

# Challenges in Forming Successful Mixed Matrix Membranes with Rigid Polymeric Materials

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**ABSTRACT:** Mixed matrix materials comprised of molecular sieve domains embedded in processable polymer matrices have the potential to provide membranes with higher permselectivity and equivalent productivity compared to existing membrane materials. It has been shown that successful mixed matrix materials can be formed using relatively low glass transition ( $T_g$ ) polymers that have a favorable interaction with the sieves. This article extends this earlier work to include the use of more practical rigid matrix polymers with high  $T_g$ s that can ultimately be used in forming high-performance mixed matrix layers for composite membranes. Initial attempts to form mixed matrix materials based on high  $T_g$  polymers with a type 4A zeolite resulted in poor adhesion between the polymer and sieve. Correcting this problem was pursued in this study by forming the

composite material close to the  $T_g$  of the polymer by addition of a plasticizer to match the matrix  $T_g$  with the solvent volatility. Forming the films at elevated temperatures presented substantial challenges, and this work discusses overcoming these challenges in detail. With some modifications in the film casting procedure, successful materials were achieved. Promising oxygen/nitrogen transport results are presented for these zeolite 4A–Matrimid®/plasticizer membranes, and this data compares favorably with predictions of the well-known Maxwell model for composite systems. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 881–890, 2002

**Key words:** membranes; gas permeation; composites; zeolites; gas separation

## INTRODUCTION

One of the immediate challenges facing membrane material design is achieving higher permselectivity with equal or greater productivity compared to existing materials. Molecular sieving membrane materials, such as zeolites, are capable of overcoming this challenge, but not in an economical way. With current manufacturing constraints, it is reasonable to expect ceramic, glass, carbon, and zeolitic membranes to cost between one and three orders of magnitude more per unit of membrane area compared to polymeric membranes. The high cost of these pure molecular sieving alternatives compromises their application relative to nonmembrane alternatives in many cases for large-scale applications.

Mixed matrix materials are a blend of molecular sieving domains within a polymer matrix. These ma-

terials combine the processability of the polymer phase with the superior transport properties of the molecular sieving phase, thereby resulting in the best of both worlds. The proposed construction, material selection issues, as well as the potential of this material have been presented in earlier work.<sup>1</sup> The proof of concept of this approach was presented in recent publications for flexible polymer matrices.<sup>2,3</sup> Truly general application of the concept requires implementation using rigid, high  $T_g$  matrices, and this extension is the topic of the present article.

## BACKGROUND

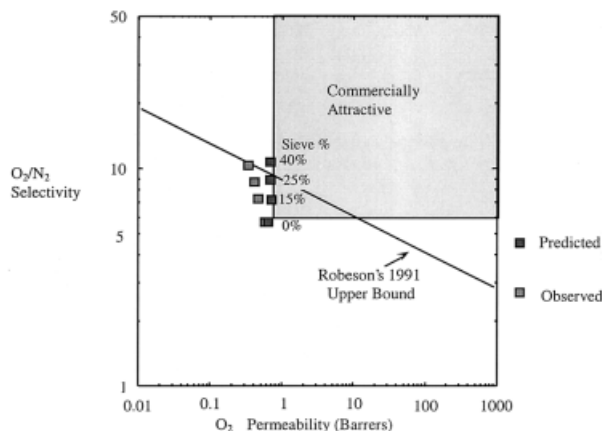
To form successful mixed matrix materials, certain key requirements need to be met. One way these requirements can be met is by choosing polymers that can maintain flexibility during membrane formation and have a favorable interaction with the sieve.<sup>4</sup> Although this approach has been used to form successful mixed matrix materials with flexible polymers such as polyvinyl acetate, such polymers have not conventionally been used for commercial gas separation applications. The formation of practical membranes with these materials presents significant challenges, and such flexible materials also tend to lack mechanical stability under high pressure and even moderate temperatures. Moreover, polyvinyl acetate and similar materials lack extremely attractive inherent transport properties, rel-

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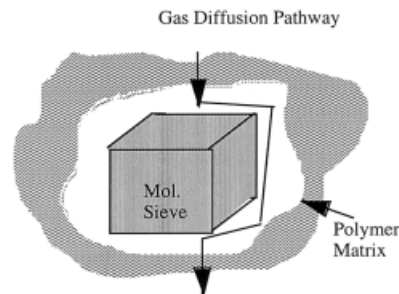
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**Figure 1** Predicted  $O_2/N_2$  transport properties using the Maxwell model compared to observed Zeolite 4A-PVAc mixed matrix membrane performance plotted on Robeson's 1991  $O_2/N_2$  "upper bound."

ative to the well-known "upper bound" performance achievable with rigid, high  $T_g$  polymers.<sup>5</sup> Because the pure polymer properties represent the base that must be improved upon by incorporation of sieves, it is desirable to work with starting matrices closer to the state-of-the-art performance polymers. For instance, even at 40% loading, the PVAc-zeolite 4A system, although significantly improved over the base case, is still slightly below the  $O_2/N_2$  "upper bound" (Fig. 1). One could presumably overcome this by using still higher sieve loading, but this seems to be a suboptimal strategy. The theoretical predictions shown in Figure 1 are based on the simple Maxwell model.<sup>3,6,7</sup> The reasonable agreement between the experimental and predicted values provide a general validation of the mixed matrix concept, proving one can improve the transport properties of a material by the incorporation of suitable sieve materials.

As noted above, polymers currently used for commercial gas separations are rigid and have properties that are much closer to the "upper bound." Formation of a mixed matrix material using such materials presents special challenges, as will be considered in the next section.



