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Jay M. S. Henis[a]; Mary K. Tripodi[a]
[a] Monsanto Company Corporate Research & Development, St. Louis, Missouri

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A NOVEL APPROACH TO GAS SEPARATIONS USING COMPOSITE HOLLOW FIBER MEMBRANES

Jay M. S. Henis and Mary K. Tripodi
Monsanto Company
Corporate Research & Development
800 North Lindbergh Boulevard
St. Louis, Missouri 63166

ABSTRACT

A method has been developed by which a porous hollow fiber which cannot separate gases to a significant extent can be made to exhibit its intrinsic separation properties by coating with an appropriate material. A unique feature of this composited fiber is that the separation properties are determined by the porous support polymer rather than by the coating polymer. The hollow fibers produced by this method have extraordinarily high rates compared to earlier hollow fibers used for gas separations. In addition, they can function under extremely high pressure gradients. Gases such as He, H_2, and CO_2 can be separated from gases like CH_4, CO, and N_2, and the system is chemically and physically stable to a wide range of typical industrial contaminants. As a result, systems based on these fibers should be useful in a variety of processes, some of which include stream splitting, gas composition control, H_2 upgrading, and purge gas recovery.

The use of membranes for gas separations has been discussed for many years.(1-3) Numerous polymers with good separation factors for gases like H_2 and He from gases like CO, CH_4, and N_2 have been reported. However, attempts to commercialize hollow fiber or other membrane systems for such separations have been unsuccessful largely because of their relatively low permeation rates and poor environmental resistance. A new type of hollow fiber membrane is described in this report which overcomes some of these earlier limitations. This fiber is a composite consisting of a porous asymmetric substrate hollow fiber made from a polymer with good intrinsic gas separating properties, and a coating polymer which has high permeabilities for gases but generally poor separating properties.

In the past, composite membranes have been made by supporting a thin separating membrane on a porous substrate to achieve high fluxes. In such membranes, the coating serves as the separating barrier, and the substrate serves only a physical support function. One of the unique features of the new composite hollow fiber membrane discussed here is that the porous substrate material, when appropriately coated, serves as the effective separating barrier as well as providing physical support for the system. It has been found that very high permeation rates for gases and excellent environmental resistance can be routinely obtained from such fibers.

A model is described below which draws an analogy between the behavior of such a composite for gas permeation and current flow through an electrical circuit. The model is referred to as the resistance model (RM), and the composite fibers are called RM composites. The model defines the term R (the resistance to gas flow) for each portion of a composite hollow fiber.

The permeation behavior of the composite hollow fiber membrane is shown to be related to the resistances to gas flow of three elements: the porous substrate material; the pores in the substrate; and the coating material. A critical factor in the behavior of RM composites is the change in the resistance of the pores in the substrate when they are filled by the coating material. By correctly using the model, a composite hollow fiber can be designed which separates through the substrate. The model predicts that many coating and substrate polymers can be combined in composite membranes which will achieve good gas separation, but only a few have the potential to be fast enough in terms of gas permeability to be economically useful on a large scale. The value of the model is that it teaches one how to utilize apparently porous fibers as separators without densifying the fiber to eliminate the pores in the surface.

Figure 1 illustrates the resistance model and indicates the key fiber structures which affect the separating properties. The resistance R of any section of the fiber is defined in Equation 1:

$$(1) \qquad R = \frac{\ell}{PA}$$

where ℓ is the thickness of that section of the membrane, P is its intrinsic permeability for a given gas, and A is the surface area. The total resistance of the fiber for a given gas, R_T, is given by Equation 2:

$$(2) \qquad R_T = R_1 + \frac{R_2 R_3}{R_2 + R_3}$$

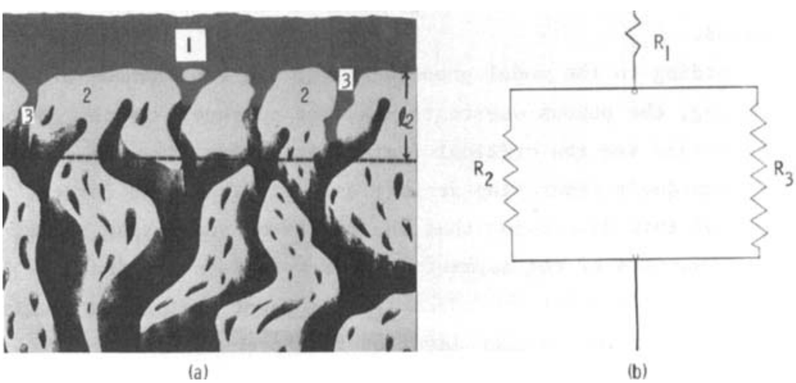

Figure 1: a) Schematic representation of the outer surface of an RM composite.

