

# Mixed matrix membranes using carbon molecular sieves

## I. Preparation and experimental results

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### Abstract

Carbon molecular sieves (CMSs) have been incorporated into two different polymer matrices to form mixed matrix membrane films for gas separations. The CMSs were formed by pyrolysis of a polyimide (Matrimid<sup>®</sup>) precursor to a final temperature of 800 °C. The CMS membrane films have an intrinsic CO<sub>2</sub>/CH<sub>4</sub> selectivity of 200 with a CO<sub>2</sub> permeability of 44 Barrers and an O<sub>2</sub>/N<sub>2</sub> selectivity of 13.3 with an O<sub>2</sub> permeability of 24 Barrers at 35 °C. The pyrolyzed CMS materials were ball-milled into fine particles, ranging in size from submicron to 2 μm, prior to dispersal in casting solvent. Mixed matrix films comprising high CMS particle loadings (up to 35 wt.%) dispersed within two polymer matrices (Matrimid<sup>®</sup> 5218 and Ultem<sup>®</sup> 1000) were successfully formed from flat-sheet solution casting. For Ultem<sup>®</sup>–CMS mixed matrix membrane films, pure gas permeation tests show enhancements by as much as 40% in CO<sub>2</sub>/CH<sub>4</sub> selectivity over the intrinsic CO<sub>2</sub>/CH<sub>4</sub> selectivity of the pure Ultem<sup>®</sup> polymer matrix. Likewise, for Matrimid<sup>®</sup>–CMS mixed matrix films, enhancements by as much as 45% in CO<sub>2</sub>/CH<sub>4</sub> selectivity were observed. Similar enhancements were observed when these mixed matrix membrane films were examined for the O<sub>2</sub>/N<sub>2</sub> separation (8 and 20% for the Ultem<sup>®</sup>–CMS and Matrimid<sup>®</sup>–CMS mixed matrix films, respectively). Effective permeabilities of the fast-gas penetrants (O<sub>2</sub> and CO<sub>2</sub>) through the mixed matrix membranes were also significantly enhanced over the intrinsic permeabilities of the Ultem<sup>®</sup> and Matrimid<sup>®</sup> polymer matrices. These encouraging selectivity and permeability enhancements confirm that mixed matrix membrane behavior is achievable with CMS particles.

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### 1. Introduction

Membranes remain attractive opportunities for many gas separation industries (natural gas processing, landfill gas recovery, olefin/paraffin separation,

air separation, hydrogen recovery, etc.) [1–4]. Because of the economic competitiveness of the existing separation technologies and the present challenges of aggressive environments for membranes, many applications seek more robust membrane materials having higher selectivities and permeabilities. Not surprisingly, membrane materials development is an important research area to synthesize both higher performance and more durable membranes [5,6]. Since

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solution–diffusion, glassy, polymeric membranes offer attractive properties for gas separation applications, they have been actively examined in the past [7,8]. However, despite concentrated efforts to tailor polymer structure to affect separation properties, current polymeric membrane materials have seemingly reached a limit in the tradeoff between productivity and selectivity [9,10]. Because of this limitation, much research is focused on forming and evaluating novel membranes, such as nanoporous molecular sieving materials (e.g. carbon molecular sieves (CMS), silica and zeolites).

Although carbon molecular sieves [11–13] and zeolites [14,15] offer very attractive permeation properties with permeabilities and selectivities significantly higher than polymeric materials, processing challenges and high costs hinder their industrial application. For example, it is estimated that a zeolite membrane module would cost around US\$ 3000/m<sup>2</sup> of active membrane area [16] compared to US\$ 20/m<sup>2</sup> for existing gas separation polymeric hollow fiber membrane modules [17]. In addition, zeolite and carbon molecular sieve membrane manufacture involves high-temperature processes [13,18,19]. Even though the processing challenges to produce defect-free membranes under acceptable processing conditions may be overcome with modifications to existing technologies, handling issues (e.g. inherent brittleness) greatly limit their cost-effective use as continuous membranes in module form due to inevitably expensive fabrication and replacement costs. Mixed matrix membranes have been proposed as an alternative approach to obtain the high selectivity benefits of molecular sieving media and to counter the costly processing of purely homogeneous molecular sieving membranes through incorporating these sieves into a processable polymeric matrix. This heterogeneous or hybrid membrane concept combines the advantages of each medium: high separation capabilities of the molecular sieves and the desirable mechanical properties and economical processing capabilities of polymers. This paper examines the use of carbon molecular sieves as the disperse phase in mixed matrix membrane films using two different continuous polymer matrices. Characterization of the mixed matrix films and permeation properties for the O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> separations are discussed. Comparisons of the experimental permeation results

to model predictions are presented in a subsequent paper.

## 2. Background

Although carbon molecular sieve and zeolites have been long known industrially and currently used as adsorbents in many adsorptive separations, their application in membrane processes is gaining increased research interest [20]. The size- and shape-selective nature of these nanoporous materials allows molecular sieving discrimination by permitting smaller-sized gas penetrants to diffuse at much higher rates than larger-sized penetrants. This ability to effectively limit degrees of freedom of penetrant molecular motion results in significantly higher entropically-based diffusive selectivity than is possible with conventional polymeric materials [12]. On the other hand, the rigid nanoporous nature of molecular sieving materials that allows for precise discrimination of gas penetrants also creates difficulties in forming continuous, defect-free membranes and currently makes them impractical for large, industrial-scale implementation. However, using these molecular sieves in a mixed matrix membrane provides a very attractive alternative, capitalizing on their superior separation properties.

Incorporation of inorganic particles or fillers into polymeric materials has been examined for many applications. These applications use such fillers to enhance the mechanical properties of the original polymer matrix and more recently to improve the separation properties over those of the polymer material for liquid separations or pervaporation. For example, inorganic fillers or fibers, such as metal or silica particles, have been integrated into polymers to increase the mechanical strength and toughness for industrial materials [21–24] and for liquid separation (reverse osmosis, ion exchange, etc.) membranes [25]. In membrane applications, activated carbon or other adsorbents have been dispersed within a polymeric matrix, resulting in enhanced filtering capabilities for microscopic, submicron particles, such as enzymes [26] or monosaccharides from polysaccharides [27].

In particular, in the past decade, polymeric mixed matrix membranes using zeolites or carbon molecular sieves have been actively pursued for pervaporation applications [28–41]. Besides zeolites, activated

carbon has also been used as dispersed adsorbents in mixed matrix films, enhancing recoveries/removal of VOCs from water or air via pervaporation [42,43].

There has however been limited research focused specifically on using mixed matrix membranes in gas separations. Paul and Kemp [44] are cited for discovery of a delayed diffusional time lag effect for CO<sub>2</sub> and CH<sub>4</sub> when they added zeolite 5A in PDMS. They observed that there was an immobilizing adsorption of CO<sub>2</sub> and CH<sub>4</sub> by the zeolite 5A that significantly increased the time lag, but had minor effects on the steady-state permeation. Later, Kulprathipanja et al. [45,46] observed that the incorporation of silicalite into cellulose acetate (up to 25 wt.%) slightly improved O<sub>2</sub>/N<sub>2</sub> selectivity from 3.0 to 4.3 at 150 psig. Jia et al. [47] also examined the permeabilities of various gases including, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>, with the silicalite–PDMS mixed matrix membrane film and observed small increases in the permeabilities of fast-gas penetrants (e.g. O<sub>2</sub> and CO<sub>2</sub>) and decreases in the permeabilities of slow-gas penetrants (e.g. N<sub>2</sub> and CH<sub>4</sub>) in comparison to pure PDMS with increasing loading of silicalite. At their highest loading, 70 wt.% silicalite in PDMS, they report O<sub>2</sub>/N<sub>2</sub> selectivity enhancement from 2.14 to 2.92 and CO<sub>2</sub>/CH<sub>4</sub> selectivity enhancement from 3.42 to 8.86 at 30 °C. While it is interesting, these results are not of practical importance compared to the available pure component glassy polymers.

Duval et al. [48] examined an array of both zeolites (5A, silicalite, 13X) and commercial carbon molecular sieves for a range of rubbery polymers (PDMS, ethylene–propylene rubber, etc.). For the CO<sub>2</sub>/CH<sub>4</sub> separation using nitrile butadiene rubber (NBR) mixed matrix films with zeolite KY, they observed significant improvement in CO<sub>2</sub>/CH<sub>4</sub> selectivity from 13.5 to 35 in one film at 46 vol.% zeolite KY loading. They also report slight enhancement for O<sub>2</sub>/N<sub>2</sub> selectivity, such as from 3.0 to 4.7 for an ethylene–propylene rubber mixed matrix film with 53 vol.% silicalite. However, they showed that mixed matrix films prepared from commercial carbon molecular sieves demonstrated no improvement—attributed to the dead-end porous nature of the commercial CMS. Unlike commercial CMS particles, CMS membranes have through porosity, which permit gas permeation, not just sorptive cavities for adsorptive processes.

As described in the previous paragraphs, early work with mixed matrix membranes predominantly used elastomeric or rubbery polymers as the continuous matrix phase. Some work did examine glassy polymers for mixed matrix films. Gür [49] unsuccessfully used zeolite 13X as a filler in polysulfone, hoping to improve gas permeation rates by favorable adsorption kinetics and surface diffusion of the 10 Å pore zeolite. Testing loadings up to 20 vol.%, Gür found no significant effect on gas permeabilities. Süer et al. [50] found some success in incorporating zeolite 4A and 13X into another glassy polymer, polyethersulfone, and showed enhanced O<sub>2</sub>/N<sub>2</sub> selectivity from 3.7 to 4.4. However, such properties remain far below the desirable selectivities of current high-performance glassy polymers. The most significant work to date was performed by Rojey et al. [51], who observed significant selectivity enhancement for H<sub>2</sub>/CH<sub>4</sub> gas mixtures using flat-sheet membranes containing zeolite 4A dispersed in an Ultem<sup>®</sup> matrix.

Many researchers [41,52,53] have identified difficulties with obtaining good polymer–sieve contact with rigid, glassy polymers, such as polyimides. Such glassy polymer mixed matrix membranes often demonstrated poor polymer–sieve adhesion, resulting in macroscopic voids and no selectivity enhancement. Vankelecom et al. [53] examined the incorporation of various zeolites (borosilicate, silicalite, and Y) into several polyimides (e.g. PMDA–ODA, Kapton<sup>®</sup>) for the pervaporative separation of xylene isomers. They found poor polymer–sieve contact to be the main difference between the polyimide–zeolite mixed matrix films and previous PDMS–zeolite films. They postulated that because of the high chain rigidity of polyimides, their “close packing is disturbed in the vicinity of the zeolite particles,” resulting in voids in the mixed matrix membrane. Such voids lead to mixed matrix membranes with little or no improvement in the selectivities over the original polymer because of bypass of gas penetrants around the sieves.