**Figure 2** Schematic representation of an undesirable gap between the polymer matrix and the molecular sieve insert, commonly referred to as "sieve in a cage" morphology.

## MATERIALS: ZEOLITE-4A-MATRIMID®

### Transport results

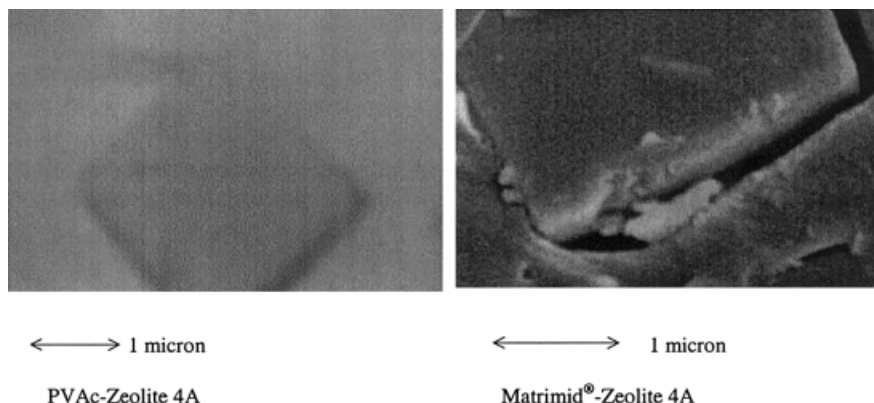
Matrimid is typical of practical gas separation polymers,<sup>8</sup> and type 4A zeolites have properties that complement those of Matrimid®, thereby potentially producing a composite material with properties above the "upper bound" (Fig. 1). Zeolite 4A and Matrimid® mixed matrix composite films were prepared using conventional film formation techniques reported elsewhere.<sup>2</sup> Pure gas permeation measurements were made using equipment and a procedure previously described.<sup>3,9</sup> Upstream pressures varied from 40–90 psia for permeation measurements. All experiments were conducted at 35°C unless otherwise noted.

Transport results for the  $O_2/N_2$  system are reported in Table I for zeolite 4A mixed matrix membrane materials. These data indicate selectivities approaching those of the native polymer at best. Also, much higher permeabilities were observed compared to the predictions of the Maxwell model. These results suggest that poor contact exists between the two phases, probably due to dewetting of polymer chains from the sieve surface. A molecular sieve enclosed in a polymer cage with void space between the two phases appears to be the picture (Fig. 2) that best explains the observed data. Because the cage is "closed," intrinsic polymer selectivities result because the gap between the sieve and the polymer provides a less resistive route to gas diffusion, and results in bypassing of the molecular sieve with higher apparent permeabilities.

**TABLE I**  
Zeolite 4A-Matrimid® Mixed Matrix Film Performance, Predicted (Using the Maxwell Model) versus Observed

Membrane	$\alpha_{O_2/N_2}$	$P_{O_2}$ (Barrers)
Matrimid®	7.2	1.32
Zeolite 4A (20% by vol.) in Matrimid® (Predicted)	8.5	1.2
Zeolite 4A (20% by vol.) in Matrimid® (Observed)	7.2	4.0

All measurements at 25°C and 50 psia feed pressure.

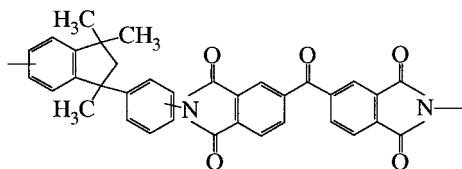


**Figure 3** Scanning electron micrographs (SEM) showing a cross-section of a PVAc-Zeolite 4A Mixed Matrix material in comparison with Matrimid-Zeolite 4A Mixed Matrix material.

SEM photographs, shown in Figure 3, support the above picture and illustrate the marked difference in polymer-sieve contact using the flexible PVAc and the rigid Matrimid<sup>®</sup>. The previously studied PVAc-Zeolite 4A material shows good adhesion between the polymer and the sieve, consistent with the results in Figure 1, while the Matrimid<sup>®</sup>-Zeolite 4A material shows poor adhesion in the SEM photograph, consistent with the results in Table I. To form mixed matrix materials with such rigid polymers, one needs to consider alternative strategies compared to those that suffice for flexible matrix polymers.

#### Possible causes of "interphase" formation

In the following discussion the term "interphase" will be used to indicate a domain extending from the sieve surface that ultimately merges with the bulk matrix phase. A significant mismatch between the properties of this hypothetical phase and the sieve or bulk phase can produce unsatisfactory mixed matrix material properties.<sup>4</sup> Two factors seem to be critical to the formation of the interphase: the nature of the polymer-sieve interaction, and the stress encountered during material preparation. The interaction between the polymer and sieve is a fundamental property of the chemical nature of the polymer and sieve surfaces, and can be attractive, repulsive, or neutral. Type 4A sieves have a hydrophilic surface due to the presence of hydroxyl groups. On the other hand, Matrimid<sup>®</sup> is relatively hydrophobic, with a mixture of polar, aliphatic, and aromatic groups (see Fig. 4), which does



**Figure 4** Chemical structure of Matrimid<sup>®</sup> polyimide.

not indicate whether the polymer will interact favorably with the hydrophilic zeolite.

