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Abstract

Mixed matrix membranes (MMMs) could provide a solution to the permeability and selectivity trade-off in polymeric membranes and bridge the gap with inorganic membranes. MMM could offer the physicochemical stability of a ceramic material while ensuring the desired morphology with higher permeability, selectivity, hydrophilicity, fouling resistance, as well as greater thermal, mechanical, and chemical strength over a wider temperature and pH range. Zeolites are fascinating and versatile materials, vital for a wide range of industries due to their unique structure, greater mechanical strength, and chemical properties. This chapter focused on zeolite-MMM and characterized various zeolite-reinforced polymeric membrane types and applications. Several key rules in the synthesis procedures have been comprehensively discussed for the optimum interfacial morphology between the zeolites and polymers. Furthermore, the influence of the zeolite filler incorporation has been discussed and explored for a range of applications. This chapter provided a broad overview of the MMM’s challenges and future improvement investigative directions.

Keywords: mixed matrix membrane, filler, zeolites, hydrophilicity, interfacial, morphology

1. Introduction

Both polymeric and ceramic membranes have been the center of interest for their tremendous contribution in water treatment industry. Despite their advantages, these synthetic membranes have limitations in terms of performance and durability. Over the years, researchers have been trying to combine the effective features of both, polymeric and ceramic, materials in one new material called mixed matrix membrane (MMM) or hybrid membrane. The sole purpose of
developing new materials has been to associate the advantageous characteristics of the two types of membranes boosting the overall process efficacy. Conventionally, objectives such as enhancement in permeability or selectivity, reduction in fouling and removal of specific contaminants have been attained either by combining two or more processes or by developing an integrated filtration process. However, material advancement in membrane technology and nanotechnology has made it possible to fine tune the process efficiency and have successfully paved the way for the synthesis of MMMs for different applications. Apart from the water purification applications, the advent of MMMs has revolutionized other areas also where separation or purification is of great significance. Some of these potential applications reported in literature include water purification, medical industry, catalytic, and gas separation. Nevertheless, MMMs have not yet crossed the lab-scale barrier because the MMM technology is still in a developmental phase and only a few lab-scale developments have been reported so far.

2. Types of MMMs

MMMs can be defined as incorporation of dispersed nanomaterials such as zeolite, carbon molecular sieve, and carbon nanotubes incorporated in a continuous polymer phase. Figure 1 presented a schematic of an ideal MMM structure including the dispersed phase and the polymer matrix [1].

MMMs could offer the physicochemical stability of a ceramic material and the membrane forming ease of polymeric materials while promising the desired morphology with higher permeability, selectivity, higher hydrophilicity, high fouling resistance, high thermal, mechanical, and chemical strength over a wider temperature and pH range [2–7]. These types of MMMs are named as inorganic filler-based MMMs, organic filler-based MMMs, biofiller-based MMMs, and hybrid filler-based

Figure 1. Schematic diagram of an ideal MMM structure [1].
MMMs, depending on the type of the dispersed fillers in the polymer matrix, as presented in Figure 1 [1]. This chapter will focus on inorganic filler-based MMM, especially zeolite-MMM.

2.1. Inorganic filler-based MMMS

The field of inorganic filler-based membrane is a promising type of membrane, which has been explored extensively over the recent years. In the polymeric matrix, the inorganic fillers attach themselves to support materials by covalent bonds, van der Waals forces, or hydrogen bonds. These inorganic fillers are prepared through processes such as sol gel, inert gas condensation, pulsed laser ablation, spark discharge generation, ion sputtering, spray pyrolysis, photothermal synthesis, thermal plasma synthesis, flame synthesis, low-temperature reactive synthesis, flame spray pyrolysis, mechanical alloying/milling, mechano-chemical synthesis, and electrodeposition. Currently, different types of inorganic fillers have been added to the polymeric phases. Some of these fillers are zeolite [8], silica [9], TiO$_2$ [10], carbon nanotubes [11], and silver [12]. There are two methods to incorporate inorganic fillers into membrane structure by blending with the solution or by attaching the fillers to the surface through different techniques [4]. Inorganic-based filler MMMS have been employed in water industry for the adsorptive removal of pollutants, disinfection and/or microbial control, catalytic degradation, and desalination [13]. They also have potentials to provide both high gas superior selectivity and the desirable mechanical and economical proper ties. Researchers believe that a suitable combination of polymers and inorganic fillers should offer superior permeability and selectivity compared to simple materials. In this review, zeolite-MMM will be comprehensively studied, as a promising membrane for several applications.

