Mixed matrix membranes with molecular-interaction-driven tunable free volumes for efficient bio-fuel recovery†

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Mixed matrix membranes (MMMs), consisting of inorganic fillers dispersed in a polymer matrix, are regarded as one of the most promising futuristic membranes. This work reports the utilization of molecular interactions to finely control the conformation and topology of polymer chains to fabricate high-performance polyhedral oligomeric silsesquioxanes (POSS)/polydimethylsiloxane (PDMS) MMMs. The influence of the incorporation of POSS on the polymer structure was systematically studied by molecular dynamics simulations combined with DSC, XRD and IR measurements. The surface and interfacial morphologies of the MMMs were observed through SEM, TEM and AFM characterizations. In particular, positron annihilation spectroscopy was employed to analyze the evolution of free volumes in the MMMs. Results indicated that facely incorporating POSS into PDMS by molecular interactions could manipulate favorable interfacial morphology and tunable free volumes in MMMs. In the PDMS MMMs, the small free volumes were reduced and the large free volumes increased; these changes were beneficial for the preferential permeation of large-sized molecules through the polymeric membrane. As applied to the bio-butanol recovery from aqueous solutions, the prepared POSS/PDMS MMMs exhibited a simultaneous increase in permeability and selectivity, breaking the permeability-selectivity trade-off limitation, moreover transcending the upper bound of the state-of-the-art organophilic pervaporation membranes. Therefore, our work demonstrates that the proposed approach based on rationally creating molecular interactions can be expected to have broad applicability in fabricating high-quality MMMs for molecular separations.

Introduction

The transport of small molecules through nano-pores in rigid materials or free volumes in soft matters continues to receive tremendous attention in the fields of batteries,1 packing materials,2 catalysis3 and organisms.4 This nanoscopic phenomenon also drives the development of membrane technologies based on molecular-scale separations, such as gas separation,5,6 pervaporation,7,8 and ion separation,9 because of the inherent advantages of energy-saving and cost-effectiveness. Recently, owing to the emerging scarcity of oil resources and the demand for environmental protection, bio-butanol (a typical biofuel) produced from biomass fermentation has become important in the development of renewable energies.10 Nowadays, the low productivity, resulting from the end-product inhibition in the fermentation process, is one of the largest obstacles for the implementation of bio-butanol. The integration of the membrane separation technology with the fermentation process for in situ butanol removal is considered as a promising approach to improve the bio-butanol productivity.11 Various studies were reported about the PV recovering n-butanol from ABE model solution or fermentation broth using silicone rubber-based membranes,12–18 poly(ether-block-amide) (PEBA)-based membranes,19,20 polyvinylidene fluoride (PVDF) membranes,21 polytetrafluoroethylene (PTFE) membranes,22 as well as MFI zeolite membranes.23 One of the great demands is to have membranes with a high butanol permeability and selectivity. However, there is a general trade-off between permeability and selectivity for state-of-the-art membranes.

Attempts to overcome the performance limitation are generally based on designing and controlling the materials chemistry or nanostructure to create more preferential adsorption and diffusion of the target permeating molecules.
Currently, incorporating nano-fillers into polymers to fabricate mixed matrix membranes (MMMs) has been proven to be an efficient approach to improve membrane permeability and selectivity.\textsuperscript{16,17,20–25} In addition to the commonly used zeolites,\textsuperscript{28–30} carbon molecular sieves (CMS)\textsuperscript{31} and metal–organic frameworks (MOFs),\textsuperscript{16,17,20,27} polyhedral oligomeric silsesquioxane (POSS) have been explored as nanoparticle fillers to fabricate MMMs in recent years.\textsuperscript{28–30,32} POSS is a type of molecular silica with a cage-like nanostructure that possesses an inner inorganic silicon and oxygen core (SiO\textsubscript{1,5})\textsubscript{n} and external organic substituents.\textsuperscript{33} The diverse functional groups and good compatibility with polymers make POSS a promising candidate for pervaporation,\textsuperscript{28–30} gas separation,\textsuperscript{30,32} as well as osmosis processes.\textsuperscript{35,36} Unlike common nanoparticles, POSS is very small (ca. 2 nm) and flexible, and it can be functionalized with various groups attached to the apex silicon atoms. Chung’s group has carried out lots of interesting work on POSS-derived MMMs.\textsuperscript{28,30,34–36} They demonstrated that POSS provided a high possibility of uniform dispersion in diverse polymer matrices even at the molecular level.\textsuperscript{8,28}

To date, how to effectively avoid inadequate particle dispersion and defective filler–polymer interfaces are regarded as the key points for achieving high-quality MMMs.\textsuperscript{37} Rational methods are critically needed to construct a desirable filler/polymer interface that provides sufficient adhesion between the filler and the polymer and maintains adequate mobility of the polymer chains. By precisely selecting the filler size and polymer structure, Merkel et al.\textsuperscript{38} proposed poly(4-methyl-2-pentyne)/fumed silica nano-composite membranes through the filler-induced disruption of the polymer chain packing to enhance both gas permeability and selectivity. The research group of Koros\textsuperscript{39} reported a deposition of inorganic nanostructures on zeolite crystals for MMMs fabrication. The adsorption and entanglement of polymer chains in the nano-whiskers on zeolite provided enhanced zeolite/polymer adhesion and yielded membranes with significantly improved separation performance. Jiang and co-workers\textsuperscript{40} took the synergy of the hydrogen bond, metal–organic coordination and π-complexation interactions between dopamine and polymer to reinforce polymer chain rigidity and facilitate the molecular transport in membranes. In addition, it has been reported that filler–polymer interactions play a critical role in determining the compatibility and dispersion of fillers in polymers, as well as the final structural, thermal, and mechanical properties of the nano-composites.\textsuperscript{39}

