Enhanced Gas Separation Properties by Using Nanostructured PES-Zeolite 4A Mixed Matrix Membranes

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ABSTRACT: The polymer–zeolite mixed matrix membranes were fabricated by incorporating nanosized or microsized zeolite 4A into polyethersulfone. A comparison of zeolite 4A nanocrystals and microcrystals was made by using SEM, XRD, N_2 adsorption–desorption measurements. Zeolite particles were well-distributed in the polymer phase, as reflected by the SEM images. The effects of the zeolite 4A particle size on the gas permeation performance were studied. Experimental results demonstrate that mixed matrix membranes exhibit decreased gas permeabilities due to the barrier effect of zeolite particles. The obtained permselectivity is greatly enhanced for He/N_2, H_2/N_2, He/CO_2, and H_2/CO_2 gas pairs, especially for nanosized zeolite 4A mixed matrix membranes. The gas permeation performance difference is observed between the nanostructured and microstructured membranes, which is attributed to a combined effect of different zeolite composition and different particle size. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3800–3805, 2006

Key words: mixed matrix membrane; gas permeation; polyethersulfone; zeolite 4A; nanostructure

INTRODUCTION

Zeolite materials have attracted considerable attention in recent years in the field of hybrid organic–inorganic mixed matrix membranes (MMMs) due to their pronounced molecular-sieving properties. Generally, MMMs comprise a dispersion of molecular sieve entities in a polymer matrix phase. The incorporation of two different materials appears promising by combining the easy processability of polymers with the superior gas separation properties of rigid molecular sieves.[1–3] However, the overall properties of formed composites are determined not only by those of the individual components, but also mainly by the organic–inorganic interfacial properties.[4–7]

Nanostructured composite membranes, formed by incorporating nanosized zeolite particles into a properly selected polymer, exhibit much better gas separation properties as compared to conventional composites, due to their unique phase morphology and high surface area.[8] In their work, the authors have applied nanosized zeolite 4A with an average particle size of 100 nm and have successfully fabricated the homogeneous zeolite 4A/polysulfone membranes. Their experimental results show that the O_2/N_2 selectivity and the O_2 permeability of the membranes are both enhanced considerably by 30% and 38%, respectively. The simultaneous increases of both the permeability and the selectivity are very attractive to potential industrial applications. Similar observations have also been reported by Süer et al. for the microsized zeolite 4A/polyethersulfone (PES) membranes.[9] However, their results show that for these microsized zeolite 4A/PES membranes both enhancements obtained are rather small (less than 10%), probably because of the relatively poor contact between the polymer and the zeolite phases. One may note that these two experimental studies have been performed at a room temperature of 25°C, lower than the commonly used temperature of 35°C. Low-testing temperature usually leads to low-gas permeability and high selectivity. Thus, the selectivity improvement at 35°C for those membranes reported[8,9] is uncertain but somewhat limited, when compared with that found in the literature.[10] As we know, for neat polymer membranes, the permeability and the selectivity are generally two competitive properties, i.e., favoring the permeability must compromise the selectivity or vice versa.[11] Therefore, it is interesting to investigate the MMMs at 35°C for better understanding the effects of the added zeolites.

In view of the pronounced effect of nanosized zeolites,[8] we attempt to fabricate nanostructured MMMs by employing self-synthesized zeolite 4A nanoparticles and PES. The apparently nanosized zeolite par-

ticles are expected to distribute well in the polymer matrix phase. For comparison, commercial microsized zeolite 4A has also been employed. Zeolite 4A was selected, since it has a pore size of 4Å,[12] close to the molecular size of the species of our interest. In this way, we aim to enhance the gas separation properties of the PES membranes.

