화학기 기여도 방법을 사용한 고분자 분리막에 대한 기체 투과도의 예측

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Prediction of Gas Permeability of Polymer Membrane Materials Using a New Group Contribution Method

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Introduction

Over the past 10 years or more an extensive body of information on permeation of gases in an extensive array of glassy polymers has been generated. Much of this work has been done in these laboratories in an attempt to learn the principles that govern this structure-property relationship driven by an interest in developing better gas separation membrane. There is an important need to develope simple means for quantitative correlations of this information since this may be useful for prediction of the behavior of new polymers and for guiding the development of new polymers.

The Bondi's group contribution method is one of general approaches to predict the behavior of polymers using the van der Waals volume of the various groups contained in the polymer[1,2]. However, this method can predict the properties of the exactly same family of polymers well. The theoretically more developed approach is Salame's method based on the polymer Permachor[3]. Bicerano[4] suggested the method considered the cohesive energy and repeat unit of polymer.

In this study the empirical factors of each chemical group included in the polymer can be obtained by the matrix method (PC-MATLAB), which are based on the chemical structure of polymers and the experimental data. Our group contribution method using these factors can predict the density and gas permeability of various glassy polymers simpler and better than the other conventional methods.

Theoretical Background

The permeability coefficient is compromised of both kinetic and thermodynamic factors which in principle depend on different aspects of the gas / polymer pair. However, for a given gas the diffusion coefficient varies from polymer to polymer a great deal more than does the solubility coefficient. While the diffusion coefficient may depend on many issues, the free volume of the polymer is among the most important. Solubility

coefficients also depend on this parameter as well. Thus, it should not be surprising that the permeability coefficient for a given gas in a series of polymers can be reasonably well correlated in terms of free volume. Indeed, extensive work from this laboratory and other groups has shown the utility of an expression or the following form

$$P = A \exp(-B / FFV) \qquad (1)$$

where A and B are constants for particular gas.

The fractional free volume, FFV, has been defined as

$$FFV = (V - V_o) / V \qquad (2)$$

Here, V is the specific volume of the polymer which is obtained from experimental measurement of the polymer density at the temperature of interest (typically 30 $^\circ$C). The term V_o is the specific volume occupied by the polymer chains. A variety of approaches may be used to obtain this, but all involve assumptions and various degrees of approximation. One of the most common approaches is to obtain this from Bondi's group contribution method[1,2]. The Bondi's method computes the occupied volume from the van der Waals volume of the various group, $(V_w)_k$, in the polymer structure using

$$V_o = 1.3 \sum_{k=1}^{K} (V_w)_k \qquad (3)$$

Using this scheme, correlation plots of logP versus 1/FFV have been constructed for polysulfone polymers by McHattie[5]. This generates good correlation using the factor A and B in equation (1). However, using the same scheme, the plots of logP versus 1/FFV have not construct good correlations for various polymers. Reasonably good correlations among a wide array of polymer structures can be generated if care is taken to ensure that accurate P and density data used and group contribution correlations are made based on a consistent and appropriate set of parameters.

It should be pointed out that some recent papers have not taken this care with the result being extremely scattered plots. Even when extreme care is taken, there is scatter in these plots that go beyond any experimental errors in the P and density data. This may stem from at least two origins. Cleary, the notion of free volume may not capture all of the factors that affect the permeability. Also, there may be errors in the values of $(V_w)_k$ available in the literature and the factor 1.3 in the Bondi's method is only an approximation for the complete packing volume of polymer. What we seek here is a group contribution method that hopefully can transcend some of these issues and lead to more accurate predictions.

We start from the framework outlined above and extend it in some purely empirical ways. We retain the forms of equation (1) and (2). However, we do not assume that FFV is the same for all gases in a given polymers or that V_o is given by equation (3). Instead, we defined for gas n

$$(FFV)_n = [V - (V_o)_n] / V \qquad (4)$$

$$V_o = \sum_{k=1}^{K} \gamma_{nk} \, (V_w)_k \qquad (5)$$

$$V = \sum_{k=1}^{K} \beta_k \, (V_w)_k \qquad (6)$$

Here, γ_{nk} is the empirical factor that depend on gas n and group k, and β_k is the empirical factor that depend on group k. We retain $(V_w)_k$ or the values of the van der Waals volumes for group k as listed in the tables by van Krevelen[2]. However, this is only a convenience and does not really affect the outcome of this approach in any way.

The work to data has been limited to a data base of 105 glassy polymers whose density (at 30 °C) and permeability to various gas (at 35 °C) are believed to be known very well. Most of these measurements were made at the university of Texas at Austin. We have defined 41 chemical groups that appear in these 105 polymers. A matrix method based on PC-MATLAB (The MathWorks, Inc.) have been used to calculate the values of the empirical factors β_k and γ_{nk} of each group for each gas from the data base of density and gas permeability for these 105 polymers.