This work reports a facile strategy of creating molecular interactions between inorganic molecules and polymer chains to fabricate high-performance MMMs. Our idea aims to finely control the conformation and topology of polymer chains through appropriate intra-molecular and inter-molecular interactions resulting from the immobilization and movement of backbone and side chains induced by the incorporated inorganic phase. We demonstrated our finding here with the example of the polydimethylsiloxane (PDMS) membrane, a benchmark for organophilic pervaporation (e.g., bio-fuel recovery from dilute aqueous solution, VOCs removal), that has a relatively low separation performance and is still insufficient for practical applications.\textsuperscript{40} POSS was selected to be the inorganic filler for PDMS MMMs, because it can act as a robust inorganic molecule that provides good interfacial adhesions and favorable molecular interactions with PDMS polymer. The resulting tunable PDMS chain structures would enable fast-selective diffusion channels in MMMs for molecular transport. Thus, the separation performance of PDMS MMMs can be expected to fulfill breaking the trade-off limitation between permeability and selectivity. Molecular dynamic simulation and experimental characterizations, such as transmission electron microscopy, atomic force microscopy, and positron annihilation spectroscopy, were carried out to systematically study the membrane microstructures. Separation performance of the as-prepared POSS/PDMS MMMs was evaluated through the bio-butanol recovery from its aqueous solution by pervaporation.

**Experimental**

**Materials**

Methyl-POSS (C\textsubscript{4}H\textsubscript{12}O\textsubscript{3}Si\textsubscript{8}, OctaMethyl POSS\textsuperscript{®}, MS0830) nanoparticles (particle size: 200–300 nm) were supplied by Hybrid Plastics Inc., USA. PDMS (\(\nu,\nu\)-dihydroxypolydimethylsiloxane, average molecular weight: 6000) was purchased from Sigma Aldrich, as shown in Fig.1. Tetraethylorthosilicate (TEOS), n-heptane, dibutyltin dilaurate and n-butanol were obtained as analytical reagents from Sinopharm Chemical Reagent Co., Ltd, China. Deionized water was used in all experiments. Tubular ceramic substrates were supplied by the Membrane Science & Technology Research Center (MST), Nanjing Tech University. They are asymmetric ZrO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} membranes with an average pore size of 0.2 μm. Their length, outer diameter, and inner diameter were 62 mm, 12 mm, and 8 mm, respectively.

**Molecular dynamics simulation**

Molecular models were constructed using the Materials Studio software from Accelrys Incorporation. The model construction and calculation parameters are described as follows. In the amorphous cell, the PDMS monomer was selected to construct the PDMS membrane model. The number of the repeat units, chain numbers, and initial density of PDMS were set to 25, 4, and 0.9 g cm\textsuperscript{-3}, respectively.\textsuperscript{15,41,42} First, the energy minimization process with 3000 iterations was performed to optimize the geometric structure of the membrane model in Forcite. Then, 150 ps NPT (fixed atom number, system pressure, and

![Image](https://example.com/image.png)

**Fig. 1** Molecular structure of (a) octamethyl–POSS and (b) \(\nu\)-dihydroxyl-PDMS used in this work.
temperature) with a time step of 1 fs was performed for the MD simulation. The Nose algorithm (controlling the thermodynamic temperature and generate the correct statistical ensemble such that the probability of the occurrence of a certain configuration obeys the laws of statistical mechanics) was used to maintain the system temperature at 313 K, and the Q ratio was set as 0.001. The Berendsen algorithm (changing the pressure by altering the coordinates of the particles and the size of the unit cell in periodic boundary conditions) was used to maintain the system pressure at 0.001 GPa, and the decay constant was set to 0.5 ps. After the MD simulation of the PDMS model, a certain number of POSS molecules were introduced into the PDMS cell for the construction of POSS/PDMS MMMs models with various POSS content, as shown in Fig. 2. Then, the abovementioned same energy minimization process and NPT calculation were adopted to perform the MD simulation of POSS/PDMS MMM systems. The condensed-phase optimized molecular potential for atomistic simulation studies (COMPASS) force field was used to carry out all the model calculations.

A radial distribution function (RDF) was used to analyze the microstructures of PDMS and POSS/PDMS MMMs. This function counts the number of two-atom species within specific distances and is defined as follows:

$$g_{\alpha\beta}(r) = \frac{V_0 N_0}{N_\beta 4\pi r^2 \Delta r}$$  \hspace{1cm} (1)

where $V_0$ is the cell volume, $N_0$ is the total number of $\beta$ atoms, and $N_\beta (r)$ is the number of $\beta$ atoms found within a spherical shell with radius $r$ to $r + \Delta r$, which corresponds to $\alpha$ atoms.