b) Electrical circuit analog of outer surface of an RM composite.

where R_1, R_2, and R_3 refer to the resistances of the designated portions of the composite shown in Figure 1. The flux Q_i for gas i is given by Equation 3:

$$(3) \qquad Q_i = \frac{\Delta p_i}{R_{T,i}}$$

where Δpi is the pressure differential for gas i across the membrane. Fluxes may be calculated for gas i in terms of the applicable ℓ's, P's and A's for each section of any given composite fiber membrane. Expected permeation rates and separation factors (ratio of the permeation rates for any two gases) can be calculated for any set of gases through any RM composite membrane, provided the intrinsic permeabilities of the gases through the coating material and substrate material can be separately determined. Using this model, it can be concluded that many materials with moderate permeabilities for most gases (e.g., polysulfone, polycarbonate, polyphenylene oxides, styrene copolymers) can be used as effective substrates with coating materials of high permeability such as silicone or hydrocarbon rubbers to yield composite membranes with high gas fluxes and good separating properties.

According to the model proposed here, the resistances of the coating, the porous substrate near the surface, and the pores at the surface are the critical factors in determining the composite membrane's separating properties. It is assumed for the purposes of this discussion that the matrix or supporting region below the surface of the asymmetric substrate is sufficiently porous that it does not represent a significant resistance to gas flow relative to the surface layer of the porous substrate. This can generally be achieved in asymmetric substrates by appropriately controlling the dope composition and coagulation conditions in the casting or spinning process. A more detailed description of the model, including matrix resistance, is presented elsewhere.(4) Typical fiber structures for good RM composite fibers are given in Figures 2-4.

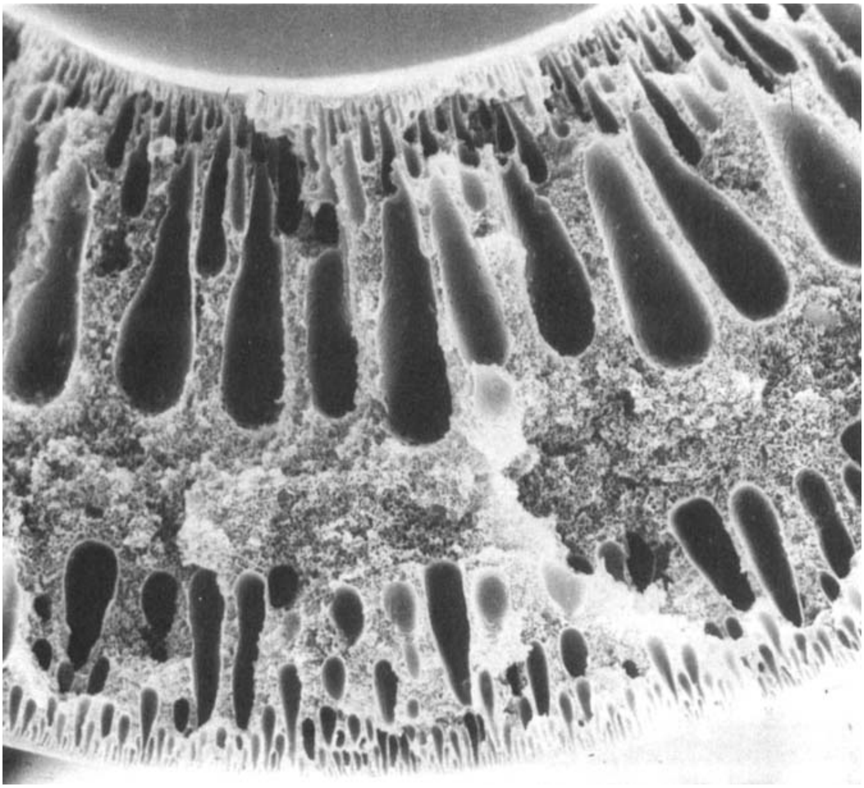

Figure 2: Cross-sectional view from inner (bore) to outer edge of RM composite hollow fiber.