2.1.1. Zeolite-MMMs

Zeolites are microporous crystalline aluminosilicate materials with uniform pore and channel size, thus they are used in various fields such as catalysts in the petrochemical industry, ion-exchangers, and absorbents for softening and purification of water [14–16]. Incorporation of zeolites into a polymer matrix has attracted great attention in membrane technology, due to several excellent advantages such as permeability improvement of the selective component, in addition to the enhancement of the thermal stability and the mechanical strength of a polymeric membrane, [17] and its molecular sieving property, thermal resistance and chemical stability [18–20]. On the other hand, zeolites are expensive. Limitation in both polymeric and zeolite offers the need to synthesize the novel polymer–zeolite MMM. The interaction of zeolites in the membrane matrix and its shape-selective catalytic properties could improve permeability and selectivity separations [21]. There have been numerous attempts to incorporate zeolite particles in polymer matrices for gas separation due to its superior separation and size exclusion and in water purification applications [22, 23].

Rezakazemi et al. [24] studied the gas transport properties of zeolite-reinforced polydimethylsiloxane (PDMS) MMM. They evaluated the feasibility of this zeolite-MMM for hydrogen purification and natural gas sweetening, and also the permeation rates of CH$_4$, H$_2$, C$_3$H$_8$, and CO$_2$ were assessed. The filler was dispersed homogenously in the matrix without any voids at the zeolite–polymer interface. It was confirmed that the homogenous incorporation of filler in the matrix resulted in higher gas permeability for the MMM, as compared with the polymeric membranes.
Ciobanu et al. [25] reported that zeolite-polyurethane membranes demonstrated improved properties. The good interaction between the polymer and the zeolite at the interface was confirmed and the membrane swelling was reduced. Consequently, the water flux through membrane increased with increasing zeolite concentration.

Hoek [26] studied the formation of mixed matrix reverse osmosis membranes by the interfacial polymerization of thin film nanocomposite polysulfone supports impregnated with zeolites. Figure 2 represents the cross-section image of zeolite nanocomposite reverse osmosis membrane, which is utilized for water purification through desalination process. It was found that increasing the zeolite nanofillers concentrations resulted in smoother, more hydrophilic, and more negatively charged MMM. As a consequence, the MMM membrane demonstrated high flux and a slight improvement in salt rejection compared to TFC membrane without zeolite nano-particles due to changes of membrane morphology.

3. Interfacial morphology of zeolite-MMMs

To obtain the optimum interfacial morphology between the zeolites and polymer, several key roles should be considered. The first one is to promote the adhesion between polymer matrix and molecular sieve phases by modifying the zeolite surface with silane coupling agents [27–29]. The second one is to introduce low molecular weight materials to fill the voids between polymer and molecular sieve phases [30, 31]. The third one is to apply high processing temperatures close to glass transition temperature (Tg) of polymeric materials to maintain the polymer chain flexibility during the membrane formation [32]. The fourth one is to prime the surface of zeolites by polymer [33].

The polymer matrix plays an important role for permeability and the inorganic filler has a controlling factor for the selectivity of the separation process. As a result, interfacial compatibility between the two phases has profound impact on the separation performance for such membranes. The addition of inorganic fillers has key impacts on the interfacial void formation, aggregation, pore blockage of the morphology, and the transport phenomenon. Consequently, the impregnation of zeolites has a significant influence on the overall performance of the newly developed MMMs. The formation of these interfacial voids is attributed to two main phenomena, the interaction between the polymer phase and the filler and the stress exerted during preparation [1, 32]. The presence of interfacial voids creates additional
channels that allow the solvent to pass through the membrane [34]. However, mechanical strength and rejection rate are also concerned by the channel density [35].