The second factor cited above, stresses generated during removal of solvent, will tend to be large for a rigid material like Matrimid<sup>®</sup>. To better understand how the flexibility of the matrix can affect the final mixed matrix material morphology, one can consider a simple example. For simplicity, consider a sieve with a neutral interaction, i.e., neither attractive nor repulsive with two different polymers that differ in their flexibility. If one polymer is extremely flexible, while the other is very rigid the formation of a mixed matrix film using conventional solution casting techniques can be expected to provide rather different outcomes. When the film is cast, one can envision a polymer solution in intimate contact with the sieve. As the solvent evaporates, the overall film will shrink due to solvent loss, but in both cases, the highly solvent-swollen polymers are expected to maintain adequate contact with the sieve. This is again a reasonable assumption, because in the swollen condition both polymers are flexible and can easily conform to the sieve surface as the film shrinks. Ultimately, however, solvent loss will cause the swollen rigid polymer to become a glass and lose flexibility. At this time, most but not all of the solvent would have left the polymer. When the remaining solvent leaves the system, further shrinkage can induce huge stresses in the high modulus matrix and cause a tendency to detach from the sieve surface. This rigid phase shrinkage is probably manifested as defects along the polymer sieve boundary, leading to the formation of the interphase. Even when all the solvent has left the intrinsically flexible polymer, it can conform to the sieve surface, and any residual stresses can be relieved, thereby suppressing a defectively packed "interphase." This simple picture is shown as a schematic in Figure 5.

The above simple picture, based on neutral interaction between the sieve and polymer, will be complicated somewhat for flexible polymers with a repulsive



**Figure 5** Hypothetical picture of mixed matrix material formation leading to formation of defects with rigid polymeric materials and defect-free materials with flexible polymers.

interaction or for rigid polymers with a strong attractive surface interaction. In this latter case, even if the polymer cannot completely detach from the sieve surface it may be highly stressed at a segmental level, leading to the formation of a region of disturbed packing. On the other hand, for a flexible material with repulsive interactions, the polymer may or may not conform to the sieve surface, but the tendency to form a “sieve in a cage” would be less pronounced than for a similarly repulsive glassy polymer matrix.

In any case, for a given polymer, the flexibility of the matrix during the solvent removal will be the key issue considered in the following study. Detailed polymer–sieve interaction issues will be considered in a separate publication. The glass transition temperature ( $T_g$ ) provides an indirect measurement of the degree of flexibility of polymeric materials at room temperature; the lower the  $T_g$ , the more flexible the material. Therefore, the  $T_g$  of the matrix can be used as an engineering tool to tailor the polymer–sieve interphase.

## FLEXIBILITY DURING MEMBRANE FORMATION

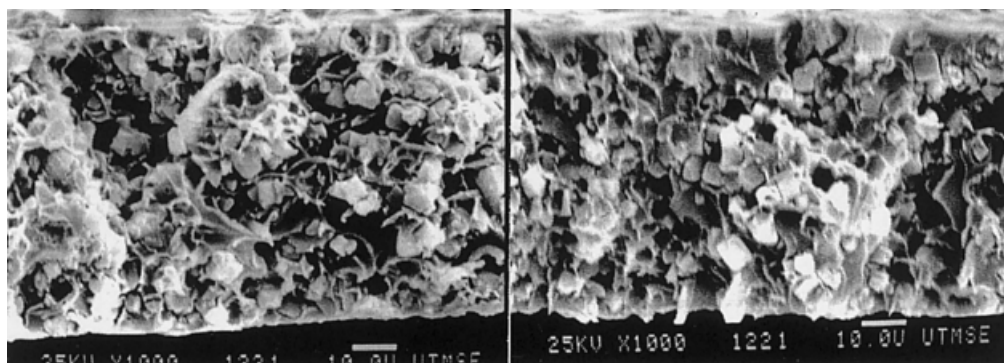
### Strategies to eliminate “sieve in a cage” morphology

The foregoing analysis supports the suggestion that flexibility of the polymer matrix is a key factor to control “sieve in a cage” morphology. With this understanding, an initial attempt to “heal” apparent defects was tried by annealing already formed mixed

matrix membranes above the glass transition temperature. A Matrimid®–zeolite 4A mixed matrix material was prepared using conventional film formation techniques described earlier,<sup>2</sup> and these samples maintained their sieve-in-a-cage morphology. The same material was heated to 400°C in an inert atmosphere. This temperature is well above the glass transition temperature of the polymer (305°C); however, annealing the defective membranes *did not lead* to any significant improvement in the morphology as shown in SEM photographs (Fig. 6). This experiment indicated that once the “sieve-in-a-cage” morphology is formed, it is extremely hard to create a material with good contact between the polymer and the sieve. Clearly, membrane material preparation should aim at preventing the formation of “sieve-in-a-cage” morphology rather than healing it.

Another approach to achieving flexibility during membrane formation is to mimic the use of a low  $T_g$  polymer by actually forming the membrane *close to the glass transition temperature* of the polymer used as the matrix. An obvious limitation in such an approach is the common tendency of using convenient casting solvents that boil at temperatures below the  $T_g$  of a typical rigid polymer like Matrimid®. Table II lists some common solvents that can be used for these engineering polymers along with the  $T_g$ s of typical engineering polymers. As one can observe from Table II, the only engineering polymer that could be used in a conventional atmospheric cast environment with commonly used solvents would be Udel® (polysulfone); however, an analysis published earlier indicated that Udel® does not have a very favorable interaction with the sieve surface,<sup>4</sup> so this material does not seem to be an attractive candidate.

