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F. -J. Tsai[a]; D. Kang[a]; M. Anand[a]
[a] Air Products and Chemicals, Inc, Allentown, PA

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THIN-FILM-COMPOSITE GAS SEPARATION MEMBRANES: ON THE DYNAMICS OF THIN FILM FORMATION MECHANISM ON POROUS SUBSTRATES

F.-J. Tsai, D. Kang and M. Anand
Air Products and Chemicals, Inc
7201 Hamilton Boulevard
Allentown, PA 18195-1501

ABSTRACT

A wide range of gas separations of interest in energy applications are carried out using membranes. Growing attention has been paid to the technology of making thin-film-composites(TFCs) membranes. Understanding the polymer solution and substrate property is key to successfully preparing TFCs membranes. This paper reports on some fundamental issues of coating hollow fibers with polymer from solution by dip coating. Polymeric porous hollow fibers with varying porosities and permeances were coated with polymer solutions of different viscosities in a continuous process. In addition, the fibers were coated dry and by presoaking in the coating solvent. It was found that the thickness of the coating on the low permeance/porosity/wet and dry fibers could be approximated by the Deryaguin model ($h/R = 1.33\ (Ca)^{0.67}$). For dry fibers, as the fiber porosity increased, the measured coating thickness was significantly underestimated by the Deryaguin equation. It is believed that the pores in the fiber allow rapid capillary suction of the solvent into the fiber walls and the bore, thus increasing the solution viscosity near the fiber wall, resulting in an increase in the coating thickness. Significant differences in the rate of solvent uptake were observed in these fibers by wicking experiments on a microbalance to support the above hypothesis.

INTRODUCTION

A wide range of gas separations of interest in energy applications are carried out using membranes. A few typical applications are: removal of acid gases from natural gas, purification of CO_2 in enhanced oil recovery, and recovery of chlorofluorocarbons from volatile organic compound streams (1-3). Conventional membranes take the form of asymmetric hollow fibers or spiral-wound flat sheet membranes. However, for advanced separation, the specialty polymer may not easily be fabricated into the desired asymmetric structure and they are often expensive. Substantial cost reduction can be achieved by preparing hollow fiber thin-film-composites (TFCs) for advanced separation. This route allows the flexibility of using an inexpensive hollow fiber support coated with a specialty polymer for the targeted gas separation. The specialty polymer includes conventional as well as active transport material.

Understanding the polymer solution and substrate properties is key to successfully preparing TFCs for gas separation. This paper reports on some fundamental issues of coating hollow fibers with polymers from solution by meniscus (dip) coating. The objective of this work was to investigate the effect of fiber porosity on the dynamics of coating a dilute polymer solution on a porous fiber via dip coating. Thus, porous hollow fibers of different porosities and pore sizes were coated with a polymer solution under different process conditions and the thickness of the coating was measured after removal of the solvent. The role of the fiber porosity in affecting solvent suction into the fiber was investigated and used in understanding coating thickness deviations from the Deryaguin model (4). It should be noted here that the porosity is comprised of both pore size and number density of pores.

The coating of a liquid on a moving substrate by dip or meniscus coating has been investigated by several researchers (4,5). Such coatings are of interest in numerous applications such as wire coating, fiber finishing and hollow fibers for gas and liquid separations. Deryaguin model (Equation 1) has been found to be a good fit for representing the coating of a Newtonian fluid on a non-porous fiber.

$$h/R = 1.33 \ (U\eta/\sigma)^{2/3} \qquad (1)$$

where h = liquid coating thickness, R = fiber radius, U = coating speed, η = liquid viscosity, σ = surface tension of the coating liquid. The term $(U\eta/\sigma)$ is known as Capillary number, Ca.

The above equation holds for Capillary numbers in the range of 10^{-5} to 10^{-2} (4,5). The model indicates that the coating thickness increases with increased fluid viscosity and coating speed, and decreases with increased surface tension of the coating liquid. Rigorous and empirical models have been developed for coating non-porous fibers and other shapes, e.g. slabs (6-13) with both Newtonian and non-Newtonian fluids. Few open literature example (6) has been found on models describing the coating of porous flat sheet substrates. This is a first effort in understanding the role of porosity in a hollow fiber substrate as it affects the coating dynamics, especially due to the coating solution penetration of the fiber pores. It is expected that an improved understanding of the parameters which control the coating thickness will be achieved by this work.