In a subsequent work, Vankelecom et al. [54] used a silane coupling agent, (γ-aminopropyl)triethoxysilane (i.e. APTS), to improve the adhesion between the polymer–sieve interface. The silylation of borosilicate molecular sieves and their incorporation in PMDA–ODA polyimide (with reaction of the silylated sieve and the polyamic acid precursor) resulted in higher tensile strength for the mixed matrix

membranes, supporting the authors' view that covalent bonds were formed between the sieve and polyimide. No permeation experiments were performed, but their xylene sorption experiments indicated no change in the sorption characteristics between the mixed matrix films using either silylated and unsilylated sieves.

Other researchers have also investigated techniques to improve polymer–sieve contact and promote compatibility. Duval et al. [52] studied various silane coupling agents on silicalite for a range of glassy polymers (polysulfone, Ultem®, Udel®, etc.). Although improved polymer–sieve contact was observed with SEM micrographs, no improvement in selectivity from gas permeation measurements resulted. They also attempted film formation above the glass transition temperature of the polymer and high-temperature post-treatment of mixed matrix films with no success. Berry et al. [55] also investigated crosslinking techniques (thermal and UV curing) with two silanes on zeolite 3A and 13X and found some evidence of bonding with the silane gel matrix from infrared spectroscopy. Recent work by Mahajan and coworkers [56,57] has identified some key issues for mixed matrix membrane formation with rigid, glassy polymers. They emphasize appropriate selection of the sieve and matrix phases as important considerations to match the fast-gas permeabilities. Having a highly permeable polymer matrix phase can result in bypass of the selective sieve phase, while a low-permeability polymer underutilizes the sieves and results in poor productivity. So, the polymer matrix phase must have sufficient permeability for gas molecules to have continuous pathways through the sieves.

Choosing a sieve with dimensions capable of discriminating gas penetrants of interest is also an

important issue. For example, for the O<sub>2</sub>/N<sub>2</sub> separation, they recommend zeolite 4A (3.8 Å) instead of zeolite 13X (10 Å) or silicalite (5.2–5.8 Å) because its pore dimension is between those of O<sub>2</sub> and N<sub>2</sub>. Table 1 lists the molecular dimensions of typical gas penetrants. Even though Mahajan and Koros also used silane coupling agents to improve zeolite surface adhesion to the polymer matrix, they still found poor permeation results. One possible solution they propose is to have greater polymer flexibility during membrane formation. This approach was successfully demonstrated using zeolite 4A and the flexible, low *T<sub>g</sub>* poly(vinyl acetate) matrix. Poly(vinyl acetate) is, however, not an attractive material for membrane formation, and other approaches, such as use of plasticizers and formation at high temperatures using conventional rigid-chain polymers, are not industrially attractive; so, alternative approaches would be more desirable.

As discussed in the preceding section, research with mixed matrix membranes has almost exclusively examined various zeolites as the sieve phase in a polymeric matrix. There is relatively limited literature using such mixed matrix membranes for gas separation, and these primarily consider the O<sub>2</sub>/N<sub>2</sub> separation. In these studies, some success has been achieved with rubbery or elastomeric polymers, showing a general trend of increased permeability with slight or moderate increase in O<sub>2</sub>/N<sub>2</sub> selectivity. However, the reported mixed matrix membranes do not exhibit the anticipated performance enhancements necessary for commercial application, i.e. near or exceeding the Robeson upper bound [58]. Current work to extend the incorporation of zeolites into more attractive, high-performance glassy polymers has

Table 1  
Molecular dimensions of gas penetrants

Gas molecule	Critical temperature (K)	Molecular diameter (Å)	Molecular width (Å)	Lennard–Jones diameter <sup>a</sup> (second-virial coefficient data) (Å)	Kinetic diameter <sup>b</sup> (Å)
O <sub>2</sub>	154.6	3.75 <sup>c</sup>	2.68 <sup>c</sup>	3.58	3.46
N <sub>2</sub>	126.2	4.07 <sup>c</sup>	3.09 <sup>c</sup>	3.69	3.64
CO <sub>2</sub>	304.2	5.10 <sup>d</sup>	3.70 <sup>d</sup>	4.42	3.30
CH <sub>4</sub>	190.6	–	4.20 <sup>d</sup>	4.01	3.80

<sup>a</sup> [67].

<sup>b</sup> [15].

<sup>c</sup> [12].

<sup>d</sup> [79].

yielded significant and unresolved problems with poor polymer–sieve contact due to the polymer chain rigidity of these high  $T_g$  materials. This study proposes to investigate the use of carbon molecular sieves for incorporation into these high  $T_g$  glassy polymers. Also, in contrast to one prior unsuccessful finding with commercial, dead-ended CMS in rubbery polymers [48], this study uses synthesized CMS membrane material formed via pyrolysis in the research laboratory.

### 3. Experimental

Preparation of the CMS mixed matrix membrane films involved three primary steps: (1) generation of sieve particles; (2) preparation of the polymer–sieve slurry mixture; and (3) casting the polymer–sieve mixture to form a mixed matrix membrane film. This section describes the materials used for these three stages, the procedures to prepare these materials, and the analytical and experimental techniques to characterize these materials.

#### 3.1. Materials

##### 3.1.1. Polymers

Two glassy polymers were used as the continuous matrix phases in the mixed matrix membrane films: Matrimid<sup>®</sup> 5218 and Ultem<sup>®</sup> 1000. Their chemical structures and physical properties are shown in Table 2. Densities were obtained from product information data sheets [59,60], while glass transition

temperatures ( $T_g$ ) were experimentally determined (see characterization techniques described later in this section). Matrimid<sup>®</sup> 5218 is a commercially available polyimide (Vantico Inc., Luxembourg) made from the monomers 3,3',4,4'-benzophenone tetracarboxylic dianhydride and diaminophenylindane and is currently used as a gas separation membrane material. Ultem<sup>®</sup> 1000 is a commercially available polyetherimide (GE Plastics, Mount Vernon, IN) made from the monomers of 2,2'-bis[4-(3,4-dicarboxyphenoxy)phenyl] propane dianhydride (BPADA) and 1,3-phenylenediamine (mPDA). Like other polyimides, Matrimid<sup>®</sup> 5218 has a high glass transition temperature ( $T_g$ ) with the characteristic rigid polymer chain backbone. Ultem<sup>®</sup> 1000, on the other hand, has a lower  $T_g$  with a more flexible polymer backbone. Both polymers exhibit high permselectivities for the O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> separations, as will be shown in the next section. Matrimid<sup>®</sup> 5218 has considerably higher permeabilities than Ultem<sup>®</sup> 1000.

##### 3.1.2. Carbon molecular sieves

The carbon molecular sieves used as the dispersed particle phase in the mixed matrix films were generated in our laboratory from the high-temperature pyrolysis of the polyimide, Matrimid<sup>®</sup> 5218. Before pyrolysis, the Matrimid<sup>®</sup> precursor material was first prepared as a dense, flat polymer film from solution casting using dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) solvent (chromatographic grade, EM Science, Gibbstown, NJ) to dissolve Matrimid<sup>®</sup> 5218 to prepare 5–10 wt.% polymer solution. The Matrimid<sup>®</sup> 5218 films were

Table 2  
Chemical structures and physical properties of polymers used

Polymer	Chemical structure	Density (g/cm <sup>3</sup> )	$T_g$ (°C)
Matrimid <sup>®</sup> 5218		1.24	302
Ultem <sup>®</sup> 1000		1.27	209

cast on a smooth glass surface into a circular ring mold or with a uniform thickness film applicator (Paul N. Gardner Co., Pompano Beach, FL). After slow evaporation at room temperature (approximately 12 h), the dry films were generally 2 mils (1 mil = 0.001 in.) in thickness. To remove residual solvent, the films were heated in a vacuum oven at 100 °C overnight.

The polymeric precursor films were pyrolyzed in a quartz tube furnace. The samples were cut first into small sections (less than 4 cm in width or diameter) and placed on a rectangular quartz plate (1/4 in. thick, Heraeus Amersil, Austin, TX) that was approximately 4 cm in width and 24 cm in length. The quartz plate had 1/4 in. wide and 1/8 in. deep grooves that aided in the removal of volatile components during the pyrolysis process. The detailed description of the pyrolysis procedure used is reported elsewhere [13,18]. After pyrolysis, the permeation properties of the CMS films may be evaluated.

For use in mixed matrix films, the CMS films were further formed into very fine particles (submicron to micron). A ball mill/mixer was used to crush the CMS films into fine particle sizes. First, the CMS films were dried at 250 °C in a vacuum oven for at least 12 h. Then, the CMS films were loaded into a 2.25 in. diameter, 3 in. high hardened steel vial set (model 8001, SPEX Certiprep, Metuchen, NJ). Stainless steel ball bearings (two 1/2 in. and four 1/4 in. balls) were placed inside the container before sealing the container with an O-ring top and cap. Prior to use, the steel vial, the top (without the O-ring), and the stainless steel balls were heated in a vacuum oven (approximately 150 °C) under vacuum for at least 2 h to dry and remove residual moisture in the container. The container was next placed inside a ball mixer/mill (SPEX model 8000, Metuchen, NJ), which provided rapid shaking of the vial container and mechanical force for the ball bearings to crush the films into very fine particles. Generally, the CMS particles were milled for at least 1 h on the mixer/miller. The vial was allowed to stand for approximately 2 h to cool down and to let airborne CMS particles inside the vial settle. After milling, the fine CMS particles were heated to 250 °C under vacuum for at least overnight prior to any use or characterization. The purpose of this heat treatment was to remove moisture that may have been sorbed by the CMS particles during storage. As a result of the milling, the distribution

of particle sizes typically ranged from submicron to 10 µm in size, as verified by scanning electron microscopy (SEM).