Figure 3 represents various structures at the polymer/zeolite interface region [36]. Figure 3a demonstrates a homogenous blend of polymer and sieve, indicating an ideal interphase morphology. Figure 3b shows polymer chains rigidification due to the shrinkage stresses generated during solvent removal. Figure 3c confirmed poor compatibility between zeolite and polymer matrix morphology, due to the formation of voids at the interfacial region. Figure 3d indicates sealing surface pores of zeolites by the rigidified polymer chains. Overall, the interaction between polymer and zeolite is related to chemical nature of the polymer and sieve surfaces, and the stress encountered during material preparation, which are the critical factors to form the interphase.

These features are a challenge and should be controlled or avoided for the synthesis of the targeted zeolite-MMM for several applications. The formation of relatively nonselective defects at the interface between the zeolite particles and the polymer medium will result in MMMs, which fail to demonstrate their performance [37]. Therefore, despite the good properties of the polymer-zeolite membranes MMMs, they still face some challenges to overcome.

4. Interfacial modification of zeolite-MMMs

Several strategies have been offered to improve the polymer–zeolite interaction; hence to avoid nonselective voids. These methods are included incorporation of a plasticizer into
the polymer solution that can decrease the polymer glass transition temperature (Tg) [32]. Consequently, polymer chain flexibility maintains during membrane preparation either by annealing the membranes above glass transition temperature of polymer [38, 39] or external surface of zeolites can be modified by coupling agents. The surface-initiated polymerization is a most frequent technique to improve the polymer–filler adhesion in polymer-zeolite MMMs [40]. Furthermore, adding the low molecular-weight (LMWAs) to the membrane formulation can act as a compatibilizer or a third component to prepare glassy polymer/ LMWAs blend membranes [31, 41], priming method can be also used to reduce the stress at the polymer-particle interface, and to minimize agglomeration of the particles. Consequently, the interfacial interaction between the two components will be improved through coating the surface of the filler particles with a dilute polymer dope [31], to minimize the zeolite-solvent/non-solvent interaction, especially for the use of modified zeolite in asymmetric membranes [42]. Therefore, the obtained hydrophobic surface can suppress the zeolite particles from acting as nucleating agents. As a result, it will minimize the voids induced by the unfavorable interaction between polymer and zeolite particles.

4.1. Interfacial modification with silane agents

Silane coupling agents were commonly proposed to modify the zeolite surface in order to improve the compatibility of the inorganic filler with the polymeric matrix [43, 44]. It is known from literatures related to the silanation of zeolites that silane coupling agents have two types of reactive groups. First, the hydroxyl groups of zeolites, which could make hydrogen bonds with the amino silane agent [43]. Second, the organo functional group, such as amino and epoxy, which could be used to bond polymer chains to the zeolite. Therefore, improving adhesion between the zeolite and the bulk polymer phase in the membrane was achieved [42]. Figure 4 shows a schematic silanation of zeolite surface with 3-aminopropyldimethylethoxysilane (APDMES) coupling agent [42].

Koros [45] indicated that the glass transition temperature of MMMs is influenced by silane modification. In other words, the Tg of the zeolite-MMMs increased with the increasing of silane concentration on the surface of the zeolite particles. As a result, the silane modification of zeolite affects the mechanical properties of continuous phase due to the formation of the hydrogen bonding between the zeolite particles and polymer matrix and the movement reduction of the polymer chains [29, 41].