EXPERIMENTAL

Materials

Nanosized zeolite A was synthesized by using a molar batch composition of 1.0 Al_2O_3: 6.0 SiO_2:14.0 tetramethylammonium hydroxide (TMAOH): 0.16 Na_2O: 345 H_2O. Based on the formula given, 4.25 g $Al_2(SO_4)_3·18H_2O$ was added into a 250-mL polypropylene bottle, where a clear solution was obtained with 2 mL 1M aqueous NaOH, 32 mL aqueous TMAOH (25 wt %), and 10 mL deionized water. Ludox TMA colloidal silica (34 wt %) was added once the solution became clear under agitation. The resultant mixture, tightly capped in the polypropylene bottle, was stirred for 2 days at room temperature and then heated to 100°C in a silicon oil bath to begin a 2-day crystallization process. The product was thoroughly washed with deionized water and was then centrifuged at 40,000g for 30 min per time till a suspension with ph less than 8.5 was got. The template removal was performed by using a recently reported polymer-networking method.[8] This method has been claimed to be able to produce highly dispersible zeolites; therefore, it has been adopted here with a slight modification. The polymer-networked zeolite particles were directly calcinated at 500°C for 6 h at a scanning rate of 5°C/min to burn off the template and the polymer in air. The nanosized zeolite 4A thus obtained was denoted as N-A.

Polyethersulfone (PES) was purchased from Amoco Performance Products, GA (~15,000 Da). The dope solvent used for preparing mixed matrix membranes (MMMs) was N-methyl-2-pyrrolidone (Merck, Germany; >99%). Dichloromethane was purchased from Merck, Germany (>99.8%). The commercial microsized zeolite 4A was supplied by Sigma–Aldrich, USA, and is denoted as M-A.

Membrane preparation

The zeolite/PES MMMs were fabricated by using the solution casting method. The procedure of casting films is similar to that in the work of Mahajan,[7] except the annealing treatment. The membrane annealing was carried out by increasing the temperature from the current 200 to 250°C at a rate of 0.5°C per minute, then holding the film overnight at 250°C under vacuum, and finally taking the film out of the oven immediately and quenching it in the air. Two MMMs, i.e., PES-N-A membrane and PES-M-A membrane, thus were made using different-sized zeolite A. The zeolite loading is reported to strongly affect the structure and properties of MMMs.[9,13] Low zeolite loading (<10 wt %) could not obviously affect membrane properties, while high loading (>30 wt %) led to poor zeolite–polymer contact and decreased separation selectivity. Thus, the zeolite loading used here was 20 wt %. For a comparison, the neat PES dense flat-sheet membrane was prepared by using a 2 wt % polymer solution that was cast on a glass wafer followed by gradually evaporating the solvent dichloromethane at room temperature.

Characterization methods

Powdery X-ray diffraction (Shimadzu XRD-6000 diffractometer using Cu Kα radiation) was used to confirm zeolite A structures. Simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) measurement (Shimadzu, DTG-60) of the as-synthesized nanoparticles was carried out at 10°C/min in air and was used to observe water content and the decomposition of TMA in the zeolite 4A framework. The sample was recovered from suspension and dried at 90°C overnight before thermal analysis. Nitrogen adsorption–desorption measurements were carried out at 77 K on a Quantachrome Autosorb-1 instrument to determine the Brunaer–Emmett–Teller (BET) surface area and the pore volume. The particle size of zeolite nanocrystals and microcrystals was examined with a scanning electron microscope (SEM, JEOL JSM-6700F). Elemental dispersive spectroscopic analyses of nanocrystals and microcrystals of zeolite 4A were carried out with a simultaneous module on SEM JEOL JSM-6700F.

The membrane gas permeation was measured using variable-pressure constant-volume method with a precalibrated permeation cell described elsewhere.[14] The measurements were all performed at 35°C. The operational pressure used was 2 atm for He and H_2 gases, and 10 atm for the other gases, respectively. The selection of 2 atm for the former two gases was based on two aspects: (1) the container used here had a relatively low volume for He and H_2; (2) He and H_2 are the two gases possessing very high permeate rate and are usually independent to the pressure.[11]