### 3.2. Preparation of mixed matrix membrane films

Mixed matrix films were prepared by solution casting a slurry of fine CMS particles dispersed within a polymer solution. Generally, the slurry concentration was about 15–20 wt.% solids (CMS particles and polymer) in solvent. The following steps were used: After preconditioning the CMS particles at high temperature (about 250 °C) in a vacuum oven for at least 12 h, a measured quantity of CMS particles was immediately dispersed in 3 ml of dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) in a 40 ml vial with a Teflon®-lined septum cap (ICHEM, Fisher). Generally, 0.2–0.4 g of CMS particles were used. After dispersal in CH<sub>2</sub>Cl<sub>2</sub>, a high-intensity ultrasonic processor (VibraCell™, Sonics & Materials Inc., Newtown, CT, 50 Watt model) with a 1/4 in. titanium probe is inserted in the vial to sonicate the slurry for about 1 min. This sonication step provided powerful shearing of the CMS particles breaking up aggregates of particles and enhancing homogeneity during the intense agitation.

After sonication, the vial was allowed to stand for about 6 h to let larger CMS particles settle to the bottom of the vial. The finer CMS particles still dispersed in the slurry were decanted into a new 40 ml vial with a glass transfer Pasteur pipet (Fisherbrand), leaving behind larger particles in the original vial. This sedimentation and decantation procedure empirically gave smaller particles in the resultant mixed matrix films. This finding was determined by visual inspection using SEM and comparing those mixed matrix film samples employing the decantation procedure to those that did not. In addition, mixed matrix films that were formed without this decantation procedure generally had wider particle size distributions, as well as the presence of large aggregates (10–20 µm particles). Having smaller sieve particles and a narrow size distribution gave better dispersion and more uniformity within the polymer matrix of successful mixed matrix films and also minimized the aggregation and stratification phenomenon observed in early films.

Mass measurements of the dried original vial and the Pasteur pipet before and after the transfer to the



new vial permitted calculation of the new mass of CMS particles in the new vial. Generally, approximately 80–90% of the original CMS particle amount was captured in the new vial.

After sonication and isolation of finer CMS particles, the CMS particles were “primed” (or “sized”) with the matrix polymer or “sizing” agent (e.g., another polymer). The purpose of “priming” or “sizing” was to promote compatibilization of the sieves with the polymer by introducing a thin layer of the polymer onto the sieve surface. Also, “priming” may aid in minimizing aggregation of CMS particles at high loadings. Extensions of this technique, though not used for the CMS mixed matrix films in this study, can include chemical/reactive grafting of the priming polymer onto the sieve surface or adding a non-polar, non-solvent (i.e. hexane) to the slurry to promote precipitation of the polymer onto the sieves [61]. With the non-solvent technique, the precipitated sieves may then be removed through filtration and dried by any conventional means prior to re-dispersion in the solvent. For “priming” the CMS particles, typically 10 wt.% of the total amount of matrix polymer to be added to the slurry is used.

After “priming” the CMS particles, the slurry was well mixed by rolling the vial on rotating parallel rollers for at least 12 h. The remaining amount of matrix polymer was finally added to the slurry, and the final slurry was again well mixed by the rotating parallel rollers at a reduced velocity (due to the higher viscosity of the mixture) for at least 12 h. The quantity of CMS particles and the amount of polymer added determined the “loading” (or solid particle concentration) in the final mixed matrix membrane. Also, generally, the slurry concentration was about 15–20 wt.% solids (CMS particles and polymer) in solvent.

The polymer–sieve slurry was poured onto a flat, level, clean horizontal glass surface placed inside a controlled environment (e.g. plastic glove bag). To decrease the evaporation rate, the controlled environment was first near-saturated with  $\text{CH}_2\text{Cl}_2$  solvent over a 3–4 h period prior to casting the polymer–sieve slurry. A stainless steel film applicator (i.e. casting/doctor blade from Paul N. Gardner Co.) was used to draw/spread the polymer–sieve slurry to a uniform thickness. An inverted glass funnel was also used to cover the wet film; however, the tip of the funnel was lightly covered with aluminum foil to further decrease

the evaporation rate. Solvent vapor left through the small gap between the glass funnel and glass surface.

The solvent from the mixed matrix film slowly evaporated over about a 12 h time period. The resulting dried film had an approximate thickness of about 30–60  $\mu\text{m}$ . For almost all cases, the mixed matrix films automatically became delaminated from the glass surface during the evaporation process; so, removal was easy. Sometimes, the mixed matrix film remained attached to the glass surface, and it was necessary to use a razor blade and slight peeling of the film from the glass surface to initiate delamination. Because water can physisorb or chemisorb to the carbon sieves, water was not used to delaminate the film as sometimes done for homogeneous, dense polymer films. The final membrane film was further dried after initial evaporation at a temperature of about 100 °C for at least 12 h in a vacuum oven to remove residual solvent.

### 3.3. Characterization of mixed matrix films

Several characterization techniques were performed on the CMS films/particles and mixed matrix membrane films. The CMS films/particles were analyzed with wide angle X-ray diffractometry (Rigaku, rotating anode X-ray diffractometer using a Cu  $\text{K}\alpha$  source), helium pycnometry (Micromeritics, AccuPyc 1330 density analyzer, Norcross, GA), and  $\text{CO}_2$  adsorption (Micromeritics accelerated surface area and porosimetry (ASAP) 2010).

For wide angle X-ray diffraction (WAXD) testing, the CMS materials were first crushed into powder form using either a mortar/pestle method or by ball-milling (as described previously). The CMS powder was then mounted onto a microscope glass slide using a small drop of amyl acetate (Aldrich, reagent grade) as a dispersant to secure the powder onto the glass. Measurements were taken in scan mode from  $2\theta = 5$  to 70 at 0.05° increments with 3.0 s dwell times. These measurements allow for qualitative comparisons of the  $d$ -spacings of the CMS materials prepared from different pyrolysis operations. For helium pycnometry and ASAP measurements, carbon samples were heated to 250 °C in a vacuum oven for at least 12 h to remove moisture and then crushed into small particles, weighed, and loaded into a 1  $\text{cm}^3$  sample container. These techniques provided direct measurements

of skeletal or true density (helium pycnometry), micro-pore volume (accelerated surface area and porosimetry), and bulk density (by calculation).

The mixed matrix membrane films were characterized with scanning electron microscopy (Hitachi S-4500 field emission scanning electron microscope) and differential scanning calorimetry (DSC) (Perkin-Elmer DSC 7 connected to thermal analysis controller (TAC) 7/DX, Norwalk, CT). For scanning electron microscopy characterization, the mixed matrix films were cryogenically fractured in liquid nitrogen and mounted on small half cylinder stainless steel sample holders with double-sided adhesive, electrically conductive carbon tape (8 mm wide  $\times$  0.16 mm thick, SPI Supplies, West Chester, PA) to view the cross-sections of the films or fibers. The samples were then sputter-coated under argon plasma with  $<15$  nm of gold/palladium using a sputter coater (model S150B, BOC Edwards, Wilmington, MA) to provide a conductive coating that enhances the images under SEM. SEM images were examined using an accelerating voltage of 15 kV. SEM micrographs provided qualitative assessments of polymer–sieve contact and homogeneity and distribution of CMS particles.

For DSC analysis, small sections of pure polymer or mixed matrix film were cut, weighed, and placed into pre-weighed aluminum DSC pans (Perkin-Elmer, Norwalk, CT). Samples were first heated from 50 °C to about 50 °C above the reported glass transition temperature of the pure polymer at a rate of 20 °C/min in the first cycle to remove thermal history. The glass transition temperature of the sample was determined in the second heat cycle by examining the inflection of the heat flow versus temperature curve using the onset method. The glass transition temperatures determined from the first heat cycle gave similar results as those from the second heat cycle, but were rougher estimations because of the very broad peaks observed in the first heat cycle. The glass transition temperature provided a qualitative measure of the flexibility of polymers. It was a useful tool for comparisons of the polymer chain rigidity of mixed matrix films at various CMS loadings to that of pure polymer films.

### 3.4. Permeation testing apparatus

Permeability measurements of the flat mixed matrix membrane films and pure polymer films were made

using a manometric (or constant volume) method [62–64]. The method relies on maintaining a constant pressure of a gas penetrant on the upstream face of the membrane film and measuring the flux across the membrane film of known thickness and area on the downstream (or permeate) face. The flux or permeation rate was measured from the pressure rise from the permeating gas in a known constant downstream (permeate) volume. The pressure rise was plotted on a strip chart recorder, and the ideal gas law is used to calculate flux. A schematic of the permeation testing apparatus is shown in Fig. 1. Detailed description of this apparatus and the membrane masking procedure are discussed elsewhere [65].

Both the upstream and downstream sections of the permeation cell and system were evacuated for about 24–48 h to remove (“degas”) any gases or vapors sorbed into the membrane. Permeation tests of the membrane were performed by introducing the upstream with the desired gas at the desired pressure. The permeation rate was measured at steady state (typically, after 5–10 times the diffusional time lag for the gas penetrant through the known thickness of that polymer material). The diffusional time lag,  $\theta$ , is

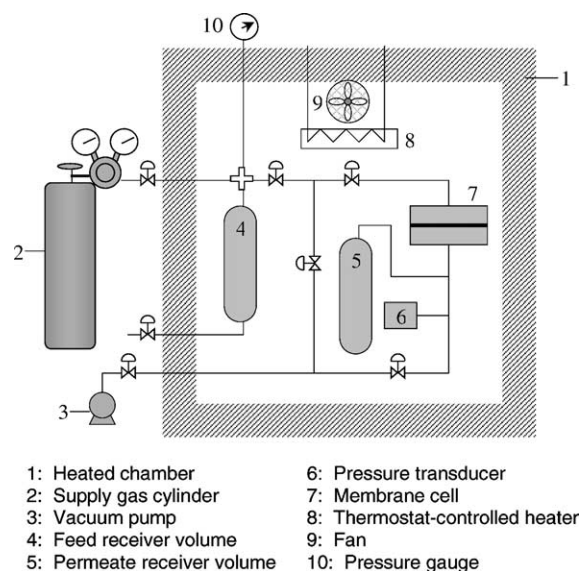


Fig. 1. Schematic of pure gas permeation apparatus for flat membrane films.



calculated from [66]:

$$\theta = \frac{\ell^2}{6D_{\text{eff}}} \quad (1)$$

where  $\ell$  is the membrane film thickness and  $D_{\text{eff}}$  the effective diffusion coefficient of the gas penetrant in the material. Following the permeation testing of a given gas, both the upstream and downstream sections were evacuated for about 12–24 h before permeation testing of the next gas.