Leo [46] investigates the effects of silane-grafting on the separation performance of MMM for gas permeation. The 3-aminopropytrimethoxysilane (APMS) was added to modify SAPO-34 zeolite before the impregnation into the asymmetric polysulfone (PSf) MMMs through dry–wet phase inversion method. Both PSf/modified SAPO-34 membranes showed great enhancement in terms of selectivity and permeability, compared to the original PSf membrane. The increment of CO₂ selectivity and permeability was correlated to the diminishing of the interfacial voids, when SAPO-34 zeolite was modified using APMS in ethanol.

Pechar et al. [47] studied the use of 3-aminopropytrimethoxysilane (APTMS) influence to modify ZSM-2 zeolite to synthesize polyimide MMMs. Although micrographs showed the absence of voids, however, the modified ZSM-2-MMMs performance for CO₂ selectivity and
permeability was dropped relatively, similarly, to the performance of pure polymeric membrane, due to the pore blockage of the ZSM-2 zeolite [48]. In order to overcome this problem, other researchers such as Li et al [28] modified zeolite 3A, 4A, and 5A using 3-aminopropylmethyldiethoxysilane (APMDES) in toluene solvent. Hence, rigidification of polymer chain and partial pore blockage reduced through this modification process. As a result, they showed high improvement for both of the selectivity and permeability of CO₂ than those MMMs containing zeolite without the modification and without major blockage the zeolite pores. Therefore, in some cases, surface modification by the silane coupling agents was recommended to enhance interfacial adhesion but hardly improve permselectivity.

4.2. Addition of low molecular weight materials (LMWMs)

Adding low molecular weight additives (LMWAs) to the membrane formulation acts as a compatibilizer or a third component to improve the compatibility between zeolite and polymer matrix. The low molecular weight materials induce a hydrogen bond with hydroxyl and carbonyl moiety. In addition, the formation of hydrogen bond confirms its solubility in the solvent used to make the polymer dope solution. It should be noted that LMWMs should be solid at room temperature, in order to prevent their evaporation during membrane fabrication, and consequently losing their ability of forming interfacial voids [31]. Once hydrogen bonds are formed between polymer chains and LMWMs, the free volume of polymers decreases, which results in a decrease in their gas permeability whereas increase in their gas permselectivity.

Yilmaz [49] reported mixed matrix membranes for the use in gas separation by blending poly-carbonates (PC) with an additive p-nitroaniline (pNA) and incorporating zeolite 4A particles as filler. The permeability of all gases was measured using differential scanning calorimetry (DSC) analysis through PC/(pNA)/zeolite 4A membranes, which were lower than those through pure
PC membrane. The incorporation of pNA was essential, since pNA acts as a facilitator for provision of better interaction between rigid, glassy polymer PC and zeolite 4A particles. Therefore, the incorporation of a molecular-weight additive with functional groups into zeolite-MMMs can be used as a tool to improve the structure and performance properties of the membranes.

One of the examples of LMWMs is 2,4,6-triaminopyrimidine (TAP) that contained three primary amine groups, which are able to form hydrogen bonds with both hydroxyl and carbonyl groups [31]. Furthermore, it had been reported that the carbonyl groups of polyimides (PI) could interact with amine groups of urethanes through the hydrogen bond formation. Park [31] used TAP to obtain the interfacial void-free PI membranes filled with zeolites. TAP enhanced the contact of zeolite particles with polyimide chains presumably by forming the hydrogen bonding. As a consequence, the void-free PI/zeolite 13X/TAP membrane showed the higher gas permeability for He, N₂, O₂, CO₂, and CH₄ with little expense of selectivity compared to the PI/TAP membrane having the same PI/TAP ratio, while the PI/zeolite 4A/TAP membrane showed the lower permeability but higher permselectivity. The difference between both membranes was influenced by the pore size of zeolites. In addition, the molecular sieving effect of zeolites seemed to take place when the kinetic diameter of gas penetrants approached the pore size of zeolites.

