Journal of the European Ceramic Society 17 (1997) 359–366
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0955-2219/97/$17.00

PII: S0955-2219(96)00107-0

Preparation of Alumina Membranes by Tape Casting and Dip Coating

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(Received 15 September 1995; accepted 10 June 1996)

Abstract

The preparation of an alumina ultrafiltration membrane with a mean pore size of 6·5 nm was performed by slip casting or tape casting of the support, dip coating or tape casting of the intermediate layer, followed by dip coating of the top layer. Controlled porosity and pore size in the support were obtained by the addition of starch particles which were subsequently burned out. A conventional process based on dip coating to create the intermediate layer was used initially. An alternative process was developed, based on tape casting of the support and the intermediate layer, followed by lamination and sintering in one step. Very good linkage between the support and the intermediate layer was obtained by the alternative process, as well as an excellent control of the intermediate layer thickness and surface finish. Pore size, pore size distribution and porosity were determined for each part of the membrane. The gas and liquid permeabilities were also measured. © 1996 Elsevier Science Limited

1 Introduction

Interest in separation by the use of membranes has gradually increased during the last 10–15 years. The use of membranes increases the effectiveness of already existing processes and opens new possibilities for separation.[1] One example is the cleaning of waste water and another the recovery of chemicals. Ceramic membranes are especially suitable for applications in which high temperature and corrosive or organic media are used.

Generally, a membrane is built up of a porous support, a few millimetres thick, with pore sizes in the range 1–10 μm; an intermediate layer, 10–100 μm thick, with pore sizes in the range 0·05–0·5 μm; and a top layer, 1–10 μm thick, with pore sizes in the range 2–50 nm, see Fig. 1.[2] The top layer can be modified by deposition of a phase inside the pores to further decrease the pore size or to add a certain function to the membrane (for example, a catalyst). The actual separation process takes place at the top layer. The support provides mechanical strength to the membrane while the intermediate layer acts as a transition phase, preventing the top layer from penetrating into the pore structure of the support. It should be mentioned that the support and intermediate layer can be used as a membrane for microfiltration, which is mainly a separation of microscopic particles (0·1–1·0 μm). The membrane with a top layer can be used for ultrafiltration, which is a separation of macromolecules and colloidal particles. Separation of smaller molecules and ions requires reverse osmosis.

The dominating geometry of ceramic membranes is the tubular shape or tubes combined to a honeycomb structure. The honeycomb structure is effective because a large membrane area is obtained in a small volume. Flat membranes are not as common as the tubular-shaped ones, but a large membrane area can be achieved by stacking flat membranes and the 'dead volume' can be minimized.[3] Tubular shapes and honeycomb structures are extensively used for liquid separation processes while the flat shape is more suitable for gas separation, low-pressure liquid processes and catalytic processes.

Flat membranes can be prepared by several forming methods. Slip casting, calendering and tape casting are all examples of forming methods suitable for making flat shapes. These methods can also be combined so that the support is prepared by tape casting and the intermediate layer by dip coating, which is actually a slip-casting process. Slip casting is a well-known forming method, while the forming of water-based systems with tape casting is still under development. There is a wide range of water-soluble binders conceivable for tape casting[4] but several requirements must be met: (i) the binder system must provide a suitable pH so that a well-dispersed slip is obtained (ii) a flexible film must be obtained which

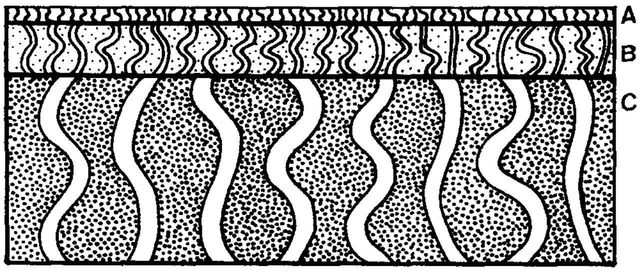


Fig. 1. Schematic representation of a membrane: (A) top layer, (B) intermediate layer, and (C) porous support.