The *permeability* or *permeability coefficient* of a gas penetrant  $i$  is a pressure- and thickness-normalized flux of the component through the membrane and is defined by the expression:

$$P_i = \frac{N_i \ell}{\Delta p_i} \quad (2)$$

where  $P_i$  is the permeability of component  $i$ ,  $N_i$  the component  $i$ 's flux (molar flow rate per unit membrane area) through the membrane, and  $\Delta p_i$  the partial pressure (or fugacity) driving force of component  $i$  (partial pressure or fugacity difference between the upstream to the downstream). The downstream is maintained at vacuum. Permeability is often expressed in the customary unit of Barrer (1 Barrer =  $10^{-10} \text{ cm}^3(\text{STP})\text{cm}/\text{cm}^2 \text{ s cmHg}$ ). The permselectivity is determined by taking the ratio of the permeability of one penetrant over that of another penetrant.

Following the permeation testing of a given gas, both the upstream and downstream sections were evacuated for at least 12 h before permeation testing of the next gas. For the pure gas permeation tests, compressed gas cylinders of  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  were supplied by Air Liquide or Praxair (Austin, TX). The purity grade on these gases was ultrahigh purity (UHP) or instrument grade: 99.999% for  $\text{N}_2$ , 99.993% for  $\text{O}_2$ , 99.97% for  $\text{CH}_4$  and 99.99% for  $\text{CO}_2$ .

For permeation experiments using the 10%  $\text{CO}_2$ /90%  $\text{CH}_4$  gas mixture (Air Liquide, certified grade), the permeation system consisted of a smaller downstream volume ( $<100 \text{ cm}^3$ ), and the downstream was connected to a gas chromatograph (Hewlett-Packard 5890 Series II, Atlanta, GA) using a thermal conductivity detector (TCD) with a packed column for  $\text{CO}_2/\text{CH}_4$  separation (HayeSep Q 80/100 mesh, Hewlett-Packard). The top of the permeation cell was also modified to include a retentate (or residue) stream. The retentate flow rate was set

so that the permeate flow rate was less than 1% of the feed flow rate. This condition specifies that the “stage cut” is less than 1%, which ensures that the feed or upstream composition does not vary during the permeation run.

In mixed gas experiments, high feed gas pressures (up to 900 psia) were examined. For these experiments, permeability coefficients for  $\text{CO}_2$  and  $\text{CH}_4$  were calculated on a fugacity driving force with the fugacity coefficients of  $\text{CO}_2$  and  $\text{CH}_4$  in the binary mixture computed from the virial equation of state [67] using the pure component second virial coefficients [68] and the second virial coefficient for the binary mixture [67].

Permeability and permselectivity measurements of mixed matrix films reported in this study come from singular films for each CMS loading, although replicate permeation experiments were performed on these single mixed matrix films. Although several replicate films were made during our investigation and often gave comparable results to those reported in this study, the preparation and formation procedures for the CMS particles themselves and the resulting mixed matrix films were fundamentally different from those described in this study. Discussion of these issues is beyond the scope of this paper. It is not justified to provide a statistical confidence interval from the available data. However, there was no special order of sample preparation and testing of the numerous mixed matrix films that are reported in this study. Yet, as will be discussed in the upcoming sections, a systematic trend exists in the experimental results. These facts strongly suggest that variability is likely on the order of the size of a data point presented in the plots, or else systematic trends would not have been observed.

A propagation-of-errors analysis was performed to estimate permeability measurement uncertainty based on uncertainties in: ( $dP/dt$ ), the permeation rate through the membrane (Torr/min);  $V$ , the downstream permeate volume ( $\text{cm}^3$ );  $\ell$ , the membrane thickness (mil);  $T$ , absolute temperature (K);  $A$ , permeation area ( $\text{cm}^2$ ); and  $\Delta p_i$ , the pressure or fugacity driving force (psi). The measurement uncertainties in the downstream volume ( $V$ ) and temperature ( $T$ ) were found to have negligible contributions to the uncertainty in the permeability calculation, while measurement uncertainties in the area ( $A$ ) and thickness ( $\ell$ ) of the membrane film had the most significant contributions.

For permeation data in this study, the uncertainties are approximately 2% of the permeability measurement values for Matrimid<sup>®</sup> and CMS–Matrimid<sup>®</sup> mixed matrix films, while the uncertainties are approximately 1% of the permeability measurement values for Ultem<sup>®</sup> and CMS–Ultem<sup>®</sup> mixed matrix films.

#### 4. Results and discussion

Several mixed matrix membrane films were prepared using Ultem<sup>®</sup> 1000 and Matrimid<sup>®</sup> 5218 as polymer matrices over a range of CMS loadings (15–38 vol.%). This section presents pure gas permeation results, as well as characterization of the CMS films and particles and the resulting mixed matrix films. In addition, experimental mixed gas (10% CO<sub>2</sub>/90% CH<sub>4</sub>) permeation results are discussed for an Ultem<sup>®</sup> 1000 mixed matrix film.

##### 4.1. Characterization of carbon molecular sieves and mixed matrix membranes

After preparing CMS membrane films via pyrolysis, their permeation properties were evaluated with pure gas permeation experiments at 35 °C. Research in our group [18,69,70] has investigated the effects of pyrolysis conditions for several polyimide precursors, including Matrimid<sup>®</sup> 5218—the polyimide precursor used to generate CMS particles incorporated into the mixed matrix films presented in this paper. Work with Matrimid<sup>®</sup> 5218, in particular, has yielded valuable information demonstrating the “tailorability” of the permeation properties of CMS membranes. Table 3 presents the permeation properties of CMS membranes at 35 °C using Matrimid<sup>®</sup> 5218 precursor films under different pyrolysis conditions.

As shown in Table 3, the typical permeability–selectivity tradeoff is observed, but all the permeation properties offer extremely attractive values for both the O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> separations. In particular, the CMS membrane pyrolyzed to 800 °C for 2 h (CMS 800-2) was a good candidate for incorporation into mixed matrix membranes because it offered the highest selectivities (O<sub>2</sub>/N<sub>2</sub> selectivity of 13.3 and CO<sub>2</sub>/CH<sub>4</sub> selectivity of 200) while still possessing high fast-gas (O<sub>2</sub> and CO<sub>2</sub>) permeabilities. The CMS 800-2 films were analyzed with helium pycnometry to determine the skeletal density (1.69 g/cm<sup>3</sup>) and with CO<sub>2</sub> adsorption analysis and the Dubinin–Astakov equation to estimate the micropore volume (0.186 cm<sup>3</sup>/g) [18]. With these quantities, the bulk density of CMS 800-2 was calculated to be 1.29 g/cm<sup>3</sup>.

It can be envisioned that adding these highly selective sieves (CMS 800-2) within an already selective polymeric matrix, such as Ultem<sup>®</sup> 1000 and Matrimid<sup>®</sup> 5218, has the potential of substantially improving the effective O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> permeation properties of the mixed matrix film. For example, Fig. 2 plots the CO<sub>2</sub>/CH<sub>4</sub> permeation properties of the two polymeric matrices explored in this paper (Ultem<sup>®</sup> 1000 and Matrimid<sup>®</sup> 5218) and those of CMS 800-2. The bold, dashed line delineates an empirical boundary representing the performance constraints and the tradeoff between CO<sub>2</sub> permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity for existing conventional polymeric membranes [71]. Since its revision in 1991, there has not been significant improvement in synthesizing new polymer materials having properties beyond this empirical “upper bound” despite considerable work in this area [58]. In contrast, as shown in Fig. 2, the CMS membrane, CMS 800-2, lies well beyond this upper bound. Integrating these sieves (CMS 800-2) into a polymeric matrix can potentially yield mixed matrix membranes with enhanced effective properties

Table 3  
Permeation properties of carbon molecular sieve films pyrolyzed from flat polymer films of Matrimid<sup>®</sup> 5218

Carbon molecular sieve	Pyrolysis conditions	Permeability (Barrer)				Permselectivity	
		CO <sub>2</sub>	CH <sub>4</sub>	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	O <sub>2</sub> /N <sub>2</sub>
CMS 550-2	550 °C (2 h); vacuum	1250	20	435	50	63	8.7
CMS 550-8	550 °C (8 h); vacuum	375	4.2	166	18.2	89	9.1
CMS 800-2	800 °C (2 h); vacuum	43.5	0.21	24	1.8	200	13.3

Data obtained from [18]. Pure gas permeation with 50 psia for CO<sub>2</sub> and CH<sub>4</sub>, 21 psia for O<sub>2</sub>, and 79 psia for N<sub>2</sub>. Temperature: 35 °C.

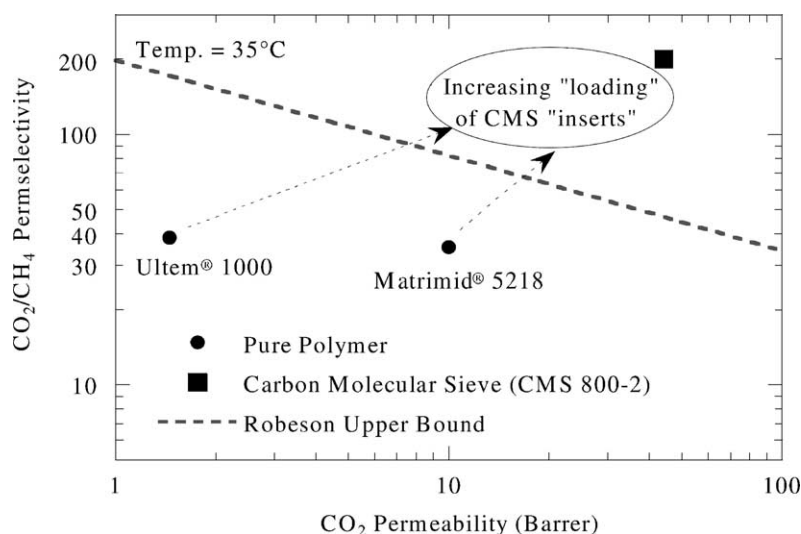


Fig. 2. Permeation properties of polymer matrices Ultem® 1000 and Matrimid® 5218 and carbon molecular sieve (CMS 800-2). Incorporation of CMS particles in a polymer matrix is expected to yield enhanced permeation properties as a mixed matrix membrane.

lying beyond this “upper bound” and offering very commercially attractive opportunities for the industry.