4.3. Annealing

One of the largest challenges in designing zeolite-MMMs is the poor contact between polymer and zeolite defects. Many efforts made to overcome to this problem associated with the zeolite-MMMs through the annealing of zeolite-MMMs above the glass transition temperature (Tg) [32]. In other words, Tg is considered as a qualitative estimation to compare the polymer chain rigidity of mixed matrix membranes at different zeolite types with simple polymer membrane and it also leads to better contact between zeolite and polymer chain [50]. Annealing process at temperature above the Tg results in the formation of stronger bond between polymer matrix and zeolite. Despite advantages of annealing in relaxing the stress imposed to the hollow fiber membrane, it results in higher packing density of polymer chains. Therefore, there are drawbacks associated with annealing. In addition, it did not lead to significant improvement in the morphology of the membranes. Annealing at high Tg formed sieve-in-a-cage morphology, which will be difficult to create a good contact between the polymer and the sieve [32]. In order to overcome to this disadvantage of annealing, incorporation of a plasticizer into the polymer solution can decrease the polymer Tg and thus maintain polymer chain mobility and flexibility during membrane fabrication [51]. Therefore, to develop membrane fabrication technology, a quench method after annealing membranes above Tg can be effective in gas separation process by forming frozen polymer chains quickly [52]. Therefore, it will have a higher free volume in the polymer matrix and subsequently higher gas permeability without the loss of selectivity.

4.4. Priming method

The dilute polymers are the same as the bulk polymers used for the preparation of MMMs. Coating the surface of the filler particles with a dilute polymer dope is known as the priming
method [45]. The agglomeration is considered as responsible for defects between polymer matrix and zeolite particle phases [53]. Since more agglomeration occurs in the polymer matrix when smaller particles are used, especially at high particle loadings, and large zeolite particles are used to form practical mixed matrix membranes. Therefore, zeolite particles were primed by increasing amount of polymer. It should be considered that polymer effectively coats the zeolite particles before adding remaining bulk polymer and mixing with the priming polymer [54]. The purpose of priming is to reduce stress at the polymer-particle interface, increase the compatibility between zeolite and polymer in MMMs, and to minimize agglomeration of zeolite particles [55, 56].

5. Applications of zeolite-MMM

The advent of zeolite-MMMs enhances the separation or purification performance of the membranes significantly. The review represents various applications of zeolite-reinforced polymeric membranes. Some of these potential applications reported in literature include water purification, gas separation, medical, catalytic, and biomedical applications.

5.1. Zeolite-MMM for water purification

Water treatment is increasingly important to remove water pollutants and solve water problems. Drinking water may comprise of hazardous substances such as toxins and endocrine disrupting compound. Therefore, it would be urgent to invent more sustainable and reliable treatment process to remove water contaminations and to regulate the quality of drinking water. The development of cost-effective membranes is in a great need to effectively replace the conventional water treatment technologies to produce water that meet or exceed stringent standards.

Recent studies have demonstrated that the zeolite-MMMs were applied to design reverse osmosis membrane to enhance the membrane properties such as permeability, selectivity, stability, surface area, or catalytic activity in water purification and separation processes [57, 58]. Nevertheless, there are only few studies performed on zeolite-MMMs for water treatment, it is determined that the size of zeolite was designed to match the expected polyimide active film thickness, thereby providing a preferential flow path through the nanochannels of zeolites [26, 59].

For example, thin film nanocomposite (TFN) reverse osmosis (RO) membranes have been used by incorporating zeolite particles into the PA rejection layer. It has shown that the incorporation of zeolite in a PA layer could improve its water permeability without significant loss of salt rejection under high pressure during RO process [60]. Main reason for that is nanochannels of zeolites with great sub-nanometer pores in zeolite nanoparticles that behave as preferential flow channels for water molecules. The zeolite-PA-based TFN membranes are considered as superior separation performance for RO applications due to their enhanced water permeability of active layer [61].