One can also achieve flexibility during membrane formation with a wide range of high  $T_g$  polymers by the incorporation of a plasticizer (to decrease the  $T_g$ ) coupled with the use of a low-volatility solvent (to increase the temperature of membrane formation). The mixture can be kept below its effective  $T_g$  by



**Figure 6** SEM's showing effect of annealing a mixed matrix membrane material (Matrimid®/20% zeolite 4A) with “sieve-in-a-cage” morphology above the glass transition temperature.

**TABLE II**  
**Normal Boiling Point of Common Solvents Used**  
**for Engineering Polymers and the  $T_g$**   
**of Engineering Polymers**

Solvents	B. P. (°C)
a. Boiling points of common solvents	
Methylene chloride	40
Tetrahydrofuran	65.4
Dimethylformamide	153
2-Methoxyethyl ether (Diglyme)	162
Dimethylacetamide	165.2
Dimethylsulfoxide	189
1-methyl-2-pyrrolidinone	202
Polymer	$T_g$ °C
b. Glass Transition Temperatures	
Udel® Polysulfone	185
Ultem® Polyetherimide	220
Matrimid® Polyimide	305

keeping the  $T_g$  of the plasticizer polymer mixture below the boiling point of the solvent. The next section examines mixed matrix material formation using this approach.

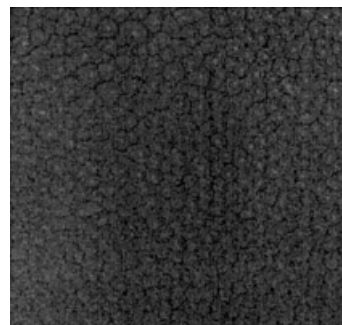
### MIXED MATRIX MATERIALS USING PLASTICIZERS TO PROMOTE FLEXIBILITY

#### Forming films at elevated temperatures

Three different plasticizers were used with Matrimid®. The plasticizers were selected such that they were compatible with Matrimid®. Compatibility was checked by the fact that the mixtures had a single glass transition temperature. Also, it was verified that the mixture led to the formation of a single phase (ascertained by SEM and optical clarity in the film without sieves present). The glass transition temperatures of the Matrimid®/plasticizer mixture were measured using a Perkin-Elmer 7 DSC. The mixtures used for all three plasticizers were 75% polymer and 25% plasticizer by weight, and in all cases the glass transition temperature of the plasticized polymer was less than 161°C, as shown in Table III. Based on these  $T_g$ s and Table II, 1-methyl-2-pyrrolidinone was chosen as the solvent. Clearly, the incorporation of plasticizer changes the properties of the matrix, and therefore Matrimid®/plasticizer transport properties were de-

**TABLE III**  
**Observed  $T_g$ s of Matrimid® and 25 wt %**  
**Plasticizer Mixtures**

Plasticizer	$T_g$ of 25 wt % Plasticizer–Matrimid® mixture
RDP Fyroflex®	161°C
Di-Butyl Phthalate	150°C
4-Hydroxy Benzophenone	144°C



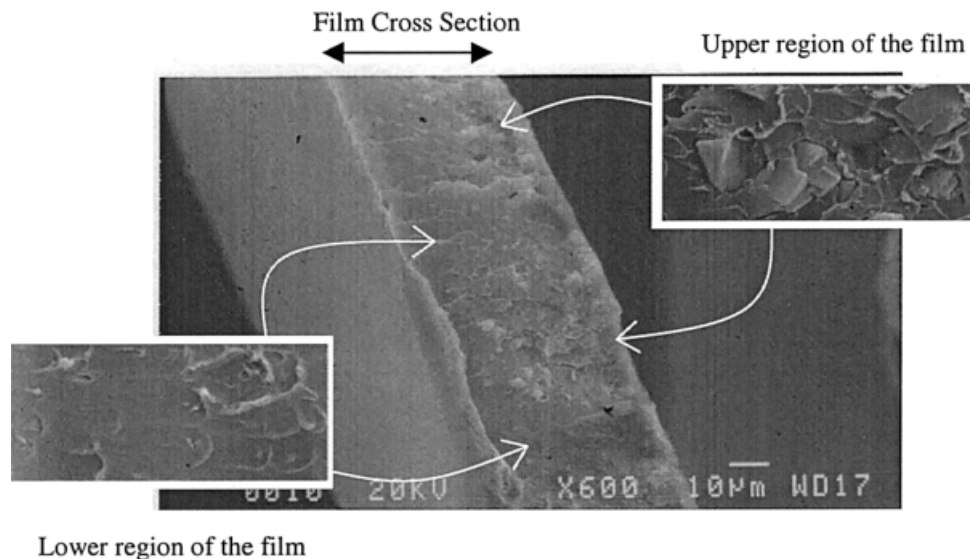
**Figure 7** Photograph depicting the formation of discernable patterns on the surface of mixed matrix films (75/25 Matrimid®/Di-ButylPhthalate with 15% zeolite 4A) cast at elevated temperatures using a heat source on the bottom surface of the film.

termined for each mixture. This was then followed by the formation of mixed matrix membranes at low loading using the above-mentioned approach. The solution was prepared by dispersing the sieves in a solvent and rolling on a standard roll mill after sonication, as described previously.<sup>3</sup> This was followed by the addition of an appropriate amount of plasticizer after which the polymer was added. It is possible that, due to plasticizer volatilization during film formation at elevated temperatures, the plasticizer polymer ratio might have changed. However, due to the low volatility of the plasticizers this loss is anticipated to be minimal; furthermore, the  $T_g$ s listed in Table III are for films that were prepared at the elevated temperatures.

