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Comments on “Highly selective polymeric membranes for gas separation” by Y. Seo, S. Kim and S.U. Hong [Polymer 47 (2006) 4501–4504]

In the paper titled ‘‘highly selective polymeric membranes for gas separation’’, the authors proposed a novel concept of a (universal) ‘‘organic molecular sieve’’ and, based on this concept, they developed membranes with a multiphase structure using a semi-crystalline polymer (nylon 6, Ny6) as a dispersed phase, an amorphous polymer (poly(2,6-dimethyl-1,4-phenylene oxide), PPO) as a matrix and an random copolymer (poly(styrene-*co*-maleic anhydride), PSMA) as a compatibilizer. They claimed that the composite membrane they developed had very good O_2/N_2 separation performance when the membrane contained 78% PPO, 20% Ny6 and 2% PSMA. The permeability of the membrane was about 3 Barrers ($1\ \text{Barrer} = 3.35 \times 10^{-16}\ \text{mol}\ \text{m}^{-1}\ \text{s}^{-1}\ \text{Pa}^{-1}$) and the selectivity for O_2/N_2 separation was 9.77. It was explained that the compatibilizer around the dispersed impermeable Ny6 phase worked as an organic molecular sieve and thus endowed the composite membrane high selectivity. I am very interested in that paper, but unfortunately I have found several problems in that paper.

1. It is said in that paper that ‘‘after diffusing through the compatibilizer, the permeants diffuse across the membrane until they meet the next impermeable barrier. This process results in the higher diffusive selectivity after each passage around the dispersed Ny6 phase than that of the homopolymer membrane. The same selection step occurs on and on. The thickness of the dispersed impermeable phase (Ny6) having optimized morphology is about 150 ± 50 nm. Thus, the composite membrane of 100 μm can have 500–1000 layers of the dispersed phase. With increasing number of passes around Ny6 phase (hence passing through PSMA phase), the selectivity goes up and up much higher than the value previously considered to be the upper-bound’’.

   According to this statement, permeates first diffuse through the compatibilizer between the matrix and the dispersed impermeable phases in the composite membrane and then diffuse across the matrix of the composite membrane. If some permeates do diffuse through the compatibilizer that has a higher selectivity for the separation of O_2 and N_2 than the matrix homopolymer (PPO), the selectivity of the composite membrane will be equal or little lower than the selectivity of the compatibilizer but higher than the selectivity of the homopolymer. There is no question about this. But how can ‘‘the same selection step occurs on and on’’ and ‘‘selectivity goes up and up’’? It should be remembered that the separation process inside a membrane is a continuous process. As a condition for a continuous process, the materials that transport through the membrane surface on the feed side should have exactly the same quantity and the same composition as the materials that transport through the membrane surface on the permeate side. In other words, if a membrane consists of many imaginative layers parallel to the surface of a membrane, all these imaginative layers have the same selectivity in a steady state. The selectivity (strictly speaking, the ideal separation selectivity) of a membrane is the characteristic of a membrane material and it is not affected by the feed composition. All membrane samples that are made from the same material should have exactly the same selectivity for a given separation task if they are all defect-free. So if you put in series pieces of membrane that are made from the same material, all these pieces of membrane will have the same selectivity. If you put in series pieces of membrane that are made from different materials, all these pieces of membrane will also have the same selectivity in a steady state and this selectivity will be equal or lower than the highest selectivity of all these pieces of membrane used. The selectivity cannot go up and up whether you put different membranes or same membranes together. Even in a non-continuous process and in an unsteady state, it is not possible to combine different membranes to get a selectivity of a membrane system that is higher than the highest selectivity of all the membranes used. The highest selectivity of all the membranes used will be the limit of the selectivity that can be obtained in a membrane system. For the composite membrane discussed, the selectivity of the compatibilizer will be the limit of the selectivity of the composite membrane and the selectivity of the composite membrane will not be higher than the selectivity of the compatibilizer (according to the paper, the selectivity of the compatibilizer is 7.77 and that of PPO is 4.1). We may also consider this point in another way. If the selectivity in that composite membrane does go up and up, then we can continuously increase the selectivity of that composite membrane to 10, 20 and even higher by increasing the thickness of that membrane (i.e. the number of the dispersed impermeable

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layers). Obviously this is absolutely impossible. So the statement that “the selectivity goes up and up” is totally wrong. If the selectivity cannot go up and up inside a membrane as it was claimed by the authors, the selectivity of the obtained composite membrane will be equal or lower than 7.77. While the selectivity of the composite membrane reported that contains 2% of the compatibilizer is 9.77. It is difficult to justify the high selectivity of that composite membrane.