The CMS 800-2 films were ball-milled into fine particles ( $<1\text{--}10\text{ }\mu\text{m}$ ) for use in mixed matrix film slurry preparations. Besides forming the CMS 800-2 inserts from dense, flat Matrimid® 5218 films, CMS 800-2 particles in this work were also generated directly from Matrimid® 5218 powder using the same pyrolysis protocol without having to cast flat Matrimid® films first. Such a modification provides the advantage of generating more CMS 800-2 sieves for each pyrolysis and eliminating an entire processing step for forming mixed matrix films. However, it is necessary to ensure that the CMS 800-2 particles obtained in this manner have comparable permeation properties to those formed from cast Matrimid® 5218 films. Although it is not possible to directly measure permeation properties of CMS 800-2 particles as with CMS 800-2 films, replicate mixed matrix films prepared with the two different sieves give very similar effective mixed matrix film permeation properties using powder-pyrolyzed sieves versus the film-pyrolyzed sieves. WAXD was performed on the CMS 800-2 films and powder, as shown in Fig. 3. The WAXD diffractograms show very similar peaks and  $d$ -spacings, suggesting similar planar dimensions between the film-pyrolyzed CMS and the powder-pyrolyzed CMS.

During the initial stages of CMS 800-2 mixed matrix film formation, three primary problems were encountered: surface pattern effects, sedimentation/aggregation, and poor polymer–sieve contact. The first problem, surface effects, arose due to rapid evaporation of the solvent and temperature gradients in the wet film. With rapid evaporation, surface tension-driven (i.e. Marangoni) forces form convective flow cells that result in uneven clustering of CMS particles and the appearance of irregular patterns on the surface.

Sedimentation of CMS particles led to aggregation with nearby sieve particles due to the low viscosity of mixed matrix slurries used initially. Sedimentation of the zeolite particles has also observed to be a problem for zeolite–polymer mixed matrix films, especially at higher loadings [53]. Lastly, like previous work with zeolites and rigid, glassy polymers [56], poor polymer–sieve contact was also observed with initial preliminary mixed matrix films. Fig. 4 shows representative SEM micrographs of a cross-section of an early mixed matrix film revealing submicron gaps ( $\sim 0.1\text{--}0.2\text{ }\mu\text{m}$ ) around the sieves due to poor adhesion between the polymer and CMS particles. Here, it was hypothesized that the evaporation rate of the casting solvent was an important factor, since fast evaporation rates may prevent polymer chains from relaxing and conforming to the sieve surface.

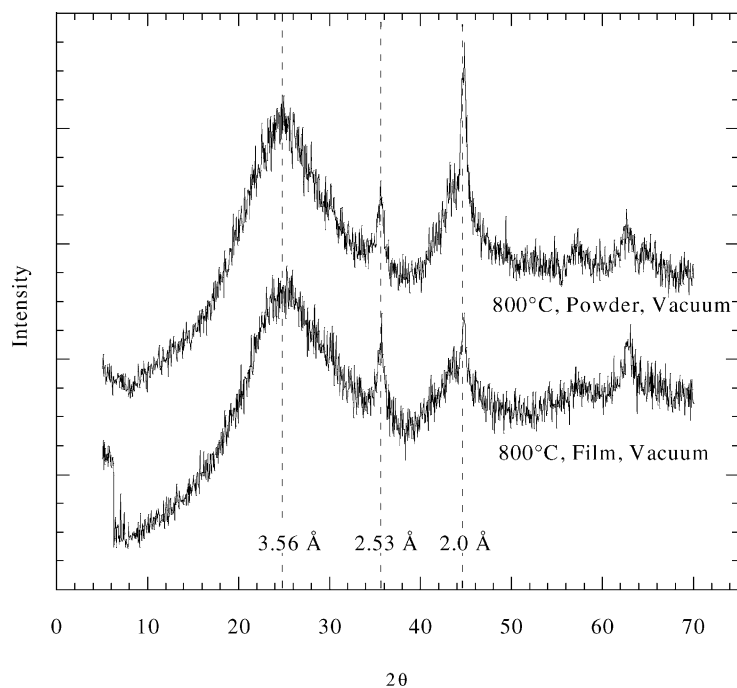


Fig. 3. Wide angle X-ray diffraction spectra of CMS materials formed via pyrolysis with different polymer precursor forms (film vs. powder). Precursor polymer (Matrimid® 5218) and pyrolysis temperature protocol are the same for both cases.

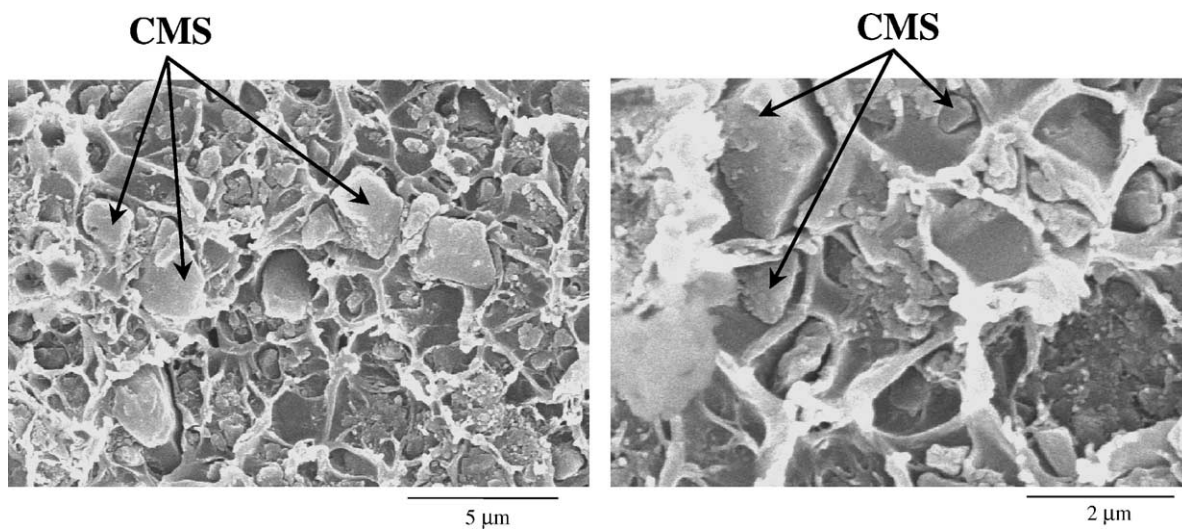


Fig. 4. Scanning electron micrographs (cross-section) of an early mixed matrix film containing carbon molecular sieve “inserts” (CMS 800-2). Continuous polymer matrix is Ultem® 1000 with CMS loading of 35 vol.%. Poor polymer–sieve contact is observed.

As discussed in Section 3, several modifications were implemented to resolve all three problems. Sonication and decantation of the smaller CMS particles, and forming more viscous mixed matrix slurries all significantly reduced the sedimentation and aggregation problems. Priming (or sizing) the sieves with a small quantity of polymer also aided in compatibilizing the sieves and the matrix polymer for improved adhesion and also minimized aggregation at high sieve loadings. Reducing the evaporation rate by casting in a glove bag near-saturated with casting solvent also helped correct all three problems. Solvent evaporation of the mixed matrix film was slowed to about a 12 h period. Fig. 5 shows representative SEM micrographs of a mixed matrix film after these modifications. These micrographs demonstrate smaller CMS particles (mostly  $<1\ \mu\text{m}$ ) and a better distribution of these particles, as well as very good polymer–sieve contact.

The glass transition temperatures of Ultem® 1000 mixed matrix films (16, 20, and 35 vol.% CMS 800-2) and Matrimid® 5218 mixed matrix films (17, 19, 33, and 36 vol.% CMS 800-2) were determined by DSC according to the procedure described in Section 3. All films (pure and mixed matrix) were cast from  $\text{CH}_2\text{Cl}_2$ . The  $T_g$  for each film was determined from the heat flow versus temperature curve using the onset method. The results are shown in Fig. 6.

The  $T_g$  of the matrix polymers increased with the incorporation of the CMS particles. This  $T_g$  elevation phenomenon is observed in semi-crystalline polymers with proportionate increases in crystallinity [72] and polymer blends [73,74]. In the semi-crystalline polymer field, it has been suggested that “steric constraint imposed by crystalline regions on neighboring, otherwise mobile polymer segments might result in an increase in  $T_g$ ” [72]. The experimental results presented in this paper suggest that the presence of a dispersed constituent (e.g. CMS particles) can affect the fundamental properties (e.g.  $T_g$ ) of the continuous polymer matrix phase when good segmental-level attachment exists between these two phases. Increases in  $T_g$  have also been observed with organic–inorganic hybrid materials employing in situ growth of dispersed nano silica in silicone rubber and in polyetherimide (i.e. Ultem®) matrices [75]. The nano silica in these hybrid materials were grown in the polymer solution via a sol–gel process and used amino silanes to form chemical linkages between the inorganic phase and the organic polymer matrices. Whereas these materials involve chemical preparation methods, it is likely that the polymer–sieve adhesion for the CMS-Ultem® case considered here is derived through strong physical adsorptive attractions between the polymer and the dispersed solid surface.

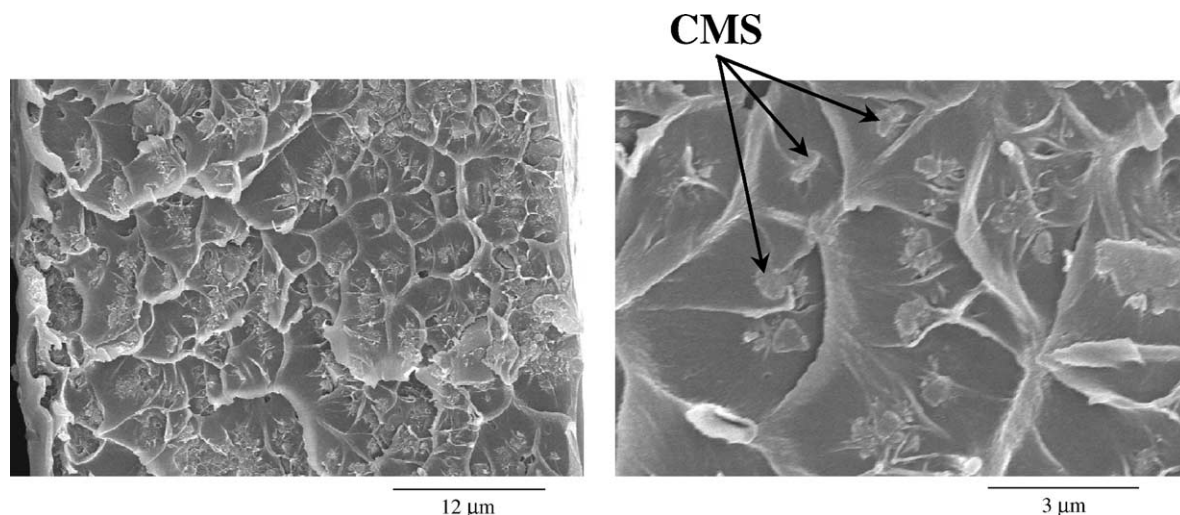


Fig. 5. Scanning electron micrographs (cross-section) of successful mixed matrix film containing carbon molecular sieve “inserts” (CMS 800-2). Continuous polymer matrix is Matrimid® 5218 with CMS loading of 19 vol.%. After modifications, good polymer–sieve contact is observed.