When these films were formed at elevated temperatures, a discernable accumulation pattern of zeolites on the surface of the film resulted. As shown in Figure 7, there were alternating areas with aggregations of zeolites and areas with no zeolites at all. This is extremely undesirable because aggregation of zeolites causes a dramatic decline in the transport performance of the membrane. These losses occur because of a nonhomogenous morphology, as well as poor contact between the polymer and sieve at the aggregates, as shown in SEM photographs in Figure 8. To prevent this pattern formation on the film surfaces, an understanding of what causes these patterns is helpful. The next section examines the formation of these patterns from a theoretical perspective.

#### Pattern formation

It is believed the surface patterns shown in Figure 7 are the result of convection cells that form during the casting of the film. A simplified schematic of the film formation process is presented in Figure 9. After the solvent evaporates and the film forms, the convection cells lead to the deposition of aggregates of zeolites at the surface spaced at regular intervals.



**Figure 8** Scanning electron micrographs show the aggregation of zeolites on the surface of mixed matrix films (75/25 Matrimid®/Di-ButylPhthalate with 15% zeolite 4A) cast at elevated temperatures using a heat source on the bottom surface of the film.

The formation of convection cells in liquids that are heated or cooled can be due to instabilities driven by buoyancy or surface tension.<sup>10</sup> Tan and Thorpe predicted a theoretical limiting depth that differentiates between surface tension and buoyancy-controlled convection.<sup>11</sup> It was shown both theoretically and experimentally that surface tension dominates for fluid depths less than 5 mm and buoyancy predominates for depths over 10 mm. Because the largest depth encountered with these films was  $\sim 0.4$  mm (the clearance of the casting knife), it was reasonable to assume that the mechanism of instability leading to the convection cells was driven by surface tension. However, it was of some use to further investigate this issue.

The instability mechanism is illustrated in Figure 9. The film is initially at uniform thickness, and the instability begins when a small disturbance causes a point of localized heating on the surface. The result is a decreased surface tension at this point that causes a surface tension gradient to form. This gradient leads to horizontal fluid motion away from the point of local heating. Conservation of mass induces bulk fluid to

move toward the surface at the point of local heating. Because of the temperature gradient, the fluid from below is warmer than the fluid it is replacing. This leads to further increase in the temperature at the point of local heating causing the formation of a self-propagating instability. The instability can be maintained if motion due to convection can overcome viscous forces. Zeolites can then become “trapped” at the top surface, which maintains a higher viscosity than the lower bulk fluid as depicted in Figure 9.

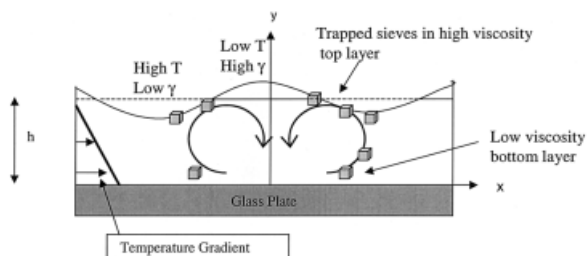
The important dimensionless quantity that emerges from doing a scaling analysis on the relevant parameters of the problem is the Marangoni number,<sup>10</sup> the ratio of surface tension forces to viscous forces. The Marangoni number is defined by eq. (1) below.

$$Ma = \frac{\left(\frac{\partial \gamma}{\partial T}\right) \beta}{\mu \alpha} h^2 \quad (1)$$

Here,  $\partial \gamma / \partial T$  is the surface tension gradient with temperature,  $\beta$  is the temperature gradient,  $h$  is the thickness of the film,  $\mu$  is the viscosity, and  $\alpha$  is the thermal diffusivity.

Pearson found that the critical Marangoni number for instability to occur is 79.6.<sup>10</sup> Tan and Thorpe recently did an analysis of convection cells in thin films, which took into account evaporative cooling.<sup>11</sup> Their analysis, in addition to providing a critical Marangoni number for the onset of instability, also predicted the wavelength of the cells, which can be compared to the measured size.

The governing equation for the wavelength of the cells is given below.



**Figure 9** Development of the instability in films cast at elevated temperature.

$$\lambda_c = \frac{831\mu\alpha}{\left(\frac{\partial\gamma}{\partial T}\right)\Delta T_s} \quad (2)$$

where  $\Delta T_s$  is the temperature difference between the bulk and surface of the film. This wavelength assumes a hexagonal shaped cell, and evaporative cooling at the surface of the film.

These parameters were quantified for the casting of mixed matrix films. The Marangoni number for our system was calculated to be approximately 320 at a temperature of 180°C (surface of the heat source), which indicates that the observed cells are, most likely, the result of surface tension driven flow. In addition, a Rayleigh number was calculated. The Rayleigh number is a dimensionless parameter that gives the ratio of buoyancy forces to viscous forces. The calculated Rayleigh number was approximately 6.5, much lower than the critical Rayleigh number of 669 needed to induce buoyancy driven convection cells.<sup>11</sup> Thus, this analysis indicates that buoyancy is not the dominant force for convection.

Furthermore, the critical wavelength was calculated to be 1.0 mm. The calculated wavelength corresponds well with the measured value of the cell sizes, which was approximately 1.0 mm (Fig. 7). The sizes of the cells were not uniform throughout the film surface possibly due to a nonuniform temperature distribution close to the edges of the hot plate. The cells were also quite often in the shape of a hexagon, which has been observed by many previous researchers.<sup>12</sup>

With the physical understanding of the problem in hand it is possible to change experimental parameters to eliminate the instability that drives the cell formation. The obvious method to do this would be to lower the Marangoni number. Decreasing the thickness of the film can most effectively do this. However, there is a limiting thickness that is needed to form a membrane film with good mechanical properties and adequate dispersion of zeolites.