EXPERIMENTAL

Polymeric porous hollow fibers were prepared by conventional dry-wet spinning. The porosity and pore size was controlled by varying the spin dope composition and the process variables (such as the coagulation bath temperature and composition). Such phase inversion spinning processes have been described in the literature extensively (14). Polymeric hollow fibers with permeances (P/l)* of 30, 1,400 and 3,500 x10^5 B/cm** were prepared by this process. Typical scanning electron micrographs of the surfaces are shown in Figure 1, where it can be seen that the very low P/l fiber has very small pores and a low pore area. As the P/l is increased, both the pore area and the pore size increase. The surface porosity of the inner bore of the fibers was also examined by scanning electron microscopy (SEM), and it showed that the porosity variations on the inside were consistent with the variations on the outside of the fiber. The fibers were dried with dry warm nitrogen prior to coating. In some experiments, the fibers were pre-wetted with the coating solvent just prior to contacting the polymer coating solution. The motivation for coating on solvent wetted fibers was to eliminate capillary suction of the solvent into the fiber porous walls and the bore. It was thus expected that the wetted fibers may behave similarly to solid or non-porous fibers.

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* P/l = (permeability,P, of fiber)/(wall thickness,l)

** B/cm = Barrers/cm where Barrer = $\dfrac{cm^3 . cm}{sec . cm^2 \ cmHg} \times 10^{-10}$

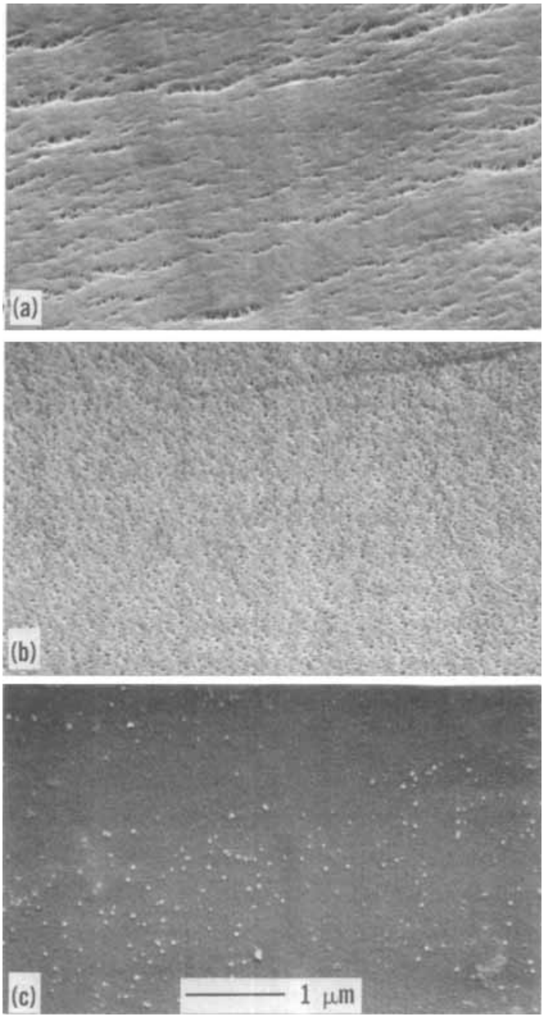

FIGURE 1. SEM micrographs of outside surface of fibers (a) P/l = 3,500 (b) P/l = 1,400 (c) P/l = 30 (x 10^5 B/cm)

The capillary suction properties of the fibers were examined by hanging a small section of the hollow fiber from a micro-balance and monitoring its weight change as a function of time immediately after contacting the polymer solution. The end contacting the liquid was closed using an epoxy resin to prevent direct flow of the liquid into the fiber capillary bore. Thus, it was possible to measure the rate of solvent suction into the fiber walls from the outside of the fiber as a function of the fiber porosity.