RESULTS AND DISCUSSION

Zeolite 4A particles

The X-ray diffraction patterns of synthesized zeolites as well as commercial zeolite 4A are shown in Figure 1. These identical XRD spectra confirmed that as-synthesized zeolites were pure zeolite 4A structure and
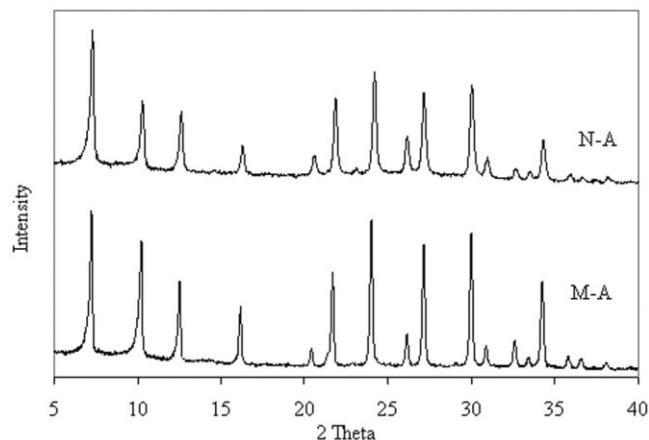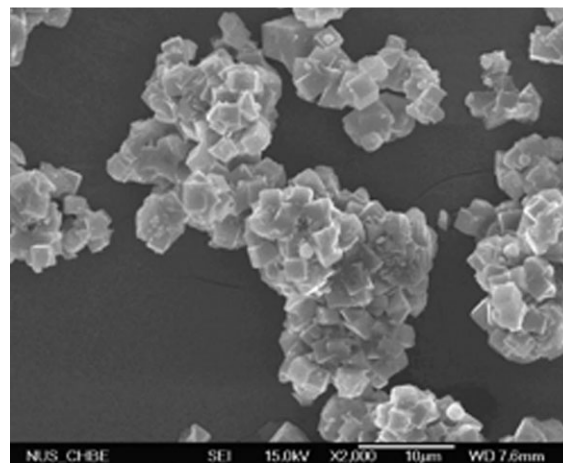
Figure 1 XRD patterns of zeolite A nanocrystals (N-A) and microcrystals (M-A).

Figure 2 SEM images of synthesized zeolite A nanocrystals and commercial microcrystals.

that the polymer introduced to form a polymer network has no effect on the zeolite 4A crystal structure. The SEM images of synthesized nanocrystals and commercial microcrystals of zeolite 4A are shown in Figure 2. Zeolite 4A nanocrystals exhibit an average particle size of 100 nm with a narrow particle size distribution ranging from 50 to 140 nm, whereas commercial 4A particles have a very wide particle size distribution of $1 \sim 5 \ \mu$m.

N_2 adsorption–desorption measurements were performed on the calcined and purchased zeolites, as plotted in Figure 3. It is shown that a sharp adsorption increase exists at very low relative pressure, as a consequence of N_2 filling of the micropores. The weak hysteresis loop observed at high relative pressures is attributed to the filling of the large mesopores. The micropore volume of the directly calcined N-A sample is determined to be 0.30 cm^3/g. The multipoint BET specific surface area is calculated to be 619 m^2/g. For microsized zeolite 4A, the micropore volume of the directly calcined sample is determined to be 0.29 cm^3/g and the multipoint BET specific surface area is calculated to be 377 m^2/g.