2. The authors suggested in that paper that all permeates first diffuse through the compatibilizer between the dispersed impermeable phase and the matrix in the composite membrane, but I think this may not be true. The quantity of the compatibilizer in the composite membrane is much less than that of the matrix and, therefore, permeates have much less chance to contact with the compatibilizer than with the matrix. At the same time, the permeability of the matrix is higher than that of the compatibilizer and the diffusion resistance in the matrix is, therefore, much lower than that in the compatibilizer. So some permeates may diffuse through the compatibilizer, but most of the permeates should diffuse through the matrix and the matrix should be the major passage for permeates. If this is true, then the selectivity of the composite membrane reported will be close to the selectivity of the matrix (4.1). And it will be more difficult to justify the high selectivity of the composite membrane that was reported in that paper.
3. Solution-diffusion and molecular sieve are different membrane separation mechanisms. Obviously the separation process described by the authors in that paper is a simple and typical solution-diffusion separation process. The separation process in the composite membrane, as claimed by the authors, “is not size selective” while size selective is the characteristic of a molecular sieve. So the separation process in the composite membrane is not related to molecular sieve at all. Therefore there is no need to fabricate a new term—(universal) “organic molecular sieve” to describe a very simple and common diffusion separation process.
4. It is said in that paper that when the quantity of the compatibilizer in the composite membrane is higher than 6%, the size of dispersed Ny6 phase will increase as the percentage of the compatibilizer in the composite membrane increases. From polymer physics principles, this is impossible. As the concentration of the compatibilizer in a multiphase system increases, the size of dispersed phase should decrease. Only when the compatibilizer does not work properly (e.g. un-sufficient mixing) in a multiphase system, the size of the dispersed phase in a multiphase system may increase as the concentration of the compatibilizer increases.
5. It is said in that paper that the permeability of the composite membrane is “high enough for this film to be used in an oxygen-enrichment process”. Again, this is not true. Permeability is the characteristic of a material. A material having a high permeability is a prerequisite to make a high productive membrane, but only high permeability is not enough. The material also needs to have good film-forming property so that the membrane made from this material will be thin enough. Only when these two requirements are met at the same time, a material can be used to make a high productive membrane. Permeability alone cannot be used to characterize the productivity of a membrane. If you want to characterize the productivity of a membrane, you have to use both the permeability of the membrane material and the thickness of the membrane. This is why I suggested using permeance, instead of permeability, to characterize the productivity of a membrane [1]. Permeance is the characteristic of a membrane. If a membrane has a high permeance, this membrane material will have both high permeability and good film-forming property. Permeability can only be used to identify potential high performance membrane materials. Back to the composite membrane discussed in that paper, that composite film cannot be used for practical oxygen-enrichment process though the permeability of that membrane material is relatively high. If we take the thickness of that composite film (100 μm) into consideration, the permeance of that composite film (membrane) is only 0.03 GPU (1 GPU $= 3.35 \times 10^{-10}$ mol m^{-2} s^{-1} Pa^{-1}) that is too low for practical application. If the thickness of that membrane can be reduced to 1 μm, then the permeance of that membrane will be 3 GPU and that membrane may have a chance to be used for oxygen-enrichment practically.

Reference

[1] Zhu Z. J Membr Sci 2006;281:754.

Zhaoqi Zhu
Petrosep Membrane Technologies Inc.
2270 Speers Road
Oakville, ON
Canada L6L 2X8
Tel.: +1 905 8253109; fax: +1 905 8253285.
E-mail address: zhaoqi_zhu@yahoo.com

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