Dip coating of polymer solution on the porous fiber was carried out by continuously pulling the fiber upward through a reservoir of the polymer solution followed by controlled drying with dry heated nitrogen. A schematic of this operation is shown in Figure 2. The fiber was coated at speeds of 2.0 and 5.5 m/min in these experiments.

The liquid coating thickness on the fiber was obtained by back calculating from the dry polymer coating thickness. The dry polymer coating thickness was obtained using X-ray florescence (XRF) measurements. A calibration curve for XRF emission intensity ratio vs. the coating thickness was obtained by measuring the florescence intensity of a specific element in the coating polymer and calibrating the signal with the coating thickness measured from SEM micrographs. The coating thickness was found to be a logarithmic function of the XRF signal intensity according to (15):

$$t = 2.3/md \log[\, 1 - \{I(s)/I(o)\}]$$

where t = coating thickness, m = mass absorption coefficient, d = density of polymer, I(s) = emission intensity from sample for specific element, and I(o) = emission intensity from infinitely thick sample of the specific element.

The liquid coating thickness, h, was simply calculated from mass balance:

$$h = \{[D_p/(D_s \cdot c)][(R + t)^2 - R^2] + R^2\}^{1/2} - R$$

where D_p and D_s are density of the polymer and the polymer solution respectively, c is the concentration of the polymer in the solution and R is the fiber radius.

In this study, a polyester was used as a model compound for the coating. The polyester to be coated was dissolved in 1,4 dioxane and the concentration varied from 1 to 5 wt.%. In this concentration range, the solution viscosity ranged from

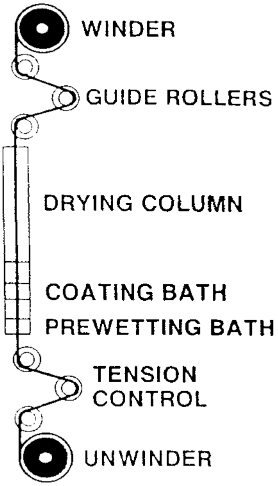

FIGURE 2. Coating Schematic

about 2 to 30 cp. at 25 °C at a shear rate of ~ 5 sec^{-1}, as measured with a cone-and-plate rheometer and a Ubbelohde viscometer. In the coating speed range of interest, a very small shear rate dependency of solution viscosity was observed and thus the solutions are considered essentially Newtonian.

The surface tension of the solutions was measured as a function of polymer concentration. In the concentration range examined, the surface tension (~ 25 dynes/cm) is independent of the polymer concentration (1 to 5 wt.%).

RESULTS AND DISCUSSION

The coating of the porous hollow fibers was carried out at different coating speeds and solution viscosities. The process parameters were plugged into the Deryaguin model to calculate the thickness of the wet coating. The coating conditions chosen for these experiments were within the window of Capillary number specified by the Deryaguin equation. The actual coating thickness was measured both by XRF and by examination of the coating cross-section under an

SEM. Plotting of the measured vs. calculated (from Deryaguin model) thickness revealed the deviations from the model.

Figure 3 shows the liquid film thickness vs. polymer solution viscosity for fibers with P/ls of 30, 1,400 and 3,500 x10^5 B/cm. In addition, the effect of coating dry vs. prewetted fibers is also shown in Figure 3. The data in Figure 3 shows that : (i) The coating thickness increases with increased polymer content in the coating solution. This is an expected result since the solution viscosity increases at higher polymer contents in the solution. (ii) For the very low permeance fiber (P/l = 30 x10^5 B/cm), there is little difference in the coating thickness if the fiber is coated dry or prewetted with the coating solvent. (iii) For the higher permeance or porosity fibers, the coating film thickness is greater when coating a dry fiber. It can also be observed that as the fiber permeance increases, the difference in the coating thickness between the wet and the dry fibers increases.

Figure 4 shows that the thickness of the coating on a dry fiber increases as the fiber permeance increases. However, this is not the case for the pre-wetted or solvent soaked fibers, where indeed a small decrease in coating thickness may occur with increased fiber permeance. This observation will be discussed later in the paper.

