complicated and mostly applied on zeolite particles.

4. Evaluation of polymer-filler compatibility through molecular dynamics (MD) simulation

MD simulation considered as an effective tool to predict molecular bonding properties of a membrane [115, 116]. A precise prediction of membrane properties such as density, FFV, binding energy, gas solubility, and diffusivity can be mathematically modelled in order to select required membrane properties with desire separation characteristic [117]. For example, in a work carried out by Wang and co-workers [118], MD simulation has been used to evaluate the impact of nano-silica towards the glass transition properties of polyethylene terephthalate membrane. First, a series of simulation runs at constant amount of particle, temperature and pressure have been performed within 220 to 480 K, so as to determine the specific volume of a membrane. The plotted temperature-specific volume was then used to determine the glass transition temperature of membrane.

This section is focused on the prediction of binding energy between individual components in a membrane system through MD simulation. Indeed, the bonding energy, ΔE , of a multi-component membrane system can be simulated, obtain their compatibility with each other [102]. The molecules of a membrane structure can be first geometrically packed in a simulation box with periodic boundary condition. Subsequently, geometry-optimized the geometrically packed membrane structure through the smart-minimizer technique. Then, the molecular bonding energy of the membrane can be estimated [119, 120]:

$$\Delta E = E_{complex} - \sum E_{individual} \quad (1)$$

$E_{complex}$ is referred to the total energy of the multi-components (polymer, coupling agent and fillers) membrane system, while $E_{individual}$ is used to determine the energy of individual component.

Ideally, a negative binding energy is preferable to represent a stable state [121], where the total energy of the multi-component membrane system is lower than the summation of energy for individual components. Hence, membrane system with higher compatibility to each other is achieved. On the other hand, the instability of a membrane system would rendered to positive

molecular bonding energy. The higher the energy level of a membrane system, the more unstable the system, where it would be susceptible to chemical changes. Similar observation has been reported by Alkorta and co-researchers [121]. In their study, interaction between two carboxylic acid molecules had formed ionic complexes with positive binding energy from 14.8 to 179.9 kJ/mol. This ionic complex was found less stable than the isolated carboxylic acid molecule.

In another work carried out by Tan and co-workers [102], APTES has been used to connect polyimide, alumina support and ZIF-8 nano-fillers. The stability of this combination has been explained using molecular dynamics simulation. As reported, a stable membrane system with lower membrane binding energy has achieved when adding APTES to bridge polyimide and alumina. 71 % lower binding energy was obtained as compared to the membrane without APTES as compatibilizer. Interestingly, in the same work, compatibility between the membrane and ZIF-8 was found improved by APTES, where the APTES membrane system showed 159 % lower binding energy when compared to the membrane without additional of APTES. A stable membrane system indicates that the polymer and nanofillers are having good compatible, whereas the interaction forces between the polymer and nanofiller are stronger than the van der Waals forces in between nanofillers. Thus, the occurrence of filler agglomeration has been reduced.

5. Conclusion and future direction

In conclusion, the successful development of a defect free nanocomposite membrane mostly depends on the interface interaction between inorganic fillers and polymers. Hence, a good understanding of the chemical properties of selected fillers and polymer is essential before applying any compatibilizer. Besides, the pore size of the fillers is another factor to be considered in order to prevent partial or fully blockage during surface modification. Although there are few techniques proposed to enhance the compatibility of organic-inorganic, each method has its advantages and disadvantages. Hence, none of them can conclude as the best solution. In our opinion, the priming method and thermal annealing process are preferable, because they do not need extra chemicals. However, for the thermal annealing process, the annealing temperature should be examined though thermogravimetric analysis (TGA) to prevent the destruction of membrane. Moreover, the chemical nature for both fillers and polymer will not significantly influence the modification procedure. Given the advanced computational modeling, simulation on membrane structure (evaluation of molecular binding energy) might able to predict the membrane separation efficiency. By developing a reliable membrane model, different fillers can be incorporated into the membrane system to predict its particular separation efficiency with lower research cost and time.

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