Mean-squared displacement (MSD) was employed to analyze the molecular mobility of membrane, which can be obtained by the Einstein relationship as follows:

$$\text{MSD}(t) = \frac{1}{N} \sum_{i=1}^{N} \left[ r_i(t_0 + t) - r_i(t_0) \right]^2 = B + 6D_t t$$  \hspace{1cm} (2)

where $N$ is the total number of atoms, $r_i(t_0 + t)$ and $r_i(t_0)$ are the positions at time $t_0 + t$ and $t_0$, respectively, $B$ is a constant, and $D_t$ is a self-diffusion coefficient.

**Membrane preparation**

After drying at 120 °C in a vacuum oven overnight, a measured quantity of POSS particles was dispersed in $n$-heptane solution under stirring at room temperature for 4 h. Then, the PDMS polymer, TEOS (cross-linker), and dibutyltin dilaurate (catalyst) were added successively to the POSS/$n$-heptane suspension ($n$-heptane/PDMS/TEOS/dibutyltin dilaurate = 10:1:0.1:0.01, weight composition). The resulting POSS/PDMS casting solution was kept stirred for another 3–4 h. Subsequently, the casting solution was coated on the outer surface of the water-pretreated tubular ceramic support for 1 min through the dip-coating method. Following the removal of the solvent at room temperature for 24 h and then curing in the oven at 120 °C for another 12 h, the POSS/PDMS membrane was finally fabricated. The POSS content of these membranes was varied as 0, 10, 20, 30, and 40 wt%, which means the POSS/PDMS membrane contained 0, 10, 20, 30, and 40 wt% POSS nanoparticles, respectively.

**Characterizations**

The morphologies of POSS particles and POSS/PDMS membranes were examined by scanning electron microscopy (Quanta-2000, FEI), atomic force microscopy (DI-NS3a, Digital Instruments MultiMode), and transmission electron microscopy (JEM-2010, UHR). For TEM characterization, membrane samples were fixed in epoxy and cut into slices by the technology of ultracryotomy (Leica EM UC7–FC7) at −160 °C with the speed of 1 mm s$^{-1}$. The ultrathin membrane samples with the thickness of 40–50 nm were then transferred to carbon-coated copper grids before observation. Thermal properties were determined with a differential scanning calorimeter (DSC, Q2000, TA Instruments) with a nitrogen flow rate of 100 mL min$^{-1}$ and a temperature rate of 10 °C min$^{-1}$. IR spectra were recorded using a spectrophotometer (AVATAR-FT-IR-360, Thermo Nicolet) in the range of 4000–400 cm$^{-1}$. 32 scans were accumulated with a resolution of 4 cm$^{-1}$ for each spectrum. The membrane crystal structures were obtained with an X-ray diffractometer (XRD, D8-advance, Bruker) using Cu K$\alpha$ radiation, in the range of 5–40° with an increment of 0.05° at room temperature. The Young’s modulus of the membranes was obtained using a dynamic mechanical analyzer (DMA, DMA-e7, Perkin-Elmer) under ambient conditions. Adsorption isotherms for $n$-butanol and water with POSS particles were obtained using an Intelligent Gravimetric Analyzer (IGA, IGA-100, Hiden analytical). The POSS particles were activated by heating to 100 °C and then tested at 40 °C by accurately controlling the pressure of vapour (water and $n$-butanol). The transient and equilibrium weight changes of the samples were measured and recorded for analysis. The static contact angles of the membranes were measured by the sessile drop method using the contact angles measurement system (DSA100, Kruss) at room temperature. The average contact angle was obtained by measuring the same sample at three different sites.

The pore radius of POSS and free volume sizes in the membranes were characterized by positron annihilation lifetime spectroscopy (PALS) at the R&D Center for Membrane Technology in Chung Yuan University in Taiwan.

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**Fig. 2** POSS/PDMS MMMs cells in MD simulation; POSS content: (a) 0 wt%, (b) 10 wt%, (c) 20 wt%, (d) 30 wt%, and (e) 40 wt%.
conventional fast-fast coincidence spectrometer with a time resolution of 250 ps was used. A radioactive source of 22 Na (0.74 MBq), sealed in between 12 μm thick Kapton films, was sandwiched in two stacks of membrane samples that consisted of several layers of free-standing POSS/PDMS MMMs. Each stack of sample had a total thickness of 1 mm. Positron annihilation lifetimes were recorded using a fast–fast coincidence timing system. A time-to-amplitude converter was used to convert lifetimes and to store timing signals in a multi-channel analyzer (Ortec System). Two million counts were collected, and the lifetime distribution was determined using the PATFIT computer program and the maximum entropy for lifetime analysis (MELT) program, which is based on the Bayesian theorem and is implemented in MATLAB software. The mean free volume radius $R$ can be related to $o$-Ps lifetime ($\tau_j$) using a semi-empirical equation based on a spherical infinite potential well model:

$$\tau_j = \frac{1}{2} \left[ 1 - \frac{R_0}{R} + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R_0} \right) \right]^{-1}$$

where $\tau_j$ ($o$-Ps lifetime, $j = 3$ or 4) and $R$ (free-volume hole radius) are expressed in ns and $10^{-10}$ m (Å), respectively. $R_0$ is equal to $R + \Delta R$, where $\Delta R$ is a fitted empirical electron layer thickness $= 1.66$ Å determined by fitting well-known cavities.