Using the coating process parameters, the coating thickness was calculated using the Deryaguin equation for each of the coating experiments. Plots were then made for the actual thickness measured by XRF vs. the thickness calculated from the Deryaguin model. Figure 5 shows such a plot for coating on low permeance wet and dry fibers. These data show that the coating thickness on the very low permeance fiber (both wet and dry) can be reasonably approximated by the Deryaguin model. The data also suggests that the very low permeance fiber behaves like a solid fiber from a coating perspective.

Figure 6 shows a similar plot for coatings done on dry and wet high permeance fibers. The key observations from Figure 6 are : (i) Deryaguin model underestimates the coating thickness for coating on porous dry fibers. The deviation from the model increases as the coating thickness increases. It should be noted that the higher coating thickness was obtained with coating from higher concentration solutions. (ii) For coating on wet fibers, the Deryaguin model overestimates the coating thickness, especially at large coating thickness.

In the above calculations, the same viscosity was used for coatings done at 5.5 and 2.0 m/min. Correction of the viscosity at the appropriate shear rate

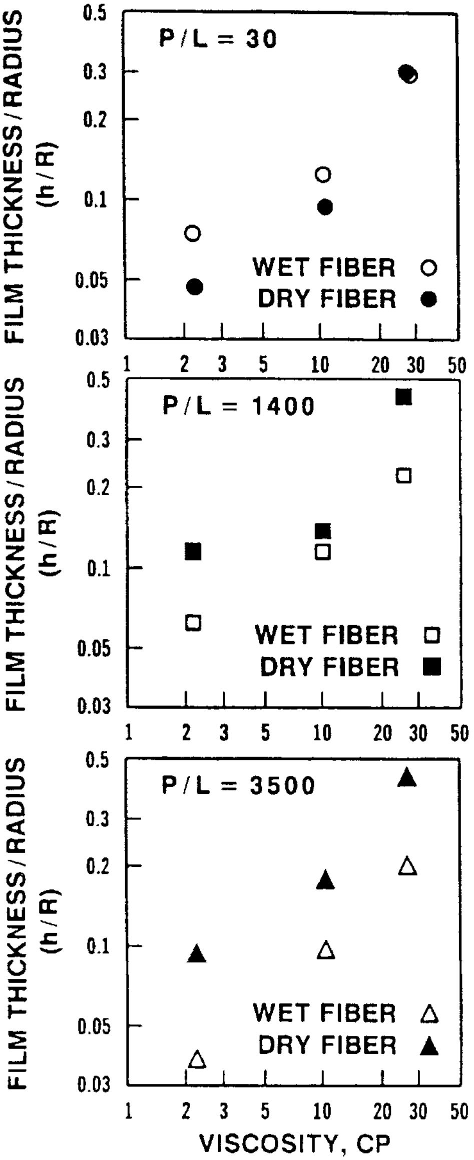

FIGURE 3. Effect of fiber preweting and solution viscosity on wet film thickness (Coating speed: 5.5 meter/min.)