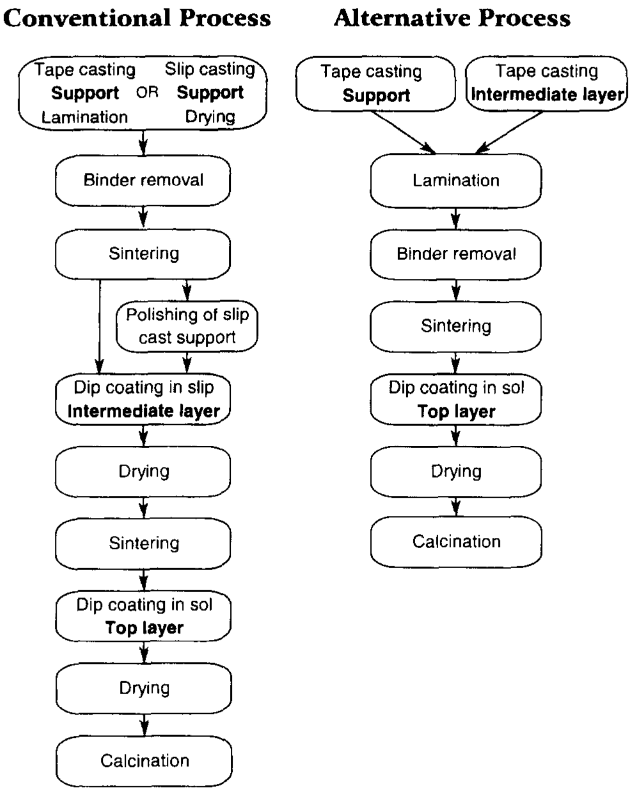


Fig. 2. Outline of the conventional and the alternative processes.

allows rolling of the tape and endures separation of tape and plastic tape carrier, and (iii) the binder must provide a good adhesion during lamination. A high binder content is often necessary to maintain good mechanical strength of the tape during processing. However, high concentrations of water-soluble binders often yield slips with high viscosity which is a disadvantage when tape casting.[5] The use of latex binder systems allows a high binder content with a maintained low viscosity. Acrylic latexes and copolymers of acrylic latexes, mainly produced for the paint industry, offer a wide variety of properties making them suitable for tape casting. Tape casting of membranes has been performed with polyvinylalcohol[3] but it required quite a large amount of binder and a long period of drying (1–5 days).

The porosity in the support is conventionally created by sintering a coarse powder with sintering aids which provide a glassy phase or formation of necks between the large particles. The intermediate layer is often applied by dip coating of the flat (or tubular) support. The raw material is a more sinteractive powder than the materials used for the support and the porosity is governed by the choice of sintering temperature. By decreasing the temperature the densification can be limited and a certain number of pores remains open.

The sol–gel technique is commonly used to obtain the desired pore sizes in the top layer. The pore size is dependent on the particle size in the sol, which means that very small particulate sols are required to obtain pores in the nanometre range. Polymeric sols have the potential of giving smaller pore sizes than particulate sols as the obtained gel layer is built up of a polymeric network. A polymeric sol is prepared by partial hydrolysis of a metal alkoxide. The hydrolysis is often a fast reaction which can be difficult to control and subsequent drying of the gel layer has to be carried out very carefully to avoid cracking. The preparation of a particulate sol is via total hydrolysis of a metal alkoxide, followed by peptization to obtain a stable solution.[6] The top layer is usually applied by dip coating. A binder is often added to the sol to prevent cracking during drying. Calcination of the top layer has to be performed very carefully. Densification with particle growth and reduction of the specific surface area must be avoided. Any possible phase transformation with volume changes must also be considered during heat treatment. Some materials can be doped by certain ions to prevent or retard phase transformation or inhibit grain growth,[7,8] but a limitation of the calcination temperature is the most common method to obtain a material with preserved porosity if no additives are used.