Pervaporation test

The pervaporation experiment was conducted using a homemade apparatus, as described in our previous work. The membrane was sealed in a stainless steel PV cell with an effective membrane region of 15.80 cm$^2$. The feed solution was maintained at a preset temperature and circulated from the feed tank through the membrane cell at a flow rate of 15 L h$^{-1}$. During experiments, $n$-butanol was added to maintain a constant feed concentration of 1 wt%. The vapor permeate was collected in a liquid nitrogen trap. The permeate pressure was below 400 Pa during the collections. $n$-Butanol concentrations were determined with gas chromatography (GC-2014, SHIMADZU, Japan) equipped with a thermal conductivity detector (TCD) using a Porapak Q packed column and helium (He) as carrier gas. $i$-Butanol was used as an internal standard. If the permeate separated into two phases, the permeate sample was diluted with deionized water to obtain a single phase prior to injection. To ensure reproducibility, all experimental results were repeated at least three times; the errors were less than 5%.

The PV performance of a membrane is usually expressed in terms of the permeate flux and separation factor. Because the permeate flux is dependent on the operating conditions, normalizing the permeate flux with respect to the driving force will be useful to further understand the permeate-specific intrinsic membrane properties changed by the addition of POSS particles in the PDMS membrane. This intrinsic membrane properties are permeability, $P_i$, and selectivity, $\alpha_i$, which are defined based on the solution–diffusion mechanism:

$$P_i = \frac{J_i \times l}{P_{i,\text{feed}} - \alpha_i \times P_{\text{permeate}}}$$

where $J_i$ is the partial permeate flux of component $i$, $l$ is the membrane thickness, $P_{i,\text{feed}}$ is the equilibrium partial vapor pressure of $i$ in the feed, $n_{i,\text{permeate}}$ is the mole fraction of $i$ in the permeate, and $P_{\text{permeate}}$ is the permeate pressure; $P_{\text{BOH}}$ and $P_{H_2O}$ are the permeability of $n$-butanol and water, respectively.

Results and discussion

Polymer chain conformation

Molecular diffusion in a dense polymeric membrane is determined mainly by the polymer chain conformation. As for mixed matrix membranes, the incorporation of inorganic fillers would affect the packing and mobility of the polymer chains. Thus, the effect of incorporating POSS on the PDMS chain conformation was studied first using both the MD simulation technique and experimental characterizations.

The packing of polymer chains could be studied using RDF analyses in MD simulation, which entails intramolecular and intermolecular behavior of the polymer chains. The RDF spectra could indicate the probability density of atoms found at a specific distance. Generally, a higher peak intensity is related to the better ordering of atoms or larger molecular interactions in the molecular model. In the MD simulation process, PDMS chains were firstly selected from the POSS/PDMS MMMs cell, and then the Si and O atoms on the PDMS chains were selected in order to be distinguished from these atoms on POSS molecules. The calculated normalized RDF curves of Si and O atoms on PDMS chains are shown in Fig. 3. Peaks that appeared at different positions correspond to different distances of Si and O atom locations in the PDMS structures. For each PDMS membrane, there are three sharp peaks in the short-distance region (0–5 Å) of the RDF curve (Fig. 3a), which are attributed to

![Fig. 3 RDF curves of Si and O atoms on PDMS chains from POSS/PDMS MMMs cells; POSS content: (a) 0 wt%, (b) 10 wt%, (c) 20 wt%, (d) 30 wt%, and (e) 40 wt%.](image-url)
the bonding distance of Si–O, Si–Si, and O–O atom pairs on PDMS chains. They reflect the intra-molecular packing and interaction in the PDMS membrane. Whereas the two broad peaks in the long-distance region (>5 Å) result from the non-bonding distance of Si and O atoms (Fig. 3b), which suggest the inter-molecular packing and interaction of the polymer chains in PDMS membrane. It is found from the MD simulation that with the increase in the POSS content of the PDMS MMMs, the RDF peak intensities increase gradually in the short-distance region, whereas they are kept almost constant in the long-distance region. These results indicate that the intra-molecular interaction of PDMS chains was promoted by the POSS incorporation, which made the packing of each PDMS chain more compact. It would lead to a smaller free volume size in the PDMS membrane. However, the inter-molecular packing and interaction of the PDMS chains were nearly not affected by the introduction of POSS. It may be attributed to the very flexible backbone of PDMS chain, as well as the good compatibility between methyl-POSS and PDMS.