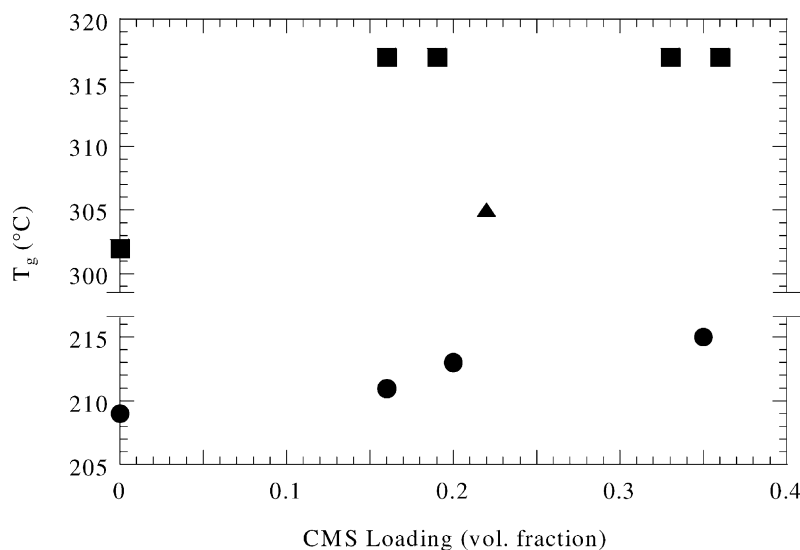


Fig. 6. Increases in glass transition temperature ( $T_g$ ) over a range of CMS loadings in mixed matrix films: (●) Ultem® mixed matrix films, (■) Matrimid® mixed matrix films, (▲) Matrimid® mixed matrix films (primed with Ultem®, 3.8 wt.%).

In Fig. 6, for Ultem® 1000 mixed matrix films, there is a gradual or slight increase in  $T_g$  of about 2–5 °C above that of pure Ultem® 1000 with incremental increase in CMS loading. In contrast, all Matrimid® 5218 mixed matrix films (17–36 vol.% CMS) show a significant 15 °C increase in  $T_g$ . This result suggests that these Matrimid® mixed matrix films may result in more rigid Matrimid® polymer chains since chain stiffness or rigidity is often empirically correlated with glass transition temperatures [76,77]. Ultem® mixed matrix films, on the other hand, show a much less significant rigidification of the Ultem® matrix. The cause for this difference is not clear at present, but some possible explanations can be suggested.

A correlation of polymer chain mobility or stiffness with  $T_g$  increases has been noted for random ionomers. Such polymers contain non-polar backbone chains with a small quantity of polar ionic groups (less than 15 mol%) attached at random intervals, and these polar ionic groups aggregate to form clusters that can exist as a separate phase from the bulk polymer. In these ionomer systems, the  $T_g$  of the material is observed to increase with increasing ion content. To explain this phenomenon, Eisenberg et al. have proposed a model that suggests that the mobility of a polymer chain in the “immediate vicinity”

of these “multiplet-clusters” can become restricted relative to the rest of the chain in the bulk polymer [77]. They propose that the multiplet-clusters with anchored polymer chains act as effective crosslinks in the bulk polymer to increase the  $T_g$  of the material. Furthermore, they observe that the rate of  $T_g$  increase for these systems is significantly higher for polymers with relatively inflexible chains than those with more flexible chains [77]. They speculate that flexible-chain ionomers have only a thin region of restricted mobility surrounding each multiplet. These findings appear consistent with the fact that Matrimid® polymer chains are intrinsically less flexible than Ultem® polymer chains; however, more work is clearly needed on this topic.

As will be discussed in the next section, there appears to be a correlation of these  $T_g$  findings, which show significant chain rigidification of Matrimid®, but not Ultem®, with observed permeability data for Ultem® and Matrimid® mixed matrix films.

#### 4.2. Pure gas permeation of mixed matrix membrane films

Pure gas permeation data (permeabilities and O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> permselectivities) of Matrimid® 5218

Table 4

Permeation properties of mixed matrix films using Matrimid® 5218 or Ultem® 1000 as matrices at various loadings of carbon molecular sieve inserts (CMS 800-2)

Mixed matrix films	Permeability (Barrer)				Permselectivity	
	CO <sub>2</sub>	CH <sub>4</sub>	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	O <sub>2</sub> /N <sub>2</sub>
Continuous phase: Matrimid® 5218	10.0	0.28	2.12	0.32	35.3	6.6
Disperse phase: CMS 800-2	44.0	0.22	22.0	1.65	200	13.3
17 vol.% CMS	10.3	0.23	2.08	0.29	44.4	7.1
19 vol.% CMS	10.6	0.23	2.41	0.35	46.7	7.0
33 vol.% CMS	11.5	0.24	2.70	0.38	47.5	7.1
36 vol.% CMS	12.6	0.24	3.00	0.38	51.7	7.9
Continuous phase: Ultem® 1000	1.45	0.037	0.38	0.052	38.8	7.3
Disperse phase: CMS 800-2	44.0	0.22	22.0	1.65	200	13.3
16 vol.% CMS	2.51	0.058	0.56	0.071	43.0	7.9
20 vol.% CMS	2.90	0.060	0.71	0.090	48.1	7.9
35 vol.% CMS	4.48	0.083	1.09	0.136	53.7	8.0

Pure gas permeation measurements with 50 psia upstream for CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, and N<sub>2</sub>. Temperature: 35 °C.

and Ultem® 1000 mixed matrix films evaluated at 35 °C are presented in Table 4. The permeation properties of the pure continuous polymer matrices and the pure disperse sieve phases (CMS 800-2) forming the mixed matrix films are also shown for comparison. For both Ultem® and Matrimid® mixed matrix films, the pure gas permeabilities of the mixed matrix films are intermediate between the permeabilities of the constituents (except for O<sub>2</sub> and N<sub>2</sub> for the Matrimid® mixed matrix film at 17 vol.% CMS). As desired and expected, the effective fast-gas, O<sub>2</sub> and CO<sub>2</sub>, permeabilities proportionately increase in permeability with increases in CMS loading: up to 42 and 26% increases, respectively, for Matrimid® mixed matrix films over those of pure Matrimid® and up to 187 and 209% increases, respectively, for Ultem® mixed matrix films over those of pure Ultem®. Correspondingly, CO<sub>2</sub>/CH<sub>4</sub> selectivity is enhanced from 35.3 (pure Matrimid®) and 38.8 (pure Ultem®) to 51.7 (for 36 vol.% CMS in Matrimid®) and 53.7 (for 35 vol.% CMS in Ultem®), representing increases of 52 and 38%, respectively, over the pure polymers. Similar enhancements are observed for O<sub>2</sub>/N<sub>2</sub> selectivity for both mixed matrix films.

The permeation properties of these mixed matrix films in relation to properties of the pure matrix polymers are plotted in Figs. 7 and 8. As shown by these figures, significant mixed matrix behavior is achieved with incorporating CMS 800-2 into these polymer matrices for both O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> separations. The

experimental data (CO<sub>2</sub>/CH<sub>4</sub>) in Fig. 7 follows the expected performance enhancement presented in Fig. 2. A similar statement can be stated for the O<sub>2</sub>/N<sub>2</sub> separation in Fig. 8. Incorporation of the highly selective, laboratory-synthesized CMS 800-2 sieve particles significantly improves the permeation properties of the polymers, Ultem® and Matrimid®.

So far, the permeation results of mixed matrix films discussed in this section have been prepared in a manner where the priming (or sizing) polymer is the same as the bulk matrix polymer. However, the priming (or sizing) polymer may be different from the matrix polymer. This modification could hypothetically be advantageous when the matrix polymer is particularly rigid and may have poor affinity and adhesion to the sieve surface but is, however, miscible in another polymer that is more flexible and has greater adhesion to the sieve surface. Following this approach, the CMS particles may be primed (or sized) with a small quantity of the more flexible and favorable polymer and then later incorporated into the more rigid matrix polymer. This hybrid approach can benefit from the synergy of the better adhesion of the priming polymer with the better permeation properties of the matrix polymer. If the matrix polymer was used alone, it might not be initially possible at all to form a successful mixed matrix film because of the resulting poor polymer–sieve contact. Since the priming (or sizing) polymer is miscible with the matrix polymer, compatibilization would not be a problem.

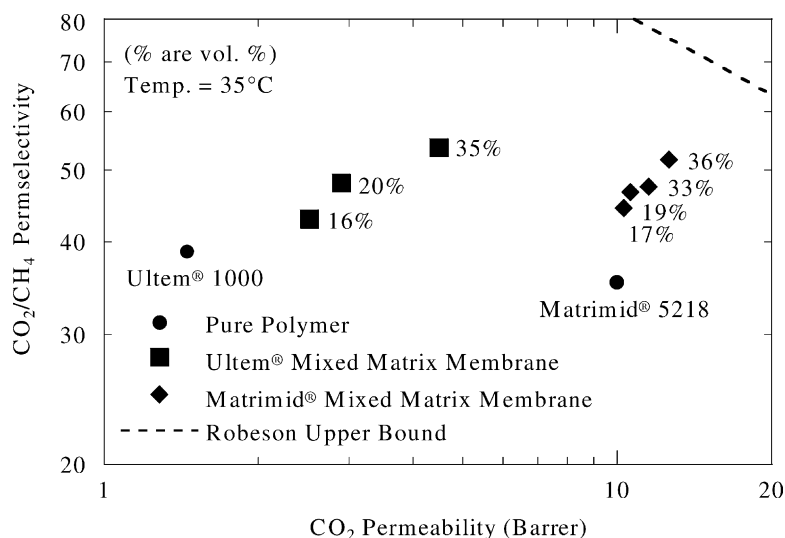


Fig. 7. CO<sub>2</sub>/CH<sub>4</sub> permeation properties of mixed matrix films using Ultem® 1000 and Matrimid® 5218 as matrices at various loadings of CMS particles. Pure gas permeation measurements (50 psia upstream for CO<sub>2</sub> and CH<sub>4</sub>). Temperature: 35°C.