Two different processes designated as the *conventional* and the *alternative process* were used to prepare flat ultrafiltration membranes in this study. The processes are outlined in Fig. 2 and will be described further below. Addition of starch with subsequent burn-out was used as an alternative to sintering of coarse particles to create porosity in the support. The need for sintering aids was therefore eliminated. The aim was to obtain a controlled porosity and pore size distribution. These factors were governed by the quality of the starch chosen and by the amount added. The objective of the study was to obtain knowledge about the critical factors in the preparation of a flat membrane and to be able to control these factors. Special attention was given to the build-up and characterization of the support and the individual layers.

2. Experimental Procedure

2.1 Materials

An alumina powder (AKP 30, Sumitomo Chemicals) with an average particle size of 0·4 μm and a specific surface area of 6·5 m^2 g^{-1} was used in this study. An ammonium salt of a polyacrylic acid (Dispex A 40, Allied Chemicals) was used for dispersion of the alumina in water. Corn starch (Lyckeby Stärkelsen, Sveriges Stärkelseproducenter) with a particle size in the range of 10–15 μm or rice starch (Remy Industries) with particles in the range 4–6 μm was used to create porosity in the support.

A water-based latex, i.e. a copolymer of styrene and an ester of an acrylic acid (Mowilith DM 765S, Hoechst Perstorp AB), was used as a binder for tape casting. This latex is stable at neutral and high pH and, therefore, it was compatible with the stable alumina slip which had a pH around 9. A styrene acrylate dispersion (Bonotex 805, Hoechst Perstorp AB) was used as a binder for slip casting. A tenside (047, Berol AB) was used to decrease the surface tension and remove entrapped air in the slips. The colloidal boehmite sol (Nyacol AL20, Nyacol Products Inc.) used for the top layer had an average particle size of 50 nm, a pH of 4 and a solids content of 20 wt%. The polyvinyl alcohol (PVA) (Mowiol 10–98, Hoechst) used as a binder in the sol had a molecular weight of 61 000.

2.2 Preparation of supports

Supports were prepared by tape casting or slip casting in the conventional process and by tape casting in the alternative process. The addition of starch to the slip created pores in the material when burned out after forming. Different sizes of starch are available which offers the possibility of governing the pore size. Slips were prepared by dispersing the alumina powder in water with the dispersing agent. The slips were homogenized by ball-milling for 12–18 h or by ultrasonification for 20 min. The starch was added during vigorous stirring which was continued for 30 min. The binder was added and slow stirring continued for about 1 h. The slips were wet sieved through a 31·5 μm cloth to remove agglomerates and entrapped air. The slips with rice starch had to be conditioned overnight with addition of a tenside to eliminate entrapped air. The amount of each substance in the slips is shown in Table 1.

Table 1. Composition of support slips

Material	*Slip casting, weight (g)*		*Tape casting, weight (g)*	
Al_2O_3	100	100	298·5	298·5
Starch rice	24·6		73·5	
Starch corn		19·9		59·4
Dispersing agent	1·2	1·2	3·7	3·7
Water	33·3	33·3	94·6	94·6
Binder	4·5	4·5	107·7	98·6

The tape casting was performed in a continuous machine from Wallace Technical Ceramics, Inc. The machine has a fixed doctor blade box and tapes were cast on a plastic tape carrier. Drying was provided by application of heat from underneath the tape and by a controlled passage of air over the surface of the tape. Tapes were cast with a sloping gap (100–500 μm) to determine the critical casting thickness (CCT)[5] above which the tapes would spontaneously crack. The CCT is dependent on the particle packing of the powder, the particle size, the nature of the binder and the binder content. Most tapes could be cast with a 250–300 μm gap. Square supports were cut from the tapes and several tapes were laminated together in a press at 60 MPa at room temperature to build up the desired thickness of about 1 mm.