Table 1 gives calculated rates (P/ℓ) and separation factors (SF) for RM composites made of several substrate and coating material combinations for H_2 and CO. The permeabilities (P's) used were determined experimentally by a technique which is described in reference 4. The permeability values obtained compare favorably to literature values, where available. The coating thicknesses (ℓ_1), effective separating layer thicknesses (ℓ_2),

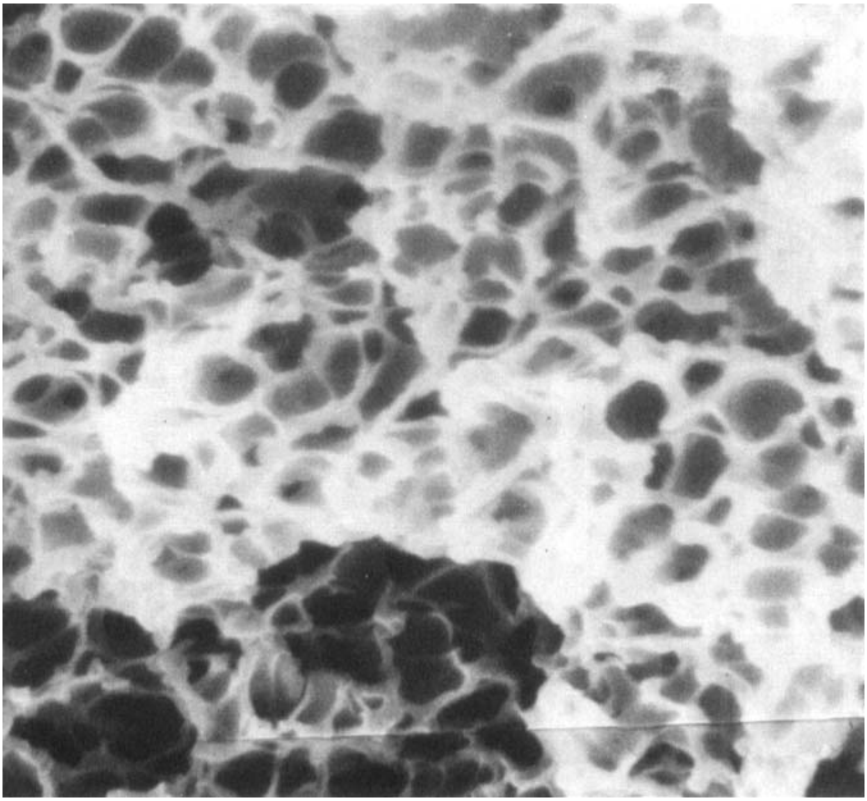

Figure 3: Close-up view of the matrix substructure halfway between the inner and outer edge of an RM composite hollow fiber.

and surface porosities (A_3) are those we have found can generally be achieved in controlled fabrication processes.

It can be seen that high fluxes and good separation factors can be expected over a range of coating thicknesses (ℓ_1) and pore cross-sectional areas (A_3) for a substrate polymer like polysulfone coated with a silicone rubber. However, for a similar composite utilizing a substrate polymer like polyacrylonitrile (PAN), calculated rates and separation factors are much more sensitive