Generally, most polymers are incompatible with each other and do not form homogenous, single-phase polymer blends. Incompatible blends display multiple phases and are characterized by having multiple glass transition temperatures ( $T_g$ s) [74]. Homogeneous polymer blends, on the other hand, exhibit only

one  $T_g$ . Relatively few binary, homogeneous polymer blends are known. Matrimid® and Ultem® is one such system [78]. As a proof-of-concept, a mixed matrix film was prepared in a protocol where the CMS particles were primed with a small quantity of Ultem®, but later dispersed in the matrix polymer Matrimid®. The

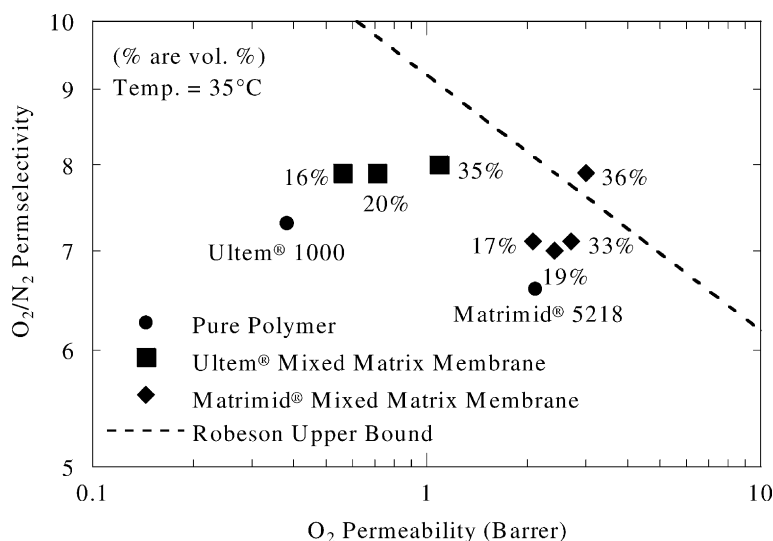


Fig. 8. O<sub>2</sub>/N<sub>2</sub> permeation properties of mixed matrix films using Ultem® 1000 and Matrimid® 5218 as matrices at various loadings of CMS particles. Pure gas permeation measurements (50 psia upstream for O<sub>2</sub> and N<sub>2</sub>). Temperature: 35°C.

Table 5

Permeation properties of mixed matrix film using a small amount of Ultem® 1000 as a “priming” polymer and Matrimid® 5218 as the continuous phase polymer matrix with 22 vol.% loading of carbon molecular sieve inserts (CMS 800-2) as the dispersed phase

Constituents	Concentration (wt.%)	Permeability (Barrer)				Permselectivity	
		CO <sub>2</sub>	CH <sub>4</sub>	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	O <sub>2</sub> /N <sub>2</sub>
Priming polymer: Ultem® 1000	0.038	1.45	0.037	0.38	0.052	38.8	7.3
Continuous Phase: Matrimid® 5218	0.732	10.0	0.28	2.12	0.32	35.3	6.6
Disperse phase: CMS 800-2	0.230	44.0	0.22	22.0	1.65	200	13.3
Mixed matrix film	22 vol.% CMS	9.40	0.21	2.14	0.293	45.2	7.3

Pure gas permeation measurements with 50 psia upstream for CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, and N<sub>2</sub>. Temperature: 35 °C.

final mixed matrix film contained 3.8 wt.% Ultem®, 73.2 wt.% Matrimid®, and 23.0 wt.% CMS 800-2. From DSC, this mixed matrix film exhibits a single  $T_g$  intermediate between the  $T_g$ s of Ultem® and Matrimid®, as observed from the first heat cycle. The permeation properties of this film are tabulated in Table 5.

Mixed matrix enhancement behavior is observed with CO<sub>2</sub>/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub> selectivities of 45.2 and 7.3, respectively, representing improvements of 28 and 11% over the respective permselectivities of the matrix polymer, Matrimid®. The pure gas permeabilities are interestingly lower than those corresponding to Matrimid®-primed Matrimid® mixed matrix films at a similar loading (see Table 4). However, these results are internally consistent with the hypothesis that the small addition of the lower-permeability Ultem® (3.8 wt.%) contributed to the reduction of the mixed matrix film permeabilities. Although this mixed matrix film contained both priming and matrix polymers that already exhibited good polymer–sieve contact and enhanced mixed matrix behavior individually, the approach, nevertheless, may be useful when other rigid, glassy polymers are found to have poor adhesion to sieves, but are homogeneously miscible in either Ultem® or Matrimid®.

Application of this approach may not be necessarily limited to cases of completely homogeneously miscible polymer blends over the entire compositional range, such as the Ultem® or Matrimid® binary pair. It is indeed difficult to get, for example, an equimolar mixture of polymer A and B when A and B are chosen at random. However, in many cases where A and B have some similarity, there is generally limited miscibility over a small range of compositions. Analogous

to the concept of “infinite dilution” mixing of low molecular weight component A in B even when they tend to be “immiscible”, some miscibility occurs for polymers in the limit of “infinite dilution”. The entropy of mixing favors this process somewhat, even when the two components do not have favorable enthalpic interactions. This study focused more on the “infinite dilution” case when the sieve is “primed” with a small amount of polymer A, and this “primed” sieve is in contact with an infinite bulk of polymer B. So, this approach may have wider applicability if only limited miscibility (i.e. “infinite dilution” case) is necessary.

#### 4.3. Mixed gas permeation of Ultem® mixed matrix membrane

The procedure and apparatus for permeation characterization of films with gas feed mixtures are similar to that for pure gas permeation and have been discussed previously in Section 3. The primary changes include a modification of the permeation testing cell to include a retentate (or residue) stream to ensure constant concentration in the upstream (<1% stage cut) and the sampling of the permeate stream to determine composition and the separation factor. Total feed pressures up to 900 psia of the 10% CO<sub>2</sub>/90% CH<sub>4</sub> gas mixture were used.

Mixed gas permeation characterization of an Ultem®–CMS mixed matrix film (35 vol.% CMS) over the 100–900 psia pressure range of 10% CO<sub>2</sub>/90% CH<sub>4</sub> feed gas is shown in Fig. 9, where the results are also compared with those of the pure Ultem® polymer film tested under identical conditions. Recall from the preceding section that this mixed matrix film has previously demonstrated successful mixed matrix

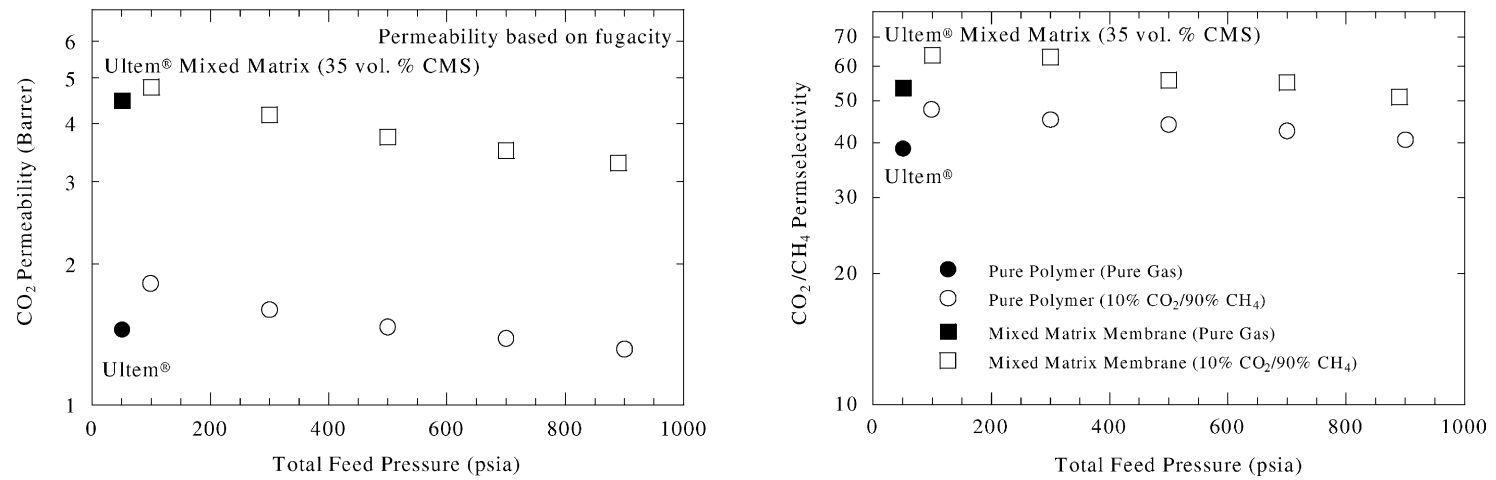


Fig. 9. Mixed gas permeation results for Ultem® mixed matrix membrane film containing 35 vol.% CMS using feed gas of 10% CO<sub>2</sub>/90% CH<sub>4</sub> at 35 °C. Results are compared with those for the pure Ultem® polymer film. Quantities were based on fugacity-defined permeability coefficients.



behavior or enhancement under pure gas permeation experiments. Results of permeation testing with 10% CO<sub>2</sub>/90% CH<sub>4</sub> in Fig. 9 confirm the impressive pure gas permeation results. The CO<sub>2</sub>/CH<sub>4</sub> permselectivity of the Ultem®–CMS mixed matrix film remains significantly higher than that for pure Ultem® (approximately 20–40% higher) up to 900 psia. CO<sub>2</sub>/CH<sub>4</sub> permselectivities for this mixed matrix film ranged from 63.6 at 100 psia to 50.9 at 900 psia total feed pressure. In contrast, CO<sub>2</sub>/CH<sub>4</sub> permselectivities for pure Ultem® ranged from 47.8 at 100 psia to 40.6 at 900 psia. In addition, the CO<sub>2</sub> permeability of the mixed matrix film is a factor of two to three times higher than that for pure Ultem®, a phenomenon that was also previously observed with pure gas permeation results.