Slip casting was performed in plastic cylinders on flat plates of plaster. The supports were dried in an ambient atmosphere at room temperature. The organic substances in tape-cast and slip-cast supports were burned out in air by rate-controlled extraction to 500°C[9] and, for the conventional process, sintering in air followed at 1550°C for 1 h with a heating rate of 5°C min^{-1}. The tape-cast supports for the alternative process were sintered at 1100°C, 1200°C and 1300°C for 1 h with a heating rate of 5°C min^{-1} to determine a suitable sintering temperature giving the support sufficient strength to be handled. The slip-cast supports were grinding machined to a thickness of 1 mm and a suitable surface finish.

2.3 Preparation of intermediate layer

Preparation of an intermediate layer by dip coating is a step in the conventional process. The slip was prepared as described above, the amount of each substance in the slip being shown in Table 2. The obtained thickness is dependent on the dipping time and the viscosity of the slip. The solids content was 25 vol% and this is one of the parameters which governs the viscosity. The dipping was performed manually in an open beaker and the dipping time was approximately 15 s. The samples

Table 2. Composition of intermediate layer slips

Material	*Dip coating, weight (g)*	*Tape casting, weight (g)*
Al_2O_3	100	100
Dispersing agent	1·2	1·2
Binder	4·5	21·5
Water	136·4	43·7

were dried in plastic boxes with a tight lid for 24 h and in an ambient atmosphere at room temperature for 24 h. Sintering was performed at 1000°C for 1 h with a heating rate of 5°C min^{-1}.

Preparation of an intermediate layer by tape casting is a step in the alternative process. The slip was prepared as earlier described and the recipe is found in Table 2. Tape casting was performed with a narrower gap (100 μm) than for the support. The lamination of support and intermediate layer was performed in one step, so that 6–8 support tapes were pressed with one tape of an intermediate layer on top at 60 MPa. Burn-out of organic matter was carried out as described earlier. Laminated samples of intermediate layers were sintered at 1100, 1200 and 1300°C for 1 h during the development of the alternative process to determine the resulting pore size distribution and porosity. The laminated membrane was sintered at 1200°C for 1 h with a heating rate of 5°C min^{-1}.

2.4 Preparation of top layer

The top layer was applied on the previously prepared intermediate layers by dip coating in a boehmite sol. PVA was added as a binder to the sol to prevent cracking during drying. A solution of 3·5 wt% PVA was mixed with a solution of the sol with 6 wt% AlOOH in the proportion of 2 : 3.[8] The thickness of the obtained layer was governed by the dipping time and the viscosity of the sol. The dipping in this step was also carried out manually in an open beaker for approximately 1 s. The top layers were dried in the same manner as the intermediate layers but could also be dried at 60°C for a few hours without cracking, which indicates that the top layer was very insensitive during drying. The top layers were calcined at several temperatures to study the effect on the pore size distribution and the specific surface area. The heating rate was 1°C min^{-1} and the temperatures chosen were 400, 600, 800 and 1000°C with a dwelling time of 1 h. The top layers applied on intermediate layers were calcined at 600°C for 3 h.

2.5 Characterization

The total porosities of supports and unsupported intermediate layers were measured by water intrusion according to Archimedes' principle and the pore size distributions were determined by mercury intrusion (Pore size 9305, Micromeritics). The pore size distributions and specific surface areas of supported and unsupported top layers were measured by nitrogen adsorption/desorption (ASAP 2000, Micromeritics). The purpose of characterizing supported top layers was to determine whether the results obtained agree with the results from characterization of unsupported top layers. The gas and liquid permeabilities were determined for slip-cast supports with corn or rice starch, and for slip-cast supports with intermediate and top layers applied by dip coating, at the Geological Survey of Denmark. The gas permeability was measured with nitrogen in the pressure range 200–1000 mbar and the liquid permeability was measured with distilled water at two flow rates. Cross-sections of the ultrafiltration membranes prepared by the conventional and the alternative process were studied by scanning electron microscopy (SEM; JEOL, JXA-8600) to determine the layer thicknesses, and to reveal any detachment between the layers or cracks in the membrane.