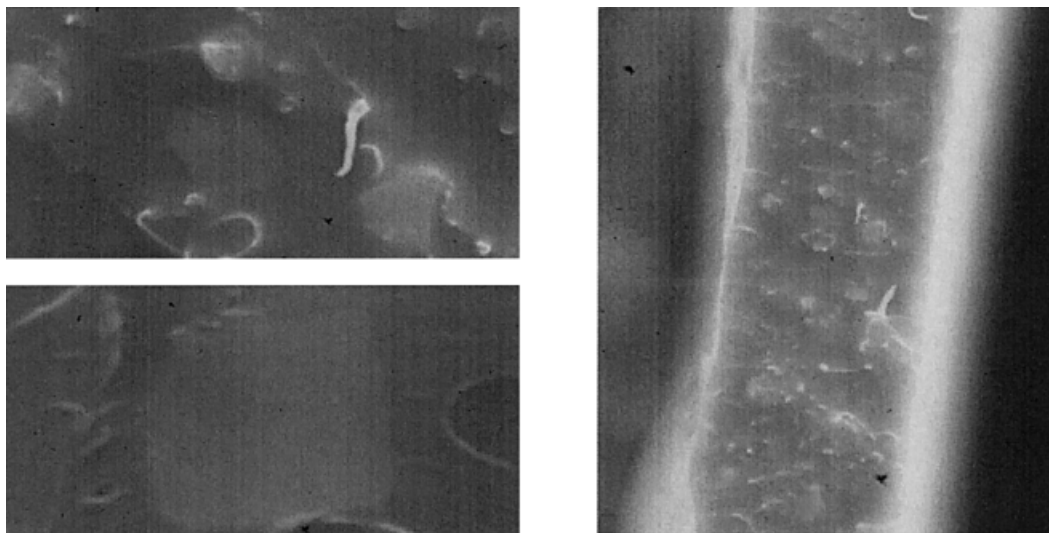
Another approach is to examine the onset of the instability. The fact that the film is heated from below causes warmer fluid to flow to the localized heating point, which maintains the instability. If the temperature gradient were reversed, and the film were heated from above, the instability would still originate in the same fashion (points of local heating). Nevertheless, in this case, colder fluid from the bulk would replace the fluid at the localized heating point and never allow the instability to propagate (as the surface tension gradient would be immediately reversed). Reversing the temperature gradient was the approach taken, and instead of casting on a hot surface, the film was heated from above during casting. The next section outlines the experimental details of the approach.

### Modified experimental setup for successful film formation at elevated temperatures

To check the hypothesis that reversing the temperature gradient could subdue the pattern formation in mixed matrix films at higher temperatures, casting was performed by heating from above using a thin flexible heater (OMEGALUX<sup>®</sup> obtained from OMEGA Inc. Stamford, CT). The heater was placed a few inches above the casting surface. The film was cast on a glass plate, which was placed on a laboratory jack. After casting, the film surface was elevated to the heater reaching a clearance of a few millimeters. Then, the film was maintained in that position until all the solvent evaporated, and this was followed by vacuum drying at 200°C. This method greatly reduced the onset of convection cells and led to homogenous mixed matrix films. The films appeared to be free of patterns and scanning electron micrographs showed well-dispersed unaggregated sieves, as shown in Figure 10.

Nevertheless, other problems remained when certain solvents were used in casting at elevated temperatures. Some of the solvents (1-methyl-2-pyrrolidinone and 2-pyrrolidinone) became discolored and possibly degraded if exposed to oxygen at high temperatures. To prevent this problem, the technique was modified. Specifically, subsequent films were simply cast in the vacuum oven. The solution was spread out on the smooth casting surface at room temperature using the casting knife. The casting surface was placed close to the top wall of the oven (the heating surface). This, in effect, achieved the required reverse temperature gradient. The oven was already preheated to a temperature that was 20–40°C less than the desired casting temperature and had inert purge gas flowing through rather than applying a strong vacuum. It was also ensured (through choice of the solvent) that the oven temperature was at least 30°C less than the normal boiling temperature of the solvent. This was necessary to ensure that the solvent did not evaporate too quickly. Once the casting surface with the solution was placed in the oven, a slight vacuum (less than 10 inches of Hg) was applied to the system with the inert purge gas still flowing. The temperature of the oven was then slowly increased (10°C per hour) to the desired temperature. A liquid nitrogen trap was used to trap solvent vapors, and the solvent was allowed to evaporate for around an hour with partial vacuum. This procedure was usually adequate to obtain a film, and after this step, the purge line to the vacuum was closed and complete vacuum was applied to the oven at the desired temperature. The film was left at the desired temperature for around 12 hours, and slowly cooled to room temperature.

At times there was considerable difficulty in removing films from the glass surface on which they were



**Figure 10** SEM photographs of mixed matrix films (75/25 Matrimid®/Di-ButylPhthalate with 15% zeolite 4A ) cast using a reversed temperature gradient. Films are free of patterns and appear to have well dispersed unaggregated sieves.

cast. Coating the glass surface with a suitable hydrophobic coating solved this problem. The coating used was GLASSCLAD® 18 obtained from United Chemical Technologies. The coating is known to reduce the polar sites on the glass surface, and therefore, lower the surface tension.

