

**PERCOLATION PROPERTIES OF POROUS CERAMIC
SUSPENSION COATINGS FOR MOLECULAR
SEPARATION MEMBRANE SUPPORTS**

Minimizing Macropore Defect Density by Multiple Coating

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Abstract

Single layer suspension coatings on extruded membrane support tubes are shown to have a relatively large density of defects with pore sizes larger than that are found in bulk material made from the same suspension. Increasing the thickness of the coating does not lead to a significant improvement. However, by applying a second layer the pore throat distribution approaches that of a bulk compact of the same suspension.

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1. INTRODUCTION

Nanoporous and microporous supported membranes for molecular separations with high selectivity demand a support structure with a sufficiently small pore size and a minimum defect density. Substrates for molecular separation membranes (MSM) are prepared by multiple coating of extruded support tubes, first with suspension coatings and then by sol-gel coating(s). Percolating voids in suspension coatings much larger than expected from bulk compact Hg porosimetry data are clearly undesired. However, such voids are commonly present in state-of-the-art coatings [1, 2].

The percolation properties of an optimum suspension coating should be determined only by the homogeneous pore void - pore throat network structure obtained by nearly random packing of the particles in the suspension. Disturbance of particle packing due to a substrate or processing effect is undesirable. How can we avoid percolating voids much larger than the size of the percolating channels in bulk compacts? Do finite size percolation effects [3, 4] play a role, and how does the defect density vary with layer thickness and number of layers? These are important questions to answer in order to be able to achieve successful upscaling of molecular separation membranes to industrial scale manufacturing as then the number of layers must be kept to a minimum from the point of view of cost. Also to further improve support processing we investigated single and double consolidated coating layers by bubble number porometry (BP) and bulk properties of casted and consolidated particle compacts by Hg porosimetry (HgP). Essential for discriminating between pores and defects is the analysis of porometry data in the light of percolation ideas.

2. THEORY

Probing the pore space of a porous material by HgP and that of coated layers by BP is in both cases a fluid displacement (in first drainage) method in which the pore space filled with a wetting fluid is invaded by a non-wetting liquid by increasing the pressure. Both processes are a form of invasion percolation [3].

The capillary pressure P_c needed to keep a wetted porous medium at a certain saturation value S_{NW} of non-wetting fluid (Hg in case of HgP and N_2 gas in case of BP) is given by:

$$P_c = \gamma J \quad (1)$$

where γ is the interfacial tension of the wetting/non-wetting fluid interface and J is the meniscus curvature. In case of a spherical meniscus in a cylindrical capillary $J = 4/d$, with d the inner diameter of the capillary.

The fraction X_{NW} of allowed pores at a certain value of P_c is given by:

$$X_{NW} = \int_0^J \alpha(J) dJ \quad (2)$$

where $\alpha(J)$ is the pore volume distribution.

The non-wetting phase saturation is given by:

$$S_{NW} = X^a(X_{NW}, N) \quad (3)$$

where $X^a(X_{NW}, N)$ is the accessibility function giving the fraction of pores that is accessible from the surface and N is the sample size [4] (i.e. layer thickness) in terms of a characteristic number of pores. The pore size distribution is then given by [5, 6]:

$$\alpha(J) = \frac{\partial S_{NW}}{\partial J} \frac{\partial X_{NW}}{\partial X^a} \quad (4)$$

This equation is implicit in $\alpha(J)$ because X_{NW} is a function of $\alpha(J)$.

Close to the percolation threshold the permeability K_{NW} of the non-wetting phase in BP measurements is proportional to S_{NW} . So qualitatively BP and HgP curves are comparable in this region. Equation (4) shows that a pore geometry and pore accessibility model is needed in principle to abstract a pore size distribution from fluid intrusion data. Applying a capillary tube bundle model for particle packing means assuming $X^a(X_{NW}, N)$ is linear in X_{NW} and independent of N . HgP and BP data interpreted this way are then a kind of weighted pore throat distribution, but underestimating the large size throats [7]. Capillary tube bundle models are still widely used in BP [8, 9, 10] but cannot explain percolation effects.

3. EXPERIMENTAL

Suspensions were prepared from a fine alpha alumina (>99.99 %) powder (mean particle size ~600 nm, coded below as A600). The powder was calcined at 600°C for two hours before use. Polyelectrolyte was used as deflocculant. Ultra pure water was used. Appropriate compositions were mixed and deagglomerated in an attritor. Test pieces (28cm length, ID/OD=8/14mm) from commercial substrate tubes (coded TSHT) were used. The pore structure of the supports was characterised by intrusion HgP and BP. Triplicate coating experiments were done on test pieces taken from the same tube.

Alumina suspensions were coated on the exterior of tubes by film (dip) coating [1] using an in house designed and built coating apparatus. The coated tubes were dried under ambient conditions and sintered above 1000 °C. The thickness of the coating was calculated from coat mass and the porosity obtained from HgP on bulk material. Bulk compacts of the coating suspension were prepared by casting and quickly drying a few ml coating suspension in a cup at 70°C, followed by sintering in the same manner as the respective suspension coatings.