The elemental analysis results show that the Na/Si/Al molar ratio is 0.6:2.1:1 for the synthesized zeolite 4A. On the basis of these results, the composition of as-synthesized zeolite 4A nanocrystals may be expressed as 0.4 $(TMA)_2O$:0.6 Na_2O:4.2 SiO_2:Al_2O_3 (in anhydrous form). The weight loss during calcination was calculated to be 14.4% due to TMA^+ decomposition. The TG analysis result of the as-synthesized sample is shown in Figure 4 together with the DTA result. The weight loss at a temperature lower than 150°C is about 3.0%, which may be assigned to the adsorbed water. The weight loss between temperatures from 150 to 500°C is ~13.9% due to the used organic template, which is correspondent to the two exothermic peaks on the DTA curve. The content of burn template
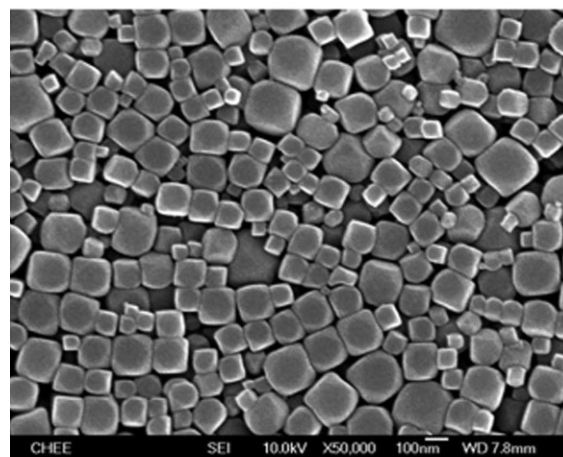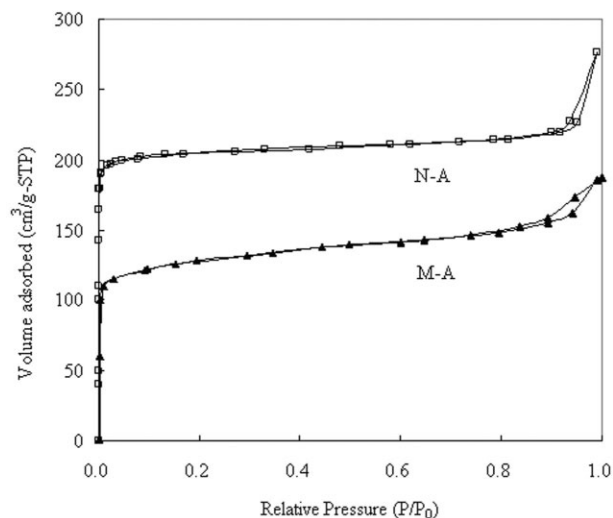

Figure 3 N_2 adsorption–desorption isotherms of zeolite A nanocrystals (N-A) and microcrystals (M-A).
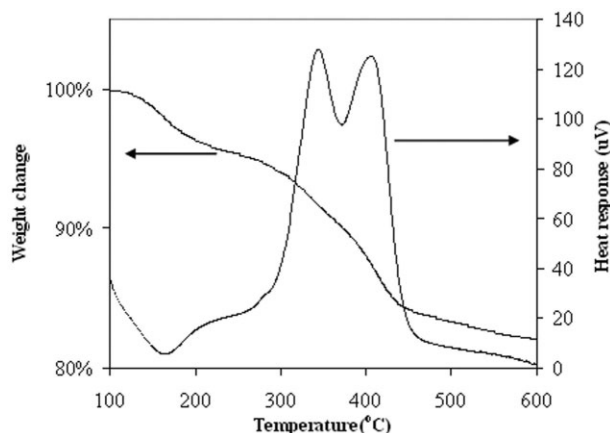
Figure 4 TGA and DTG analysis result of as-synthesized zeolite A nanocrystals.

is consistent with that based on elemental analysis. The microsized 4A zeolite is determined to have a Na/Si/Al molar ratio of 1:1:1, a true zeolite 4A.

The zeolite 4A/PES mixed matrix membranes

The gas permeation tests of two PES-zeolite MMMs were performed at 35°C on pure gases of He, H_2, N_2, O_2, CO_2, and CH_4. The permeability values obtained for these gases are presented in Table I. Compared with the pure PES dense membrane, the permeabilities of these two MMMs are observed to decrease, especially for the PES-M-A membrane. As shown in Table I, the gas permeability of the nanostructured membrane drops considerably by about 30%, except for helium, whereas that of the microstructured membrane drops significantly by around 50%. Note that the zeolite loading employed in the MMMs is only 20 wt % of the polymer matrix material. The obtained permeation results indicate that the added zeolite has taken effect in gas permeation through the membranes. For the polymer membrane, the solution-diffusion mechanism has gained widespread acceptance in describing the gas permeation results. Through the diffusion coefficient and solubility parameters, the gas