Furthermore, the MSD calculation of MD simulation could be adopted to investigate the mobility of polymers and inorganic fillers. In this work, MSD and self-diffusion coefficients \(D_c\) of Si and O atoms in the PDMS chains and POSS molecules were calculated to study the molecular mobility of PDMS and POSS in the POSS/PDMS MMMs. In general, a larger slope or displacement in the MSD diagram indicates a higher molecular mobility. As shown in Fig. 4a, incorporating POSS into the PDMS polymer leads to a significant advance in the mobility of PDMS backbone chains, which is further linearly improved by increasing the POSS content. E.g., \(D_c\) in PDMS MMMs filled with 40 wt% POSS is \(0.267 \times 10^{-10}\) m² s⁻¹, which is ca. fourfold higher than that in the pristine PDMS membrane \((0.071 \times 10^{-10}\) m² s⁻¹). The slopes were not very stable at the beginning and the end of the simulation process as the model was under unsteady state. Similar phenomena have been observed in previous studies that related to the POSS/polymer composite system. Likewise, it is found in Fig. 4b that the mobility of POSS molecules (i.e., relative motion of POSS molecules in the polymeric matrix) in the PDMS MMMs is also enhanced with the POSS content. A reasonable explanation for these phenomena is as follows: with the induction of inter-attractions of POSS molecules caused by electrostatic and van der Waals forces, the POSS molecules are prone to get closer, which increases their mobility. Moreover, in the POSS/PDMS MMMs, the abundant molecular interactions between POSS and PDMS would cause the adsorption of POSS molecules on the PDMS chains. The accelerating movement of POSS eventually improved the molecular mobility of PDMS. The advancement of chain mobility would create more cavities (free volumes) in the POSS-PDMS MMMs.

The MD simulation demonstrated that the molecular interactions in the POSS/PDMS MMMs were the major driving force for the evolution of the PDMS chain conformation. In addition, the packing and mobility behavior of the PDMS chains can be experimentally analyzed by DSC measurement; the result is shown in Fig. 5. By increasing the POSS content from 0 to 40 wt% in the MMMs, both the glass transition temperature \(T_g\) and the crystallinity \(X_c\) of the PDMS membrane are decreased linearly from −116.5 °C to −121.9 °C and from 61.6% to 34.9%, respectively (Fig. 5a); moreover, the heat of cold crystallization \(\Delta H_c\) and the heat of fusion \(\Delta H_f\) show a linear decline (Fig. 5b). Ideally, the crystallinity of the PDMS membrane is related only to the PDMS content if the PDMS chains are not affected by external conditions (e.g., filler incorporation, polymer blending). In view of this, theoretical values of \(X_c\) in MMMs were calibrated based on the PDMS weight percent, and the result is given by the dashed line in Fig. 5a. Thus, the influence of incorporating POSS fillers on the crystallinity, cold crystallization, and melting behavior of the PDMS membrane are reflected by the value difference between the solid line and the dash line. The result suggests that larger amounts of amorphous domains were produced in the PDMS membrane with the introduction of more POSS fillers, and thus the membrane crystallinity was reduced. The incorporation of POSS nanoparticles could disrupt the crystallization process of PDMS polymer such that smaller crystallite sizes are achieved as well as changing the nucleation process from heterogeneous to homogeneous where the Avrami coefficient approaches one. The resultant effect decreased the crystallization rate and extent of PDMS membrane, and thus there would be more space available for the PDMS chain mobility. The abovementioned

![Fig. 4 MSD of Si and O atoms on (a) PDMS chains (inserted diagram gives the slopes of linear fitting of MSD vs. time during 30 to 120 ps) and (b) POSS molecules.](image-url)
and the hydroxyl-terminated PDMS chain. Nevertheless, the chemical groups of POSS show a coincident redshift ($\delta$(CH$_3$); from 1270 to 1257 cm$^{-1}$; $r$(Si–O–Si): from 1115 to 1082 cm$^{-1}$; $r$(Si–C): from 776 to 767 cm$^{-1}$) in the POSS/PDMS MMMs. Similar results are also found in FTIR characterization (Fig. S1 in ESI†). It could be attributed to two possibilities: the combination effect of the characteristic peaks of PDMS, and the presence of molecular interactions between Si–CH$_3$ and Si–O–Si groups on POSS and PDMS. Because both methyl-POSS and PDMS consist of Si–CH$_3$ and Si–O–Si groups, it is difficult to confirm the primary cause just from the IR analysis.

Furthermore, XRD was used to analyze the crystal structures of POSS, PDMS, and MMMs. As shown in Fig. 6b, the characteristic peak at 12° of the cross-linked PDMS can also be found in the XRD pattern of MMMs. It indicates that the introduction of POSS fillers into the PDMS matrix has a slight influence on the original d-spacing (7.38 Å) of the PDMS tetragonal crystal lattice. This result is well in line with the RDF analysis of MD simulation, in which the inter-molecular interaction and packing density in the non-bonding region (>5 Å) almost did not change with the POSS incorporation. However, the crystalline POSS was slightly affected by the PDMS matrix, resulting in a 0.1–0.2° right shifting of the characteristic peaks and variations in the peak intensity of the POSS crystals in the XRD pattern of MMMs.

In addition, the Young’s modulus of the membranes was determined using DMA, and the results are shown in Fig. S2 in the ESI†. Because of the good mechanical strength of the POSS particles, as well as the formed interfacial interactions between POSS and PDMS, the tensile deformation of PDMS chains was effectively suppressed by incorporating POSS into the PDMS matrix. Thus, Young’s modulus of the membrane is greatly increased with the POSS loading. The improvement in mechanical strength is conducive to the installation of the membrane module and the long-term stability of MMMs.