Tanga [61] provided an additional study to confirm that thin film nanocomposite membranes can significantly improve FO water flux significant with a relatively low zeolite loading due to both the surface and intrinsic separation properties of TFN membranes. Compared with TFC membrane, the TFN membrane is potentially more favorable during the application of treating feed solutions with relative higher salinity water under AL-FS orientation.
Sridhar [62] studied reactive separation of lactic acid (LA) using a microporous hydrophobic H-beta zeolite/polyvinylidene fluoride (PVDF) mixed matrix membrane from aqueous streams. Experiments were conducted using a stirred cell assembly consisting of two bell-shaped glass pipe reducers containing aqueous LA separated by the membrane from an organic solution of tri-noctylamine (TOA) carrier in alcoholic medium. The interfacial concentrations of species adjacent to the membrane in aqueous and organic chambers are influenced by mass transfer coefficients, the concentration of TOA in organic phase and the zeolite loading, and forward extraction rates. Overall, the mass transfer rates were improved with the zeolite addition, due to the kinetics of complex formation and diffusion. The continuous separation of LA by a membrane contactor could enhance the fermentation yield of the acid, which is inhibited by LA through deactivating of the lactate dehydrogenase enzyme of Lactobacillus bulgaricus microorganism used in the production of LA.

5.2. Zeolite-MMM for gas separation

Membrane technologies, such as pervaporation and gas separation, are recognized as highly promising approaches to reduce the energy consumption of industrial processes. Compared with polymeric membranes that show Robeson upper bound between selectivity and permeability, MMM are attracting research attention, due to their high permeability and selectivity.

It is known that the permeability of a gas through an MMM depends on several factors such as intrinsic properties of the filler and polymer, the filler loading, and the filler–polymer matrix interface, and the filler loading [58]. For designing a mixed matrix system for separating a certain gas pair, the molecular sieving phase must provide precise size and shape discrimination ability to distinguish the molecules. Moreover, zeolites with three-dimensional networks are generally preferred for gas separation since they offer less restricted diffusion paths. As a result, the attractive polymer matrix materials are generally glassy with relatively lower permeability and much higher selectivities. Indeed, addition of zeolites or another highly selective media would only improve the already industrially acceptable properties, if defects can be eliminated.

Pechar et al. [63] used silanated zeolite L filler modified with 3-aminopropyltriethoxysilane (APTES) and a glassy polyimide as polymer matrix for fabricating MMMs for gas separations. Both CO$_2$ selectivity and permeability of the modified MMM dropped relatively to the neat membrane, due to the blocked zeolite pores by APTES.

Furthermore, metal–organic frameworks (MOFs), as porous fillers possessing molecular sieving properties, have been combined with polymers to give MMM with substantial enhanced separation performance of CO$_2$/CH$_4$ for natural gas sweetening or CO$_2$/N$_2$ in flue [64]. MOF-74 series recently have demonstrated superior CO$_2$ adsorption capacities, due to the presence of open metal sites. This finding positions the materials as a very promising candidate for CO$_2$ capture from flue gas. Figure 5 represents MIL-101/PSF membranes at different MOF loadings. It was found that the CO$_2$ permeability increases from about 5 to over 35 barrer from pure PSF to 24 wt % MIL-101/PSF. The increase for CO$_2$ also raises the ideal selectivity for CO$_2$/N$_2$ and CO$_2$/CH$_4$ from about 20 to 25 [65].
5.3. Zeolite-MMM for catalysis

Recently, many reports demonstrated catalytic activity of polymer–zeolite MMM, because the interaction of materials in the membrane matrix and the shape-selective catalytic properties of zeolites can improve permselective separations. Membrane also functions as a separator in gas phase between different gaseous molecules. Thus, membrane should be permeable enough to give efficient separation. For liquid phase separation, metal organic complexes and inorganic filler such as zeolite have been used [66]. It is well presented mostly that polydimethylsiloxane (PDMS) is incorporated as a polymer matrix because of high permeability, affinity for reagents, thermal, mechanical, and chemical stability [67].