transport may be modeled with the aid of thermodynamic tools. On the other hand, the gas transport through zeolites is different as a combined effect of zeolitic composition, pore size, and pore structure. Particularly, zeolite materials are known to have pronounced molecular sieving effects due to their well-defined open crystal structures and their pore sizes of several angstroms. Thus, they discriminate components of a mixture either by exclusion of competing molecules on the basis of a difference in molecular size and shape or by transition state selectivity.[15] Consequently, for the MMMs, the zeolite characteristics must be considered for the obtained permeation results. The permeability decrease for zeolite 4A, 13× filled PES membranes has been similarly reported in the study of Sür et al.,[9] where the pure PES membrane, one may notice, has very lower permeability values than that prepared in our study, probably due to the membrane preparation method difference.

The permeability decompression may be due to the relatively small pore size of zeolite 4A, which can considerably hinder the diffusion of gas molecules through the zeolite pores. The intracrystalline diffusion of gas molecules through zeolites is generally dependent on the zeolite particle size and the Si/Al ratio. Several studies have demonstrated that the small crystals may have a much lower diffusivity than the larger crystals due to the surface barrier.[16–18] However, in our work, the opposite trend has been shown to apply the microstructured and nanostructured MMMs, suggesting that nanosized zeolite 4A may have higher diffusivity than the microsized one. This distinction is probably due to the Si/Al ratio difference between the microsized zeolite A and the nanosized one. In view of molecular interactions, the rich cationic ions existing in the zeolite channels and cells are able to strongly affect the adsorbed molecules. The attractive forces among the zeolite surface and the adsorbate molecules are thus much pronounced, so that the adsorbate molecules are tough to transport forward and then desorb from the downstream side. Therefore, the higher Si/Al ratio, i.e., the lower cation content, will usually render the adsorbate

TABLE I
Permeabilities of Gases Through PES and Zeolite-4A/PES Membranes at 35°C

Membrane	He*	H_2*	O_2	N_2	CH_4	CO_2
PES	9.11	8.96	0.773	0.129	0.112	3.38
PES-N-A	10.4	8.3	0.583	0.0907	0.0743	2.32
E[a]	114.16%	92.63%	75.42%	70.31%	66.34%	68.64%
PES-M-A	5.23	4.94	0.363	0.058	0.0501	1.56
E[a]	57.41%	55.13%	46.96%	44.96%	44.73%	46.15%

* He and H_2 were tested at 2 atm and the other gases were tested at 10 atm. Permeabilities are given in terms of barrer: 1 barrer = 10^{-10} cm^3 (STP) cm/cm^2 cm Hg s.

[a] E is defined as the ratio of the property of the mixed matrix membrane over that of the pure dense membrane, correspondently.

TABLE II
Permselectivities of PES and Zeolite-4A/PES Membranes at 35°C

Membrane	P(He)/P(N₂)	P(H₂)/P(N₂)	P(O₂)/P(N₂)	P(CO₂)/P(CH₄)	P(H₂)/P(CO₂)	P(He)/P(CO₂)
PES	70.62	69.46	5.99	30.18	2.65	2.70
PES-N-A	114.66	91.51	6.43	31.22	3.58	4.48
E[a]	162.37%	131.75%	107.27%	103.47%	134.96%	166.32%
PES-M-A	90.17	85.17	6.26	31.14	3.17	3.35
E[a]	127.69%	122.63%	104.45%	103.18%	119.46%	124.39%

[a] E is defined as the ratio of the property of the mixed matrix membrane over that of the pure dense membrane, correspondingly.

having much higher diffusivity. In the study of Xiao and Wei,[19] the authors have investigated the benzene diffusivity in silicalite-1 with two different Si/Al ratios, i.e., Si/Al = 6000, and Si/Al = 110. Their result shows that the diffusion of benzene molecules in higher Si/Al content silicalte-1 is nearly twice faster than in lower Si/Al content silicalte-1. On the basis of our elemental analysis, the microsized zeolite 4A has lower Si/Al molar ratio than the nanosized counterpart, which may have rendered the PES-M-A membrane having higher gas diffusion hindrance than the PES-N-A membrane.