#### 4.4. Above $T_g$ thermal annealing of mixed matrix films

As discussed in the beginning of Section 4, early mixed matrix films displayed poor polymer–sieve contact (see Fig. 4) with corresponding poor permeation properties. Several researchers [52,61] have suggested high-temperature casting conditions and/or post-treatment to improve polymer chain flexibility and mobility that could aid in conforming the polymer onto the sieve surface. Prior to introducing the simple “priming” step described in Section 3, this approach was pursued to achieve functional mixed matrix samples. Specifically, defective (35 vol.% CMS) Ultem® mixed matrix films were annealed by heating formed mixed matrix films on a Teflon® plate to 250 °C (above the 209 °C  $T_g$  of Ultem®) for 2 h in a vacuum oven. The appearance of in-tact polymer–sieve interfaces generated either by the priming or anneal-

ing procedure seems similar under standard SEM inspection, but gas permeation results reveal some differences between the primed, unannealed and unprimed, annealed samples. The pure gas permeation results are tabulated in Table 6 for comparison to data for primed, unannealed samples.

Permeation results before and after heat treatment indicate significant improvement in both O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> permselectivities. However, the resulting 250 °C annealed Ultem® mixed matrix film surprisingly exhibits significantly lower permeabilities than even the original pure Ultem®. DSC analysis of the Ultem® mixed matrix films before and after the 250 °C thermal annealing treatment indicates no change nor increase in  $T_g$  (207 °C) that would support a rigidification phenomenon. Possible explanations may be a reduced permeability of the bulk Ultem® polymer matrix because of the above  $T_g$  treatment and/or partial occlusion or pore blockage of the nanoporous CMS particles by the Ultem® polymer chains, resulting in reduced permeability of CMS particles. At the present time, this point cannot be resolved without corresponding “control” studies of the neat Ultem®. For completeness, characterization of the effects of the presence of impermeable carbon particles loaded into Ultem® samples should also be examined to determine if the permeability changes seen in the annealed samples are influenced by the presence of the carbon phase, or whether it occurs throughout the matrix polymer during the 250 °C annealing. Such a study is beyond the scope of the present work. Nevertheless, despite the reduced permeabilities, the above  $T_g$  thermal annealing approach seems to be a possible post-treatment technique that may be pursued to improve separation properties for defective mixed matrix films showing poor polymer–sieve contact.

Table 6  
Effect of above  $T_g$  thermal annealing of a defective Ultem® 1000 mixed matrix film (35 vol.% loading of CMS) early in our work

Mixed matrix film	Permeability (Barrer)				Permselectivity	
	CO <sub>2</sub>	CH <sub>4</sub>	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	O <sub>2</sub> /N <sub>2</sub>
Continuous phase: Ultem® 1000	1.45	0.037	0.38	0.052	38.8	7.3
Disperse phase: CMS 800-2	44.0	0.22	22.0	1.65	200	13.3
35 vol.% CMS (defective)	2.74	0.097	0.60	0.095	28.2	6.3
35 vol.% CMS (after 250 °C thermal annealing)	0.88	0.018	0.27	0.035	48.3	7.7

Pure gas permeation measurements with 50 psia upstream for CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, and N<sub>2</sub>. Temperature: 35 °C.

## 5. Conclusions

It has been demonstrated that laboratory-synthesized CMS particles can be successfully incorporated into two glassy polymers, Matrimid® 5218 and Ultem® 1000, to form mixed matrix membrane films with enhanced permeation properties over those of the original polymer matrices. Unlike previous work with rubbery polymers and commercial CMS [48], where dead-end pores were present, we believe our laboratory-synthesized CMS particles formed via high-temperature pyrolysis generate molecular sieving pores and channels that allows for very high size- and shape-selective separation properties. Mixed matrix films with high CMS particle loadings (up to 35 wt.%) dispersed within Matrimid® 5218 and Ultem® 1000 were successfully formed from flat-sheet solution casting. Some modifications to the casting protocol and preparation techniques were discussed, resulting in improved polymer–sieve contact and morphologies.

As discussed in the paper, Ultem® and Matrimid® mixed matrix membranes display significant enhancements in both CO<sub>2</sub>/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub> selectivities with enhancements by as much as 45% in CO<sub>2</sub>/CH<sub>4</sub> selectivity and 20% in O<sub>2</sub>/N<sub>2</sub> selectivity. Effective permeabilities of the fast-gas penetrants (O<sub>2</sub> and CO<sub>2</sub>) through the mixed matrix membranes were also significantly enhanced over the intrinsic permeabilities of the Ultem® and Matrimid® polymer matrices. High-pressure, mixed gas permeation experiments (10% CO<sub>2</sub>/90% CH<sub>4</sub>) on a high-loading Ultem®–CMS mixed matrix film further confirm these results.

Mixed matrix membrane research into gas separations has predominantly focused on zeolites as the dispersed selective phase. However, the CMS particles discussed in this paper seemingly offer several advantages over zeolites as possible molecular sieving entities for incorporation into mixed matrix membranes. First, the CMS particles appear to have better affinity to glassy polymers, achieving good adhesion and polymer–sieve contact with minimal preparation and casting modifications. In contrast, mixed matrix work with zeolites has identified poor polymer–sieve as a significant hurdle for successful film formation. Current strategies (high casting temperatures, surface treatment of zeolites, use of plasticizers, or use of chemically reactive techniques) that have been exam-

ined or discussed introduce processing complexities (casting conditions and pre- and post-treatment) and may be industrially undesirable for scale-up. Second, the permeation properties (permeability and selectivity) of our CMS particles are tailorable by modifying the pyrolysis protocol. Such adaptability may be advantageous when other gas separations are considered.

In particular, the CO<sub>2</sub>/CH<sub>4</sub> separation discussed in this paper indicate a very promising potential in using mixed matrix membranes for natural gas purification (i.e. CO<sub>2</sub> removal from natural gas). Continuing work is evaluating other higher performance polymers as the continuous matrix phase and examining mathematical models that predict permeation behavior of mixed matrix membranes. Results of this work will be presented in future publications.

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## Appendix A

As a comparison to the laboratory-pyrolyzed CMS 800-2 used to make mixed matrix membrane films presented in this paper, a sample of commercial CMS manufactured by Takeda Chemicals in Japan was examined as the dispersed phase for mixed matrix films. The Takeda commercial CMS materials are carbonized from coconut shells through a proprietary process. The pore structure of Takeda CMS are generally considered to have “narrow pores” suitable for air separation

in pressure swing adsorption (PSA) applications. Generally, the pore structure of such CMS materials are controlled or modified by depositing carbon within the pores of the CMS surface through the cracking of hydrocarbon gas. Besides Takeda Chemicals, other major manufacturers who use similar processes to make commercial CMS materials include Air Products Inc. (Allentown, PA) and Bergbau-Forschung (now called CarboTech, Germany).

The Takeda CMS sample was in pellet form and was ball-milled with the same steps outlined in Section 3. The ball-milled Takeda CMS powder was dispersed in  $\text{CH}_2\text{Cl}_2$  solvent and was used to form high loading

(35 wt.%) Ultem® 1000 and Matrimid® 5218 mixed matrix films, as described previously for CMS 800-2 powder. Identical preparation and formation procedures (i.e. sonication, decantation, “priming”, etc.) were performed. Both mixed matrix films were characterized with scanning electron microscopy, exhibiting excellent polymer–sieve contact, similar to the SEM micrographs of successful mixed matrix films discussed in this paper. Pure gas permeation experiments were performed on the Takeda CMS–Matrimid® 5218 mixed matrix film. The results for the  $\text{CO}_2/\text{CH}_4$  and  $\text{O}_2/\text{N}_2$  separations are presented in Fig. 10. So, despite the very attractive polymer–sieve contact

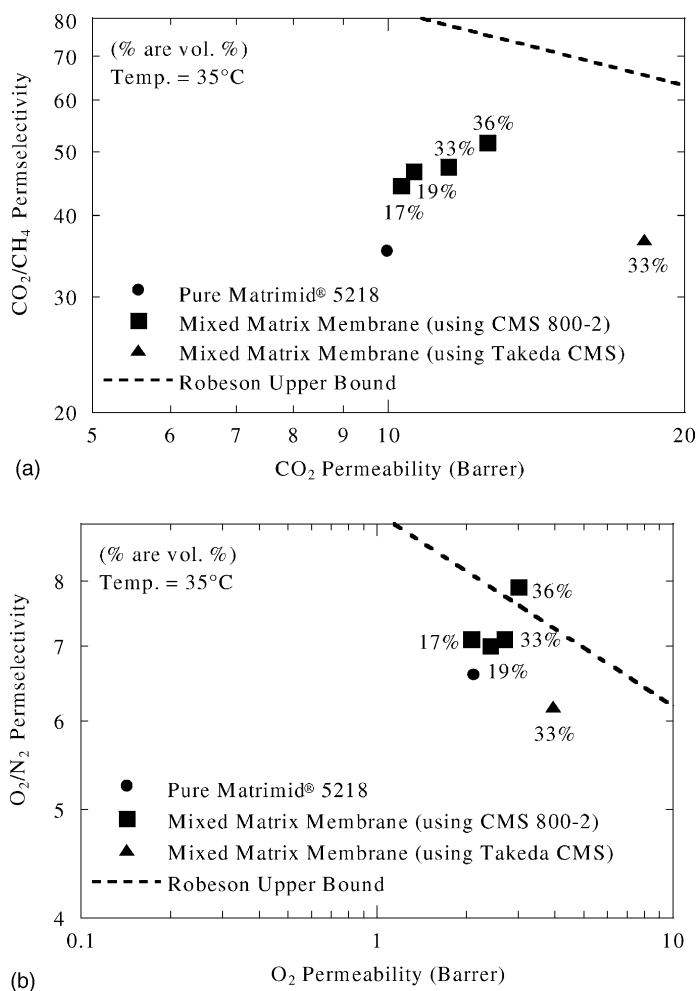


Fig. 10. Comparison of membrane properties of mixed matrix films prepared with the dispersed phase using either CMS 800-2 or Takeda commercial CMS for (a) the  $\text{CO}_2/\text{CH}_4$  separation and (b) the  $\text{O}_2/\text{N}_2$  separation. Pure gas permeation experiments at 50 psia upstream and vacuum downstream at 35 °C.

observed with the SEM micrographs, the Takeda CMS–Matrimid® 5218 mixed matrix film exhibits very poor membrane properties. It appears likely that the highly porous substrate supporting the molecular sieve pores at the surface dominate the effects of incorporation of such materials. Specifically, enhanced permeabilities without improved selectivities tend to be the primary effects observed. This is clearly quite different than observed when the essentially homogeneously molecular sieving carbons produced in this study are used in formulating mixed matrix materials.

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