**Morphology**

As reported by a number of studies, favorable molecular interactions could be beneficial for the dispersion of POSS in PDMS and the interfacial morphology of POSS–PDMS. Fig. 7a shows the casting solution and a dense POSS/PDMS MMM. It can be clearly observed that POSS particles are uniformly dispersed in the PDMS solution, and the resulting dense MMM also displays a homogeneous appearance. To improve the membrane flux for practical applications, the POSS/PDMS solution was coated on the surface of tubular porous ceramic substrates to form ceramic-supported composite polymeric membranes with a thin active layer for separation, as reported in our previous work. A typical cross-sectional SEM image of the as-prepared ceramic-supported POSS/PDMS MMM is given in Fig. 7b. The POSS/PDMS separation layer, firmly deposited on the ceramic substrate, is homogeneous and defect-free with a thickness of ca. 9 μm. From the enlarged cross-sectional SEM image (Fig. S3a in ESI†), it is more clear to find that the POSS particles are uniformly dispersed in the PDMS matrix. The fine structure of the interfacial morphology of POSS/PDMS was observed with
TEM, as displayed in Fig. 7c and d. Although both POSS and PDMS consist of Si–O–Si and –CH₃ groups, differences in molecular structures and crystallinity cause light and shade variations under the TEM characterization. The dark area is related to the POSS dispersed phase, and the light area corresponds to the PDMS continuous phase. As seen in Fig. 7c, the POSS particles are found to be tightly embedded in the PDMS domain without interfacial voids. This widespread morphology is further confirmed by a lower magnification of TEM image of Fig. S3b in the ESI.

Moreover, the enlarged image in Fig. 7d distinctly reveals good compatibility between POSS and PDMS phases. PDMS chains are well adsorbed on the POSS surface with an interfacial thickness of ca. 1–2 nm, corresponding to the length of 6–12 PDMS repeat units. By integrating the results of MD simulation, it can be reasonably inferred that this well-defined filler-polymer interfacial morphology could play two roles in determining the microstructures of MMMs: one is improving the intra-molecular interaction of segmental PDMS chains in the interface, while maintaining the flexibility of the main PDMS chains; the other is utilizing the interactions (i.e., electrostatic and van der Waals forces) between POSS molecules that adsorbed on the PDMS chain to promote the molecular mobility of the PDMS chains.

The MMMs surface morphologies were characterized by SEM and AFM, and the results are given in Fig. 8. As shown in Fig. 8a, in contrast to the smooth surface of the pristine PDMS membrane, uniform concave-convex surfaces of the POSS/PDMS MMMs are found, and the area and numbers of these sunken and bulges are increased with the POSS content. The phenomena can be seen more clearly in the 2D and 3D surface AFM images in Fig. 8b and c. By incorporating POSS fillers, the even PDMS membrane surface become wrinkled, the degree of which is magnified with the rise of the POSS loading in the MMMs. As a consequence, the membrane roughness increases linearly, i.e. the $R_q$ (mean square roughness) is enlarged from 17.4 nm to 571 nm for the MMMs filled with 40 wt% POSS. Compared with the morphology of POSS particles (Fig. S4 in ESI†), it can be inferred that no POSS particles are found in the SEM surface images (Fig. 8a). Moreover, according to the AFM phase images (Fig. 8d), only the PDMS phase was observed in the membrane surface. Thus, we speculate that the generation of the concave-convex and plicated surface of the MMMs results mainly from the variation in internal stress during the solvent volatilization of the membrane fabrication. The stress variation is probably due to the enhancement of the PDMS chain mobility, induced by the molecular interactions of POSS adsorbed on the PDMS chain.

**Free volume distribution**

The abovementioned evolution of polymer chain conformation and microstructure induced by molecular interactions would also have a significant influence on the free volume elements (i.e., cavities or holes) of MMMs. Molecular diffusion in dense polymeric membranes is strongly dependent on free volumes in polymer, which provide diffusion channels with low transport resistance. Free volumes are created by inefficient chain packing and transient gaps generated by thermally induced chain mobility.⁶⁴ Lee and co-workers demonstrated that free volume topologies of glass polymers could be systematically tailored by thermally driven segment rearrangement.⁵ Our previous work also found that centrifugal force is effective to optimize the free volumes by arrangement and orientation of molecular chains in polyamide membranes.⁶⁵

In recent years, the positron annihilation spectroscopy (PAS) technique has been proven to be an advanced and powerful tool in analyzing the free volume size and distribution for various polymers for molecular separations.⁶,₆⁸ PAS results of POSS/
POSS/MMSMs are shown in Fig. S3 (ESI†), Table S1 (ESI†) and Fig. 9 and 10. The positron lifetimes \( \tau_3 \) and \( \tau_4 \) are due to o-Ps annihilation. In polymeric materials, the annihilation lifetime is in the order of 1–5 ns, which results from the so-called pickoff annihilation with electrons in molecules. According to eqn (3), the positron lifetime can be used to calculate the mean free volume radius \( R \). Table S1† shows that the positron annihilation time in the PDMS membrane exhibits a bimodal distribution \( \tau_3 = 1.241 \text{ ns} \) and \( \tau_4 = 3.135 \text{ ns} \), corresponding to a free volume size distribution at two ranges, with an average small radius of \( R_3 = 0.202 \text{ nm} \) and large radius of \( R_4 = 0.373 \text{ nm} \). Similar results for PDMS membranes in the previous studies were found. A POSS molecule with a flexible cage structure also owns diffusion channels for molecular transport; its free volume radius \( R_4 \) is 0.362 nm. It is noted that the o-Ps annihilation intensity \( I_1 \) of POSS (4.99%) is considerably lower than that of PDMS, which is probably due to PALS data being strongly dependent on the physicochemical property of the material. Although they have similar chemical elements and groups (e.g., Si–O–Si, –CH₃), their structures are considerably different. POSS owns a cage-like structure made by single Si–O–Si unit, whereas PDMS possesses a cross-linked network consisted of several Si–O–O repeat units. This would lead to the different free volume elements, namely, lifetime and intensity of positron annihilation. Most positron annihilation in POSS may be attributed to short lifetimes \( \tau_1, \tau_2 \).