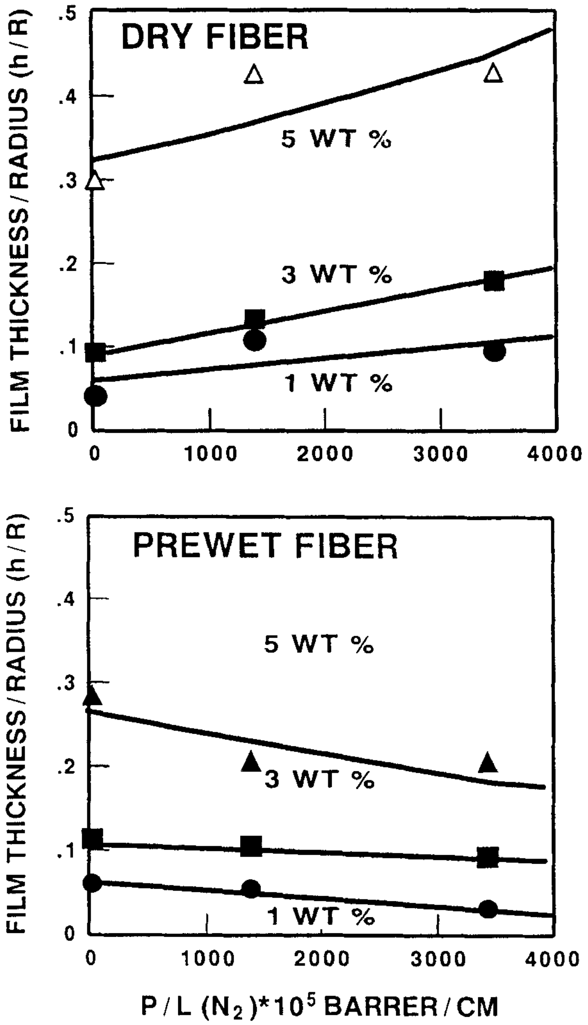

FIGURE 4. Effect of substrate porosity on coating thickness (Coating speed: 5.5 meter/min.)

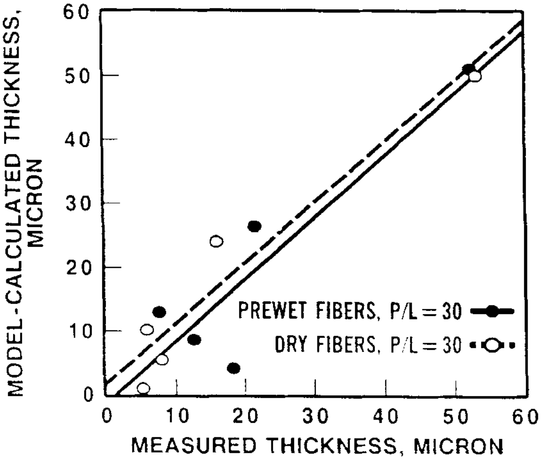

FIGURE 5. Measured vs. calculated* wet film thickness for fibers of low porosity (* Calculated by the Deryaguin model: (h/R = 1.33 (Ca) $^{0.67}$))

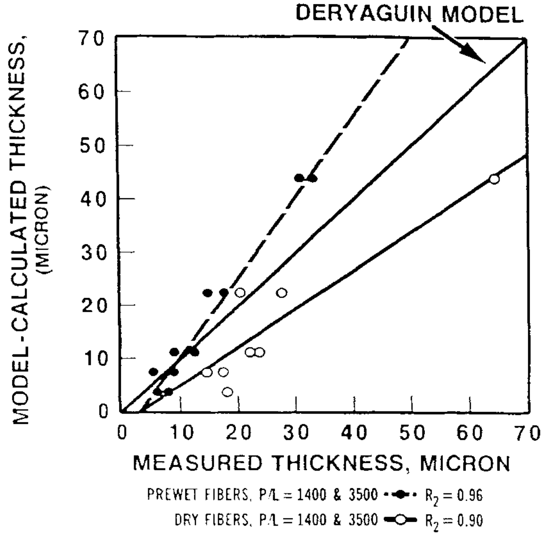

FIGURE 6. Measured vs. calculated* wet film thickness for fibers of high porosity (* Calculated by the Deryaguin model: (h/R = 1.33 (Ca) $^{0.67}$))

(corresponding to the coating speed) decreased the deviation by about 15% in the higher coating thickness range. However, it was still not possible to fit the Deryaguin model calculated thickness to the measured thickness. It was thought that the porosity in the fiber causes preferential capillary suction of the solvent into the fiber pores and bore, thus increasing the coating solution viscosity in the vicinity of the fiber. This occurrence from a simple viscosity viewpoint would result in an increase in the coating thickness. Indeed, as the solution concentration increases, the effect on viscosity due to solvent removal is greater, and hence one would expect an increased deviation from the expected thickness.