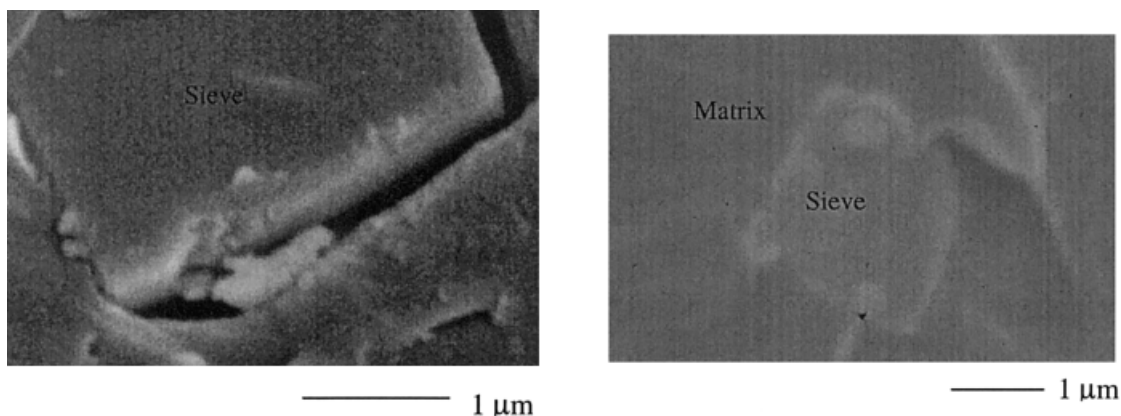
This approach eliminated surface patterns for most films; however some of the films still showed surface aggregation on the edges possibly due to heat loss along the edges. The bulk of the film was, however, pattern-free and homogenous. The homogeneous central regions of film were used for oxygen/nitrogen pure gas permeation experiments. Occasionally a distorted pattern appeared throughout the film when working with a new material or a significantly different solids concentration. This was not surprising, because even though the reverse temperature gradient prevents the instability from propagating, the temperature gradient can still lead to the formation of con-

vection currents. In these cases the film thickness was reduced and the oven was preheated to slightly lower temperatures. This modification was usually enough to obtain pattern-free films.

With these modifications, films could be cast successfully, and SEMs indicated good contact between the zeolites and the polymer. Figure 11 compares the morphology obtained earlier (sieve in a cage) with Matrimid® and the modified membranes made using plasticizers and a low volatility solvent to maintain flexibility during membrane formation.

#### TRANSPORT PROPERTIES

The matrix (plasticizer/polymer mixture) properties along with the mixed matrix properties are summarized in Table IV. The matrix was 25 wt % plasticizer, 75 wt % polymer; and the sieve loading in the mixed matrix materials was 15% by volume. The numbers in



**Figure 11** SEM photographs showing that flexibility during membrane formation leads to improved contact between polymer and sieve.



**TABLE IV**  
**Properties of Matrimid®/Plasticizer Materials and Matrimid®/plasticizer/Zeolite 4A Mixed Matrix Materials**  
**(Numbers in Parentheses Correspond to Maxwell Model Predictions)**

Plasticizer	(75/25 Matrimid® plasticizer mixture)		(75/25 Matrimid® plasticizer mixture with 15% Zeolite 4A)	
	$\alpha$ (O <sub>2</sub> /N <sub>2</sub> )	P (O <sub>2</sub> )	$\alpha$ (O <sub>2</sub> /N <sub>2</sub> )	P (O <sub>2</sub> )
RDP Fyroflex®	7.8	0.25 Barrer	8.6 (9.4)	0.2 (0.29) Barrer
Di-Butyl Phthalate	6.6	1.50 Barrer	7.1 (7.3)	1.1 (1.4) Barrer
4-Hydroxy Benzophenone	6.4	0.55 Barrer	Could not be tested; always failed during gas testing	

parenthesis next to the mixed matrix values are predictions using the Maxwell model.<sup>6,7</sup> As can be seen from the matrix observations, and shown for other systems,<sup>13</sup> the addition of plasticizers significantly changes the polymer properties. The incorporation of sieves in the polymer clearly leads to improved performance, thereby supporting the concept of maintaining flexibility during membrane formation to form ideal mixed matrix materials.

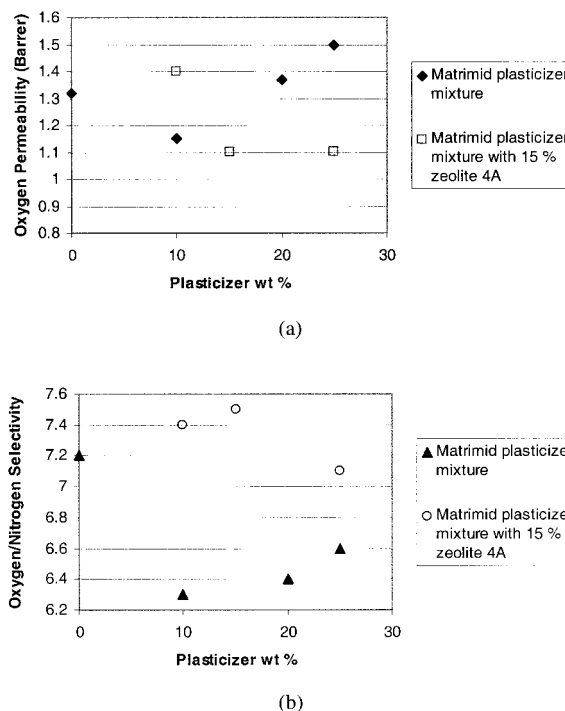
The 25/75 RDP Fyroflex®/Matrimid® film showed a lower oxygen permeability than that of the pure Matrimid®, and a larger O<sub>2</sub>/N<sub>2</sub> selectivity, which is characteristic of the effects of an antiplasticizer. The 25/75 RDP Fyroflex®/Matrimid® film with 15% zeolite 4A shows an improved O<sub>2</sub>/N<sub>2</sub> selectivity; however, the permeability is almost an order of magnitude lower than pure Matrimid® making this material unattractive in terms of transport properties relative to the O<sub>2</sub>/N<sub>2</sub> "upper bound."