Determination of the bubble point and the bubble point number density curve at higher pressures were performed on an in-house made set-up using N₂ gas for pressurising. Dry tubes were carefully immersed with pure water or ethanol.

4. RESULTS AND DISCUSSION

Coating an A600 alumina layer on a TSHT support tube means in principle a change in percolation transition from $J \approx 1 \mu\text{m}^{-1}$ (support tubes) to $J \approx 23 \mu\text{m}^{-1}$ (A600 layer with bulk properties), see figure 1. Observing much lower percolation values for a coating than the HgP bulk value shows the presence of large percolating voids (defects) that are caused by a substrate or a processing effect. The coating pore structure is then not statistically homogeneous and more $\alpha(J)$ and X^a functions are needed to describe the behaviour. Homogeneous thin layers behaving as bulk compacts (i.e. no finite size percolation effects), are expected at $N > 30$ [4]. So layers thicker than say $6 \mu\text{m}$ (10 times the average alumina particle size), are expected to be able to behave bulk like. If not (lower percolation threshold) this must be attributed to substrate/coating interaction or processing.

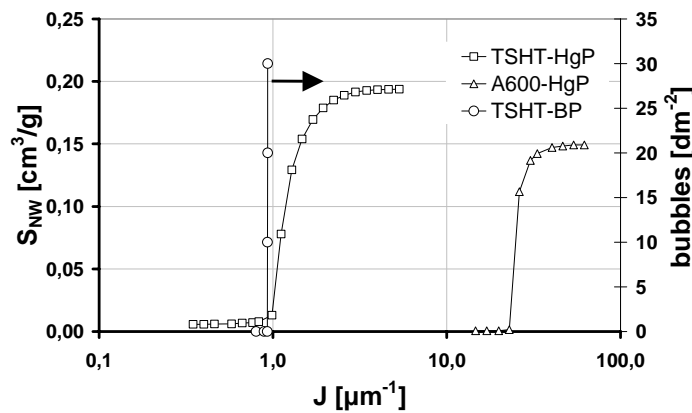


Figure 4.1 *HgP curves vs curvature J of TSHT support and sintered bulk A600 compact. The BP curve of the TSHT shows similar curvature threshold (J) as the HgP curve*

Increasing the thickness of the first coating layer does not increase the percolation transition in BP to values expected for bulk compacts. Although we observed a decreasing BP gas permeability K_{NW} with increasing thickness above the percolation threshold. So these layers still contain percolating voids not present in bulk particle compacts of the same material. Suspension drying problems occurred upon coating layers thicker than $80 \mu\text{m}$ in one step. A percolation threshold close to the HgP bulk value (figure 2) was found by coating a second layer of about $40 \mu\text{m}$ upon a consolidated first layer of the same thickness. The fact that a large improvement is obtained by coating twice shows that processing as such is not the cause of defects for layers thinner than $\sim 40 \mu\text{m}$. Coating a thin first layer and a thicker second one shifts the percolation point to higher curvature values. A thin second layer upon a thicker first layer gave to our surprise no improvement. We believe that smoothing of the tube surface by a relatively thin first layer is necessary for a less disturbed particle packing in the second layer. But if this were true bulk compact behaviour should be observed with a $10 \mu\text{m}$ second layer on top of a $\sim 40 \mu\text{m}$ first layer. However this is clearly not the case. Apparently particle packing for these thin second layers cannot be considered spatially homogeneous, questioning the random packing assumption. Weak attraction in our concentrated alumina suspension may play a role. We are further researching the need for thick second layers.

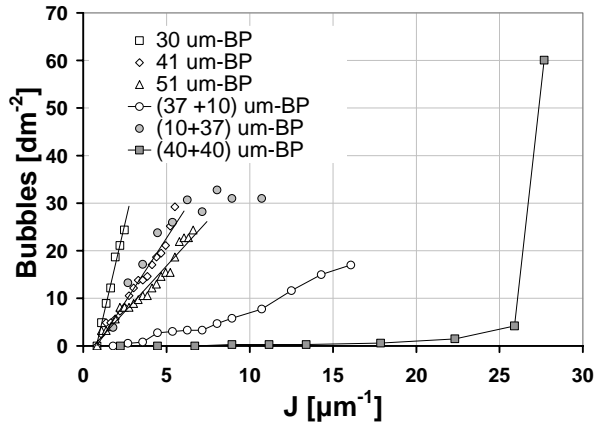


Figure 4.2 *BP curves vs curvature J (μm^{-1}) for single and double A600 coated TSHT tubes. Layer thickness as indicated*

Supports coated with two 40 μm A600 layers show bulk compact behaviour as desired. More than one layer is clearly needed to achieve this, but the optimum is not known yet. Percolation ideas need further consideration to be able to resolve particle packing and pore structure in multilayer suspension coatings and to become a valuable tool in upscaling and improving supports of inorganic molecular separation membranes. Preliminary BP investigation of mesoporous sol-gel coatings on twice-coated A600 substrates shows no shift in percolation threshold to higher curvature. This shows that the tail of the A600 intrinsic bulk pore distribution determines the percolation threshold of the sol-gel layers. Finer suspension particle compacts are obviously needed for further improvement.

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