The corresponding experiments with pre-wetting of the fibers with the coating solvent would not allow this local increase in solution viscosity; indeed one could visualize an osmotic effect resulting in a net flow of the solvent from the fiber to the coating fluid, resulting in a local decrease in polymer concentration (hence viscosity), causing the coating thickness to decrease. This hypothesis is indeed supported by the coating thickness data.

To further understand the role of sorption or suction of the coating solvent into the fiber in affecting the coating thickness, experiments were performed to measure the capillary suction rates of the coating solvent into the fibers with the different permeances (porosities).

Figure 7 shows the increase in fiber mass as a function of time when a fiber is dipped into the coating solution (Note : in these experiments, the fiber end in contact with the solution was sealed off with epoxy so that capillary suction effects only through the walls of the fibers could be measured). The data in Figure 7 shows dramatic differences in the sorption rates for the fibers with the different porosities. It should be noted that the solvent suction into the very low permeance fiber (P/l = 30 x10^5 B/cm) is negligible in the time scale of the experiment (Note: in our coating experiments, the solution contact time in the coating die is about 0.1 sec and the solvent contact time in the prewetting die is about 1 sec). This would suggest that these fibers would behave as solid fibers from a coating viewpoint. This is indeed borne out by the observation that both the prewetted and dry fibers of very low P/l are indistinguishable in their coating characteristics (Figures 3 and 5). It can also be observed from Figure 7 that as the fiber permeance and porosity are increased, the rate of solvent suction into the fiber increases (from the average slope of the weight increase vs. time curves). Thus, one would expect greater depletion of the solvent just outside the fiber walls when coating higher P/l fibers. The

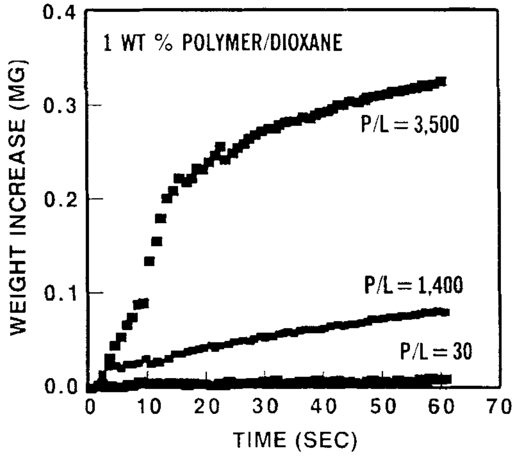

FIGURE 7. Effect of fiber porosity on capillary suction

consequence of this would be a higher local viscosity of the coating fluid adjacent to the fiber when coating higher P/l fibers and hence a larger coating thickness. The data in Figures 3 and 6 support this argument. Similarly, for pre-wetted fibers, the dilution effect would be expected to be greater with the higher P/l fibers because of a larger reservoir of the solvent being released in the fiber vicinity.

It may be possible to incorporate this capillary suction effect on the coating thickness by introducing a term in the Deryaguin equation which may account for a local increase in viscosity. Such a term should be a function of the fiber pore size and distribution, solvent wetting and sorption characteristics, the solution viscosity characteristics (i.e. concentration and shear rate dependence) and the contact time in the coating die. No effort was made to develop such a model in this work.

CONCLUSIONS

It can be concluded from the above work that : (i) Porosity in a fiber results in a greater coating thickness when coating by meniscus/dip coating. The coating thickness increases as the fiber porosity is increased. It is believed that effect is caused by capillary suction of the coating solvent into the fiber wall and bore resulting in an increase in the solution viscosity in the fiber vicinity. (ii) Prewetting the fibers with the coating solvent reduces the coating thickness, possibly due to dilution effects in the fiber vicinity. (iii) The coating thickness on very low permeance dry or prewetted fibers can be fitted by the Deryaguin model. However, the deviation from the model becomes larger as the fiber porosity and the coating solution concentration/viscosity are increased. (iv) The capillary suction effect in the fibers can be investigated by gravimetric methods. Vast differences in fiber solvent suction characteristics were observable via this technique. The differences in capillary sorption characteristics of the fibers qualitatively supported the observed variations in the coating thickness. (v) It is possible to reduce the coating thickness by prewetting the fiber to be coated.

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