Results and Discussion

The values of γ_{nk} vary a lot from group to group, but vary little from gas to gas. Conceptually this value may not vary from gas to gas because the specific volume occupied by polymer V_o in equation (5) does not depend on the gas, but depends on the polymer. The molar volume and the gas permeability of any polymers compromised of the chemical groups in this study can be estimated from the equations (1), (4), (5), (6), the γ_{nk} and the values of A and B. Calculated permeabilities for each gas and densities in the 105 polymers in our database have been compared to the experimental values. Average percent errors (APE) defined as equation (18) are compared with the correlation using the simple Bondi's approach which assumes γ_{nk} =1.3 for all gases and chemical groups. As expected, the new method results in a greatly improved APE of density and in permeability of each gas. It is the evidence of excellence of the new group contribution method.

Figure 1 shows a graphical comparison of the densities of 105 glassy polymers in the database calculated from the new method with the experimental values. We can see the nice agreement of the two values in this figure. Figure 2 show a example of comparisons of the gas permeabilities (He, H_2, CO_2, O_2, N_2, CH_4) of various polymers in the database calculated from the new method with the experimental values. Cleary, there are some polymers that still lie rather far from the correlation line. Future work will seek to understand what are the real underlying causes for these discrepancies and estimate the other properties of all glassy polymers.

The distribution of errors in the new group contribution method is

compared with that in the conventional Bondi's method in Figure 3 and Figure 4. There is a sharp peak at the point of P(exp) / P(cal) = 1, which means the calculated permeability is equal to the experimental permeability, as shown in Figure 4. However, the number polymers is dispersed widely in the range of P(exp) / P(cal), which means the Bondi's method could not predict well the gas permeability on most of polymers in Figure 3.

References

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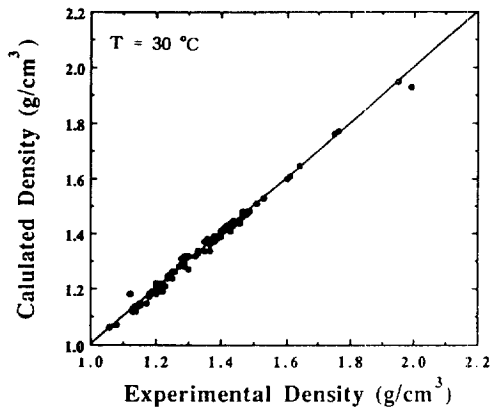5. J.S. McHattie, W.J. Koros and D.R. Paul, *Polymer*, Vol.33, pp.1701 (1991).

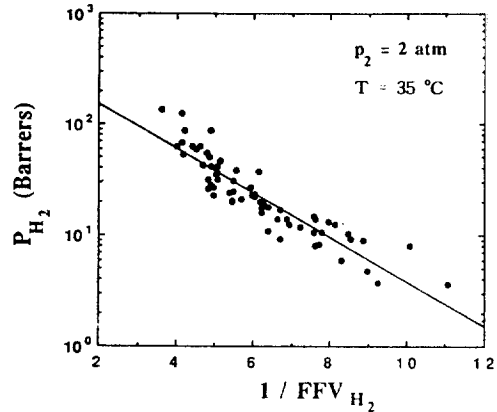Fig.1. Comparison between experimental and calculated density at 30 °C.

Fig.2. H_2 permeability coefficient as a function of calculated FFV.
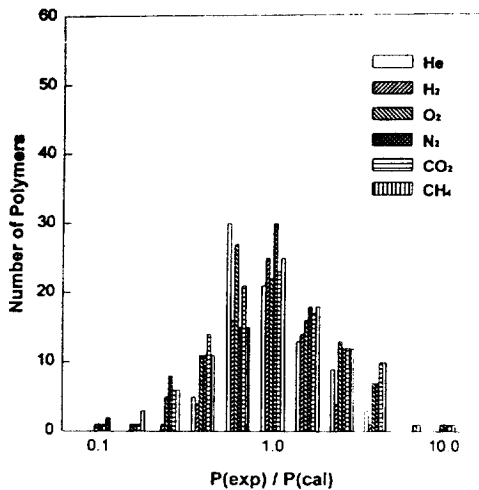
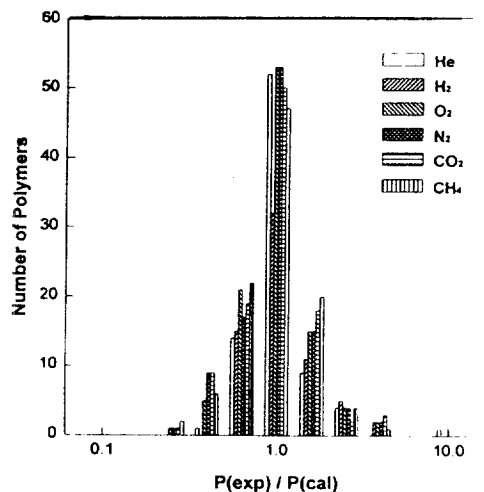Fig.3. The distribution of errors in Bondi's group contribution method.

Fig.4. The distribution of errors in the new group contribution method.