The 25/75 4-Hydroxy Benzophenone/Matrimid® film exhibited lower oxygen permeability and lower O<sub>2</sub>/N<sub>2</sub> selectivity compared to pure Matrimid®. Furthermore, when the zeolite 4A was added the mixed matrix material always failed during gas testing. For these reasons no further study was conducted using this plasticizer.

The 25/75 Di-Butyl Phthalate/Matrimid® film showed a larger oxygen permeability, and a lower O<sub>2</sub>/N<sub>2</sub> selectivity compared to pure Matrimid®, as expected. The changes in the matrix properties due to addition of the plasticizer, however, made the system less attractive in terms of separation performance. In some ways this approach leads to the same issues faced with polyvinyl acetate, i.e., the matrix properties are not optimal, so that even upon improvement by incorporation of sieves, the transport properties are less attractive than state-of-the-art polymers. The comparison of the observed properties of the mixed matrix materials with Maxwell model predictions also shows trends seen earlier with the Zeolite 4A-PVAc system. The observed O<sub>2</sub>/N<sub>2</sub> selectivities are close to predicted values, but the permeabilities are much lower. In all likelihood, the lower permeabilities are due to inhibition of polymer chain mobility near the sieve-polymer interface. Such inhibition could arise from

polymer adsorption onto the surface of the sieve. This effect has also been observed by previous researchers working on related problems,<sup>14</sup> and the same trend is observed in the PVAc-Zeolite 4A mixed matrix system.

Another possible path to achieving better matrix properties is to reduce the fraction of plasticizer used, while still ensuring that flexibility during membrane formation is always maintained. Again, this was done by casting above or around the glass transition temperature of the mixture. The solvent used was 2-pyrrolidinone, which has a boiling point of 245°C; thus, giving some additional degree of freedom in the amount of plasticizer used. Based on the results seen in Table IV, the plasticizer chosen for further study was Di-ButylPhthalate.



**Figure 12** (a) Oxygen permeability of Matrimid®/plasticizer and Matrimid®/plasticizer-zeolite 4A mixed matrix membranes vs. wt % plasticizer. (b) O<sub>2</sub>/N<sub>2</sub> selectivity of Matrimid®/plasticizer and Matrimid®/plasticizer-zeolite 4A mixed matrix membranes vs. wt % plasticizer.

Additional experiments investigated the effect of decreasing the plasticizer wt % in the polymer matrix. These results are summarized in Figure 12.<sup>15</sup> Again, all mixed matrix materials had 15% by volume loading of the sieve in the matrix. The oxygen permeability of the plasticizer/Matrimid® membranes goes through a minimum as a function of plasticizer wt % as observed in Figure 12(a). Likewise, the O<sub>2</sub>/N<sub>2</sub> selectivity extends through a minimum with increasing plasticizer concentration [Fig. 12(b)]. Similar trends have been observed by Maeda and Paul for gas permeation experiments with poly (phenylene oxide), and that work provides a more detailed explanation of these trends.<sup>13</sup>

For the mixed matrix material incorporating Matrimid®/plasticizer with 15% zeolite 4A, the oxygen permeability appears to decrease with increasing plasticizer concentration [Fig. 12(a)]. There is no clear trend in terms of O<sub>2</sub>/N<sub>2</sub> selectivity vs. plasticizer concentration. A considerable improvement in O<sub>2</sub>/N<sub>2</sub> selectivity is observed for the mixed matrix materials compared to the Matrimid®/plasticizer films. The material with 10 wt % plasticizer is actually the most optimum showing a good balance of oxygen permeability and O<sub>2</sub>/N<sub>2</sub> selectivity. These results further validate the concept outlined earlier illustrating the importance of forming the membrane at or above the glass transition temperature of the matrix.

## CONCLUSIONS

It has been demonstrated that tailoring of the interphase between the polymer and the sieve is a key requirement in forming successful mixed matrix materials. There are a number of strategies to hypothetically optimize this interphase. This work has considered forming the membrane at a temperature close to the  $T_g$  of the polymer to maintain flexibility during film formation. Adding plasticizers to the film to "match" the matrix  $T_g$  with the solvent volatility was the approach taken here. Forming films at high temperatures resulted in a number of challenges, including a dispersion of zeolites at the film surface in a

hexagonal pattern of cells. Analysis of this phenomenon indicated that the cell formation is due to surface tension instabilities. Understanding this issue led to reversing the temperature gradient during film casting, which resulted in the formation of successful mixed matrix membranes. Oxygen/nitrogen transport results indicate that zeolite 4A–Matrimid®/plasticizer membranes have adequate dispersion of zeolites, as well as good adhesion between the polymer–sieve interphase. The O<sub>2</sub>/N<sub>2</sub> transport data on films formed at or above the  $T_g$  of the matrix compares favorably with the predictions of the Maxwell model. These results provide strong validation that maintaining flexibility in the matrix during film formation is a good strategy to form successful mixed matrix membranes.

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