We found in the PAS analysis of POSS/PDMS MMMs that the addition of POSS to PDMS brought regular variations in the membrane free volumes. As presented in Table S1 (ESI†) and in Fig. 10, with an advance of the POSS loading, the small free volume elements decline progressively with \( R_3 \) moving to a smaller size, whereas the large volume elements gradually increase with \( R_4 \) moving to larger size. Moreover, the small free volume intensity \( I_3 \) increases and the large free volume intensity \( I_4 \) decreases, maybe owing to the partial pore blockage of POSS by PDMS chains. As shown in Fig. 9, there are linear relations both for \( R_3 \) and \( R_4 \) that change with the POSS content in the MMMs. As for the MMMs with 40 wt% POSS, \( R_3 \) is reduced to 0.167 nm and \( R_4 \) is increased to 0.392 nm. Although the intrinsic free volume radius of POSS is smaller than that of the pristine PDMS membrane, \( R_4 \) for the PDMS membrane was greatly enlarged after the incorporation of POSS (i.e., \( R_4 \) increases from 0.373 nm to 0.392 nm). This result suggests that free volumes in MMMs could be finely tuned by molecular interactions with two possible aspects: (i) increase in the PDMS intramolecular packing reduces the small free volumes \( R_3 \) and (ii) improvement in the PDMS chain mobility enhances the large free volumes \( R_4 \).

It is demonstrated that our proposed simple physical incorporation of nano-sized POSS could realize the true molecular-scale regulation of the polymer chain packing and mobility, because the variation in the free volume radius is just ca. 0.02–0.035 nm. For the molecular-level separation occurrence in dense polymeric membranes, only less than a 0.02 nm difference in the penetrant size is enough to yield substantial differences in the flux through polymeric membranes. For instance, although the difference in the molecular kinetic diameters of \( \text{O}_2 \) and \( \text{N}_2 \) is only 0.018 nm, the permeance ratio of \( \text{O}_2 \) and \( \text{N}_2 \) (selectivity) could be as high as 8 in strongly size-sieving polymeric membranes.

The abovementioned special characteristics of tunable free volumes in POSS/PDMS MMMs are profitable for selective-permeating larger-sized molecules. This is because the shrunken small free volumes hinder the smaller-sized molecule diffusion, whereas the extended large free volumes facilitate the larger-sized molecule diffusion. The effect of the polymer free volume on the molecular diffusion coefficient is usually modeled by the statistical mechanics description of diffusion in a liquid of hard spheres, proposed by Cohen and Turnbull as follows:

\[
D = A \exp \left( -\frac{\gamma V^*}{V_T} \right)
\]

where \( A \) is a pre-exponential factor that is weakly dependent on temperature, \( \gamma \) an overlap factor introduced to avoid double-counting of free volume elements, \( V^* \) the minimum free volume.
size that can accommodate a penetrant molecule (and is closely related to the penetrant size), and $V_i$ the average free volume in the polymer accessible to penetrants for transport. Based on the solution-diffusion model, the diffusion selectivity $\alpha_{D_{ij}}$ can be expressed as give below:

$$\alpha_{D_{ij}} = \frac{D_i}{D_j} \times \exp \left( \frac{\gamma_j V_j^* - \gamma_i V_i^*}{V_i} \right)$$  \hspace{1cm} (7)

where $i$ and $j$ represents penetrant $i$ and $j$, respectively.

According to eqn (6), with the increase in free volumes in polymeric membranes, the diffusion coefficient of penetrant increases and then the membrane permeability is enhanced. Based on eqn (7), if the molecular size of penetrant $j$ is larger than that of penetrant $i$, generally $\gamma_j V_j^* > \gamma_i V_i^*$, resulting in $\alpha_{D_{ij}} > 1$, namely, smaller-sized molecules are preferentially diffused in the membrane. However, $\alpha_{D_{ij}}$ declines with the enlargement of $V_i$ and finally approaches 1. That is to say, enlarging the membrane free volumes would be in favor of weakening the diffusion selectivity for smaller-sized molecules (i.e., size-sieving ability) to facilitate the selective diffusion of larger-sized molecules. For instance, the recovery of butanol from aqueous solution through polymeric membranes is a typical application of the selective permeation of larger-sized molecules (butanol) over smaller-sized molecules (water).

![Fig. 11](a) Contact angles of water and $n$-butanol on POSS/PDMS MMMS surfaces; (b) adsorption isotherms of water and $n$-butanol on POSS particles at 40 °C.