Langhendries and Baron [68] studied the catalytic activity of zeolite-filled poly(dimethylsiloxane) polymer membranes. The incorporation of zeolite-encaged iron-phthalocyanine partial oxidation catalysts into a dense hydrophobic polymer membrane results in a substantial
improvement in catalyst performance. Both mathematical model and kinetics determined exact concentrations in polymer and catalyst, and subsequently, the resulting catalyst activity and selectivity. Their results also indicate that hydrophobic poly-(dimethylsiloxane) is an attractive polymer for the incorporation of the hydrophilic zeolite-encaged iron-phthalocyanine catalyst. As a result, diffusion through composite catalytic membranes can be predicted using the mass transfer coefficients of pure zeolite and pure polymer material, and a tortuosity factor based on the zeolite loading as a catalyst.

Another study, Jia and Peinemann [69] investigated the incorporation of polydimethylsiloxane (PDMS) into a polymer matrix and silicalite-1, a hydrophobic zeolite in order to study the permeation of various gases. In their study, only a couple of very high zeolite loadings were investigated, and they indicated that zeolite played the role of a molecular sieve in the membrane by facilitating the permeation of smaller molecules while it prevents the permeation of larger ones.

5.4. Zeolite-MMM for biomedical application

Combination of polymer materials with zeolite particles has been attracted attention not only due to enhanced mechanical and thermal properties, but also because of antibacterial properties. Polymer hosting can provide the enhanced antibacterial activity. There are three methods such as, production of reactive oxygen species (ROS) MMM, mixed matrix membrane direct damage to cell membrane; uptake of ions from mixed matrix membrane followed by DNA replication; and disruption of adenosine triphosphate (ATP) production [70].

Siddiq [71] studied the antibacterial effects of polysulfone/polyimide (PSf/PI) mixed matrix membranes fabricated by incorporation of modified zeolite (MZ) particles through solution casting method. The antibacterial property of fabricated zeolite-MMMs against Gram-negative bacteria (Klebsiella pneumonia, Salmonella typhi) and gram positive bacteria (Staphylococcus aureus, Bacillus subtilis) were also investigated. The MMM showed good antibacterial activity and a highest activity by PSf/PI/MZ mixed matrix membrane. Therefore, the combination effect of polysulfone/polyimide and modified zeolite sufficiently increased the antibacterial effect of mixed matrix membranes.

6. Challenges and future prospects

Recently, novel zeolite-MMMs have attracted great attention in membrane technology, due to the excellent advantages such as improvement in the permeability, selectivity, thermal stability, mechanical strength of a polymeric membrane. Furthermore, the recent developments demonstrated that gas separation as well as water treatment has significantly benefited from membrane technology so far and advancements in these areas are still in progress in order of their wider use can become a reality. However, the comprehensive understanding of organic–inorganic interfaces is in a great need. Zeolite-MMMs performance suffers from defects caused by poor contact at the molecular sieve/polymer interface, the complexity of the synthesis process, high cost, identification of compatible inorganic particles, agglomeration,
inorganic particle concentration, phase separation, control of morphology and structural defects. Moreover, some zeolite-MMMs for water purification application is considered a potential hazard to humans and environmental, which also needs to more study to determine the hazardous character of these nanoparticles and mechanism of nanoparticles embedded membrane fouling in industrially water purification in the future.

One of most difficulties associated with membrane technology is fouling for a long time. Although, several strategies such as incorporation of antifouling nanoparticles, and surface modification have been used to overcome this problem, intensive investigations are needed to stop regeneration of microbial colonies on membrane surface and to reduce the leaching of filler. The next generation MMM should be developed with producing nano-size fillers without aggregation to improve their separation properties for membrane industry especially MMMs. There are several reasons to produce nano-size fillers, especially zeolite fillers such as more polymer/particle interfacial area and enhanced polymer-filler interface contact by smaller particles. The potential of incorporating fillers such as zeolite particles has not been attained up to the expectation of zeolite-MMMs performance, due to the smaller sizes, homogeneous distribution, agglomeration, price, availability, compatibility with polymer interface, their relation with water chemistry, better interfacial contact, and stability.