The apparently lower specific BET surface area and lower pore volume of microsized zeolites are not favorable to the diffusion of gas molecules either. As a combined consequence, the microsized zeolite 4A with higher aluminum content may have lower diffusivity than the nanosized one.

Table II shows the permselectivities for PES, PES-M-A, and PES-N-A membranes. As compared to the plain PES dense film, the zeolite-incorporated MMMs have demonstrated increased permselectivities, especially for He/N₂, H₂/N₂, H₂/CO₂, and H₂/CO₂ gas pairs. These resultant selectivity data suggest that at least some penetrant molecules have permeated through the zeolite pores and channels to transport across the membrane. Thus, the interactions between the penetrants and zeolite pore structures may have played an important role in affecting the membrane separation performance. The selectivity enhancement is found to be more pronounced for the nanostructured composite membrane. For example, the selectivity for the H₂/N₂ gas pair is enhanced by 62.2% for the PES-N-A membrane but only 27.9% for the PES-M-A membrane. However, the zeolite 4A/PES membrane selectivities for O₂/N₂ and CO₂/CH₄ are only marginally higher than their pure polymer counterparts, indicating that the selectivity enhancement for these two gas pairs may not be achieved by incorporating either microsized or nanosized zeolite A into the PES polymer.

The observed selectivity increase for He/N₂, H₂/N₂, He/CO₂, and H₂/CO₂ four gas pairs are consistent with our expectations, mainly because of the distinct molecular sieving effect of zeolite 4A. Table III com-

piles the molecular dimensions of the tested gases.[20] It can be seen that larger molecular size difference exists in each gas pair, which may play a major part in contributing to the increased selectivity through zeolite 4A-filled membranes. However, this sieving effect is not successful to discriminate the gas pairs with close molecular sizes like O₂/N₂ and CO₂/CH₄. As discussed elsewhere, the O₂/N₂ ideal selectivity for pure zeolite 4A materials can be reached higher than 35.[5] Thus, the incorporation of zeolite 4A should be able to enhance the selectivity. It is noted, however, that zeolite 4A is able to more preferably adsorb N₂ than O₂.[21] The different adsorption capabilities and thus the adsorption affinity of zeolite A for these gases may be responsible for our observations. For the CO₂/CH₄ pair, although CO₂ can be more adsorbed than CH₄ by zeolite 4A, its rather appreciated quadrupole is able to render it forming stronger interactions with the zeolite pore surface, and hence CO₂ molecules may be harder to leave the active sites and move forward. In contrast, CH₄ has larger molecular size but weaker interactions with the zeolite surface, and therefore, it may diffuse through the zeolite channels easier than CO₂. The competing effect of absorption affinity and diffusion preference may render the used zeolite be unable to selectively allow CO₂ molecules to permeate through the zeolite apertures.

A comparison of the gas permeation results for the PES-N-A and PES-M-A membranes shows that the nanostructured material has better performance in both of the gas permeabilities and the gas pair selectivities. Regardless of the different zeolite compositions, the polymer chain molecules may experience a different packing revolution after incorporating nanosized zeolite particles as compared to the large zeolite