**Sorption property**

In addition to the diffusion process, the separation performance is also dependent on the sorption process according to the solution-diffusion theory. Therefore, the surface sorption property of the POSS/PDMS MMMSs was evaluated by the contact angle test, using water and butanol as the contacting liquids. Because of the intrinsic hydrophobicity and organophilicity, the PDMS MMMSs general show water contact angles >90° and butanol contact angles <90°, as displayed in Fig. 11a. Thus, most PDMS-based membranes exhibited high sorption selectivity for butanol over water, as described in the previous studies. With incorporating POSS particles, the water contact angles are decreased a lot, whereas the butanol contact angles have some fluctuation. These results suggest that the hydrophobicity of the POSS/PDMS MMMSs was lower than that of the pristine PDMS membrane.

To further verify the role POSS played in the sorption process, the adsorption isotherm of $n$-butanol and water on POSS particles were measured by varying the vapor pressure from 0 to 26 kPa at 40 °C. As shown in Fig. 11b, the uptake of water is higher than that of butanol, indicating a water-selective sorption property of POSS filler. Moreover, the adsorbed amounts of both water and butanol are considerably lower than that of the porous materials such as silicalite-1 zeolite and ZIF-8 MOFs. This means that these molecules could hardly enter into the POSS cage and POSS fillers in the PDMS MMMSs would have little contribution to the sorption process when separating alcohol–water mixtures.

**Separation performance**

The as-prepared POSS/PDMS MMMSs were applied to pervaporation recovery of $n$-butanol from a 1 wt% aqueous solution at 40 °C. As shown in Fig. 12, the separation performance of the PDMS membrane is greatly improved by the POSS incorporation: both the butanol permeability and selectivity increase simultaneously with the POSS content. Particularly for the PDMS MMMSs with 40 wt% POSS, the permeability and
selectivity are 3.8- and 2.2-times higher, respectively, compared with the pristine PDMS membrane. From the SEM and TEM characterizations in Fig. 7, there are no visible interfacial defects in our POSS/PDMS MMMs. Thus it is reasonable to speculate that the rational construction of molecular interactions between POSS and PDMS could highly reduce the interfacial defects, which are generally observed in conventional zeolite/polymer MMMs. More importantly, the free volumes in the PDMS membrane could be finely regulated for the fast selective permeation of larger-sized molecules.

The kinetic diameters of n-butanol (0.505 nm) and water (0.296 nm) are just located in the ranges of small free volume diameters (2 × R1 = 0.334–0.404 nm) and large free volume diameters (2 × R4 = 0.746–0.784 nm), respectively, of the POSS/PDMS membranes. Their relationships are marked in Fig. 11. The schematic of the effects of the POSS incorporation on the membrane free volume variations and the separation of butanol/water is displayed in Fig. 13.

In the POSS/PDMS MMMs, the decrease in small free volume (R1) can effectively hinder the water diffusion, and the increase in large free volume (R4) is good for promoting the butanol diffusion. According to eqn (9), the R4 enlargement is also beneficial for improving the diffusion selectivity for butanol. Although there is a possibility of butanol molecules diffusing through the small free volume (R1) as it gets swollen by the feed, the large free volumes are considered as the main diffusion pathways for butanol molecules. Therefore, POSS/PDMS MMMs could exhibit both high butanol permeability and selectivity, breaking the existing trade-off between permeability and selectivity in polymeric membranes.

The reported separation performance of organophilic membranes for the butanol recovery from aqueous solutions is displayed in Fig. 14 and Table S1 (ESI†). To eliminate the effect of operating conditions (feed temperature and composition) on the separation performance, the membrane flux and separation factor were normalized to permeance and selectivity, respectively. Then, intrinsic membrane properties could be fairly compared. Because some of the reported membrane thicknesses are unknown, permeance was used for comparison (1 GPU = 1 × 10−6 cm3 (STP) cm−2 s−1 cmHg−1). It can be found that the POSS/PDMS MMM exhibits the highest butanol/water selectivity, as well as a very high butanol permeance. The performance of the POSS/PDMS membrane clearly transcends the upper bound of the state-of-the-art organophilic pervaporation membranes.

**Conclusions**

In summary, we have designed and fabricated high-performance POSS/PDMS MMMs with tunable free volumes driven by favorable filler–polymer molecular interactions. Molecular dynamics simulations indicated that the POSS incorporation enhanced the PDMS chain intra-molecular interactions and, at the same time, improved the PDMS chain mobility. Thus, in the PDMS MMMs, small free volumes were reduced and large free volumes increased. The feature of tunable free volumes was beneficial for the preferential permeation of large-sized molecules through the polymeric membrane. In the bio-butanol recovery from aqueous solutions, the obtained POSS/PDMS MMMs improved both the permeability and the selectivity of the pristine PDMS membrane by 3.8- and 2.2-times, respectively, which overcame the permeability-selectivity trade-off limitation characteristic of polymeric membranes. Moreover, the separation performance of the MMMs clearly transcended the upper bound of the state-of-the-art organophilic pervaporation membranes. The above-mentioned characteristics of the POSS/PDMS MMMs obtained through molecular-interaction-driven tuning of free volumes make them great promising candidates for practical applications in bio-fuel production. Moreover, the proposed approach based on rationally creating molecular interactions can be expected to have broad applicability in fabricating high-quality MMMs for molecular separations.
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Notes and references