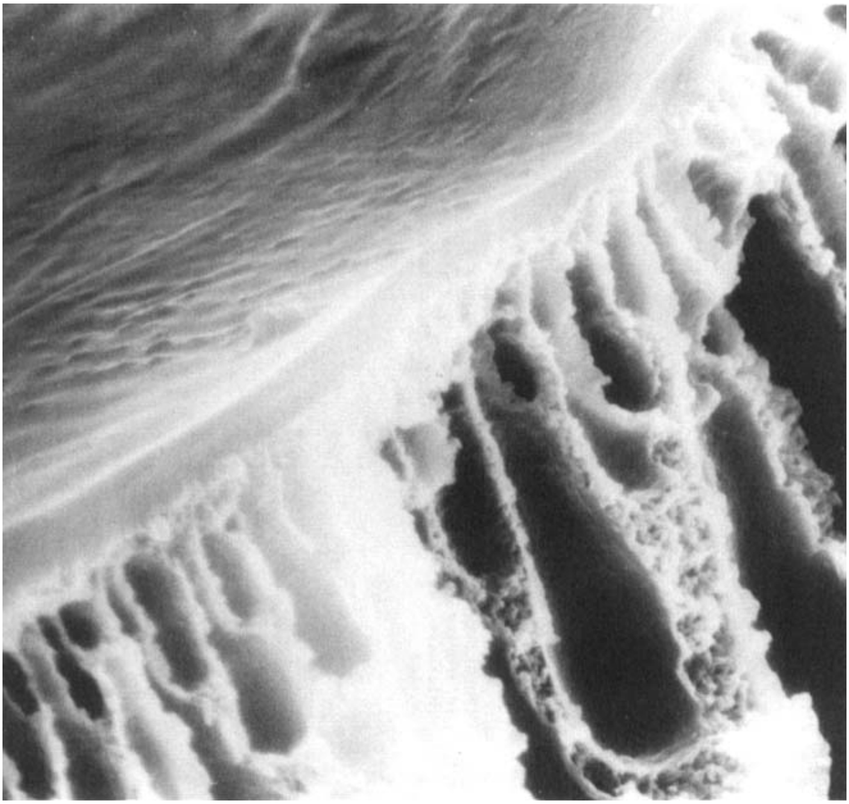

Figure 4: Close-up cross-sectional view of the outer edge of an RM composite hollow fiber. The coating is clearly visible at the surface.

to variations in ℓ_2 and A_3. The model predicts that a less porous substrate would be necessary for a PAN composite to approach its intrinsic separation factor when silicone rubber is used as the coating material, compared to polysulfone. It is interesting to note that a polymer such as polyethylene which has a lower permeability than polysulfone for H_2 would be expected to make a poor coating for polysulfone, yielding both a low rate and a low separation factor. However, due to the relative resistance relation-

TABLE 1

Calculations of P/ℓ (H_2) and $SF^{H_2}_{CO}$ for Several RM Composites

Substrate Polymer	Coating Polymer	Coating Thickness, ℓ_1 (μ)	Substrate Separating Layer Thickness, ℓ_2 (μ)	Surface Porosity, A_3 (cm^2/cm^2 of surface)	Model Predictions[1] $P/\ell \times 10^6$ (H_2) ($cc/cm^2 sec cmHg$)	Model Predictions[1] $SF^{H_2}_{CO}$
Polysulfone	Silicone Rubber	1	0.1	10^{-6}	97.5	32.9
"	"	1	0.1	10^{-4}	97.8	30.5
"	"	1	0.2	10^{-6}	53.7	36.0
"	"	5	0.2	10^{-6}	38.1	26.1
Polyacrylonitrile	"	1	0.1	10^{-6}	1.0	286.
"	"	1	0.1	10^{-4}	1.5	4.0
"	"	1	0.2	10^{-6}	0.50	286.
Polysulfone	Polyethylene	1	0.1	10^{-6}	8.1	8.5
"	"	0.2	0.1	10^{-6}	31.9	15.2
Polyacrylonitrile	"	1	0.1	10^{-6}	0.9	977.

1. The equations used to calculate P/ℓ and SF are given below and are discussed in detail in reference 4.

$$\left(\frac{P}{\ell}\right)_{\text{composite}} = \frac{\ell_1}{P_1} + \frac{\ell_2}{P_2 + P_1 A_3}$$

$$SF^{a}_{b}\ (\text{composite}) = \frac{(P/\ell)_a}{(P/\ell)_b}$$

where P_1 is the intrinsic permeability of the coating material and ℓ_1 is the coating thickness, P_2 is the intrinsic permeability of the substrate polymer and ℓ_2 is the thickness of its separating layer, and A_3 is the cross-sectional surface area of the pores as a fraction of the membrane surface area.

Values of intrinsic permeabilities used in these calculations were determined in our laboratory and are as follows (permeability units are cc-cm/cm^2-sec-cmHg):

	$P_{H_2} \times 10^{10}$	$P_{CO} \times 10^{10}$
Polysulfone	12	0.3
Silicone Rubber	520	250
Polyacrylonitrile	0.1	0.0001
Polyethylene	8.7	1.4

ships involved, it would make a better coating for PAN than would a silicone rubber.

In summary, the value of RM composites is the ease with which many polymers can be used to produce high rate, useful fibers in a reproducible manner. There have appeared many reports of asymmetric fibers and membranes produced in the laboratory which can separate gases and which have high rates. However, as workers in the field well know, it is very difficult to reproduce such results even in the laboratory, much less on a large scale. It is the nature of asymmetric membranes with thin surface layers (necessary for high rates) to be porous, and the RM composite approach appears to offer a general solution to that problem.

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