TABLE III
Diameter of Various Gas Molecules

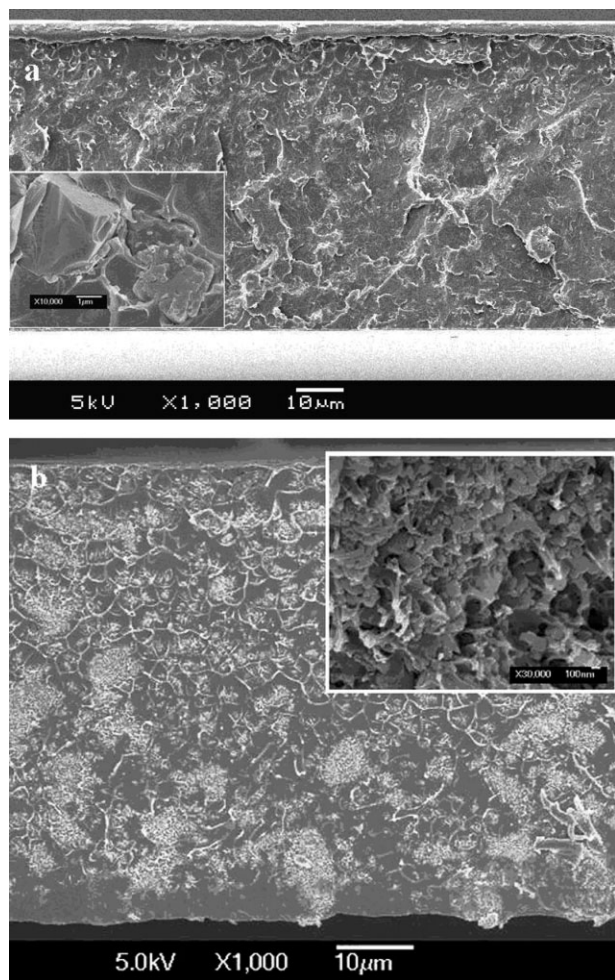|	Gas name					
	He	H₂	O₂	N₂	CH₄	CO₂
Kinetic diameter (Å)	2.60	2.89	3.46	3.64	3.80	3.30
Collision diameter (Å)	2.58	2.92	3.43	3.68	3.82	4.00

Data abstracted from Ref. 18.

Figure 5 SEM images of polyethersulfone–zeolite A mixed matrix membranes. (a,b) 20% zeolite A loading, cross-sectional view. (a) Microsized zeolite A, inset: at high magnification. (b) Nanosized zeolite A, inset: at high magnification.

particles. It may be explainable by the observed morphology and the internal texture of MMMs prepared with two different zeolites. Shown in Figure 5 are the SEM images of the zeolite 4A filled PES membranes. The thickness of the dried MMMs is determined to vary from 50 to 80 μm. The particle size of zeolite 4A is found to have a significant influence on the morphology of the fabricated membranes. SEM images of the PES-M-A membrane [Fig. 5(a)] show that zeolite 4A microparticles are homogeneously distributed in the PES matrix. At high magnification of SEM, no obvious voids between the microcrystal and PES were observed, suggesting good zeolite–polymer contact.

Figure 5(b) shows the cross-sectional view of the PES-N-A membrane. Nanocrystals are observed to be well-dispersed in the whole matrix. The most interesting observation is the island-like structures which are not observed for the formed membrane by those microparticles. The island-like structures seemingly join together in the membrane, which possibly make the

zeolite particle form a second continuous phase. At high magnification of SEM, nanocrystals and polymer were observed to closely pack with each other, indicating rather good compatibility between the zeolite and polymer.

CONCLUSIONS

In this study, nanosized and microsized zeolite 4A particles were employed to fabricate MMMs by being incorporated into PES. The SEM images show that both zeolites could be able to rather well contact with the polymer phase. Moreover, the well-distributed nanosized zeolites may form a second continuous phase through the island-like structures. The permeation experiment was performed on formed MMMs with six normal gases. The results show that the selectivities of zeolite 4A/PES MMMs for He/N_2, H_2/N_2, He/CO_2, and H_2/CO_2 gas pairs are greatly enhanced as compared with pure PES dense film. The gas permselectivity enhancement is much more pronounced for the nanostructured PES membrane, as a result of employed zeolite 4A nanocrystals. However, the permeabilities of zeolite 4A/PES MMMs for all gases are observed to decrease. Further study should be under way to investigate the interfacial properties between the polymer and the zeolite sieves so as to improve the integral property of PES-zeolite materials.

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