Despite many novel MMMs and fillers are being investigated so far but their performances are restricted due to limited synthesis processes. Previously process fails to demonstrate their performance due to the formation of relatively nonselective defects at the interface between the zeolite particles and the polymer medium on laboratory scale. Therefore, other major issue related to MMM is the interface defects that can lead to isolating zeolite fillers from the transport processes. Therefore, new techniques to achieve a perfect interface between inorganic fillers and polymers in membranes without compromising performance and scaling up these novel membranes under industrially relevant conditions is greatly needed [72].

In addition, many of these novel MMMs reported so far have been only tested on a laboratory scale and need further research to use commercially in industry. It is required to produce novel materials that can have high selectivity as well as nano-sized fillers with incredibly small sizes. There are limitations on developing novel materials due to high prices or expensive synthesis processes. The molecular dynamic simulations (MD) of mixed matrix materials could be effective approach to predict diffusive performance of MMM, especially zeolite-MMMs, and to provide experimental guidelines for tuning the membrane permeability at the molecular level without high costs. Although there are previously predicted models for predicting the processes contributing to membrane separations, however, studies in MMMs showed inadequate suitable models. Therefore, MD will be essential and effective to predict the morphology and intrinsic properties of these fillers and its interaction of the polymeric matrix.

Last but not least factor, is changing and membrane morphology could change properties of membranes, and subsequently will influence the membrane performance. Therefore, improving membrane performance in real conditions such as high temperature, high pressure, and with incorporating of a plasticizer into the polymer solution would be possible and essential in order to provide better thermally and chemically zeolite-MMMs at different operating conditions.
Although there is development success of the synthesis and the application of MMMs impregnated with zeolites for gas, water separation, and other applications, however, the mechanisms behind these phenomena require intensive investigations for more advanced MMM technology.

7. Conclusion

Mixed matrix membranes with zeolite fillers have attracted a lot of attention in membrane technology research due to its excellent advantages, such as high permeability and improved selectivity. Zeolite-MMMs could be considered an ideal candidate for purification industry since it combines the properties of polymeric matrix and zeolite inorganic fillers. Application and fabrication techniques of zeolite reinforced polymeric membranes have been comprehensively reviewed in this article with the aim of optimizing interfacial interaction between the zeolite and the polymeric matrix. Compatibility between zeolite and polymer matrix can be improved with a number of methods, such as: by applying high processing temperature during membrane formation, the silane modification, and priming on the particle’s surface, annealing that can relax the stress imposed to hollow fiber and result in higher packing density of polymer chains, and the introduction of a LMWA agent between the polymer matrix and inorganic particles.

There have been numerous attempts to incorporate zeolite particles in polymer matrices in water purification applications and for gas separation due to its superior separation properties and size exclusion. Applications of zeolite-MMMs were re-evaluated for a variety of industrial processes, including water purification, medical industry, catalytic, and gas separation. However, despite its advantages, there are still issues and difficulties associated with zeolite-MMMs that have restricted their wider applications.

It can be concluded that the advancements in the application and fabrication of zeolite-MMM needs further intensive investigations. Future research should be conducted with the aim of developing new techniques that provide better understanding of zeolite incorporation into polymer structures. New materials should also be considered as a way of reducing the fouling concerns. Additional study is necessary for an improved understanding of the basic transport mechanism occurring through the MMMs. The next generation MMMs must be developed with nano-size fillers and without aggregation so as to improve their separation properties severely needed in the membrane industry. Some results indicate that the nanosize zeolite particles incorporated in MMMs offer better performance in comparison with micron size particles. New additives and modification agents should be produced to improve adhesion between polymer and inorganic fillers. In conclusion, despite of all the identified problems, MMM technology with zeolites could be considered a strong candidate for modern purification industry due to the remarkable properties of polymeric and inorganic zeolite materials.

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