3 Results and Discussion

The results in Table 3 show that suitable porosities and pore sizes were obtained for the supports sintered at 1550°C. The rice starch particles are smaller than the corn starch particles, and addition of rice starch to the slip before preparation of the support therefore results in smaller pore sizes. The tape-cast supports sintered at 1200°C have bimodal pore size distributions with two ranges of pore sizes. The ranges with the smaller pores were eliminated at higher sintering temperatures. The ranges with the larger pores originate from addition of the starch particles. A bimodal pore size distribution could be a disadvantage resulting in decreased permeability. There is, however, a large increase in the total porosity when a support sintered at 1200°C is compared with a support sintered at 1550°C resulting in a preserved or increased permeability. The sintering of tape-cast supports at 1100–1300°C showed that 1200°C gave sufficient strength for the support to be handled without breaking. Sintering of the support at 1300°C did, of course, increase this strength.

The pore sizes and porosities of the tape-cast intermediate layers sintered at 1200 and 1300°C were in the desired range (0·05–0·2 μm, 30% porosity). The figures in Table 3 can be compared with the results obtained from sintering of a slip-cast intermediate layer at 1000°C. Although a lower sintering temperature was used for the slip-cast sample, the resulting pore size was smaller and the porosity higher. Tape casting resulted in a less dense packing of particles, which was an advantage for the alternative process. A membrane prepared by the alternative process was sintered at 1300°C and is shown in Fig. 3. The shrinkage of the intermediate layer was too great at this temperature compared with the support, and cracks appeared in the intermediate layer. The cracks in the top layer were inherited from the intermediate

Table 3. Total porosities and pore sizes of supports and intermediate layers

	Porosity (%)	*Pore size* (*μm*)
Slip/tape-cast support 35 vol% corn starch (1550°C)	35	1–5
Slip/tape cast support 40 vol% rice starch (1550°C)	36	0·8–1·5
Tape-cast support 35 vol% corn starch (1200°C)	52·5	0·70–0·1 and 0·6–1·1
Tape-cast support 40 vol% rice starch (1200°C)	57	0·07–0·2 and 0·4–1·0
Slip-cast support 40 vol% rice starch (1000°C)	59·8	0·06–0·1 and 0·45–1·0
Slip-cast intermediate layer (1000°C)	36	0·06
Tape-cast intermediate layer (1200°C)	33	0·1
Tape-cast intermediate layer (1300°C)	28	0·1

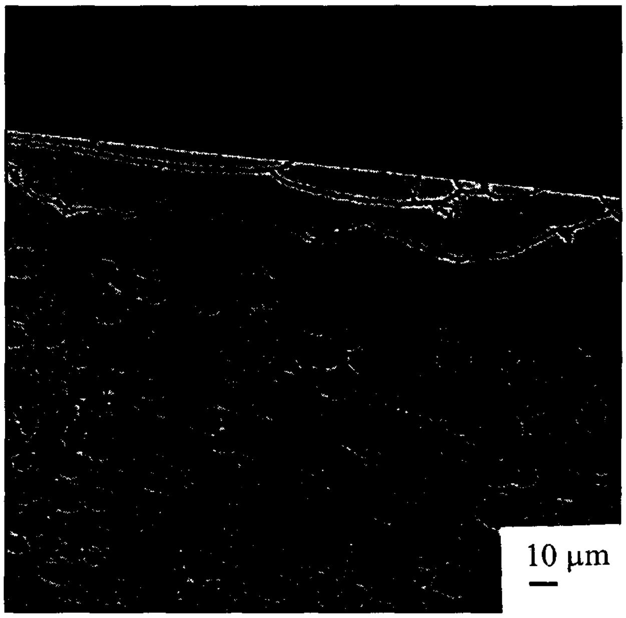
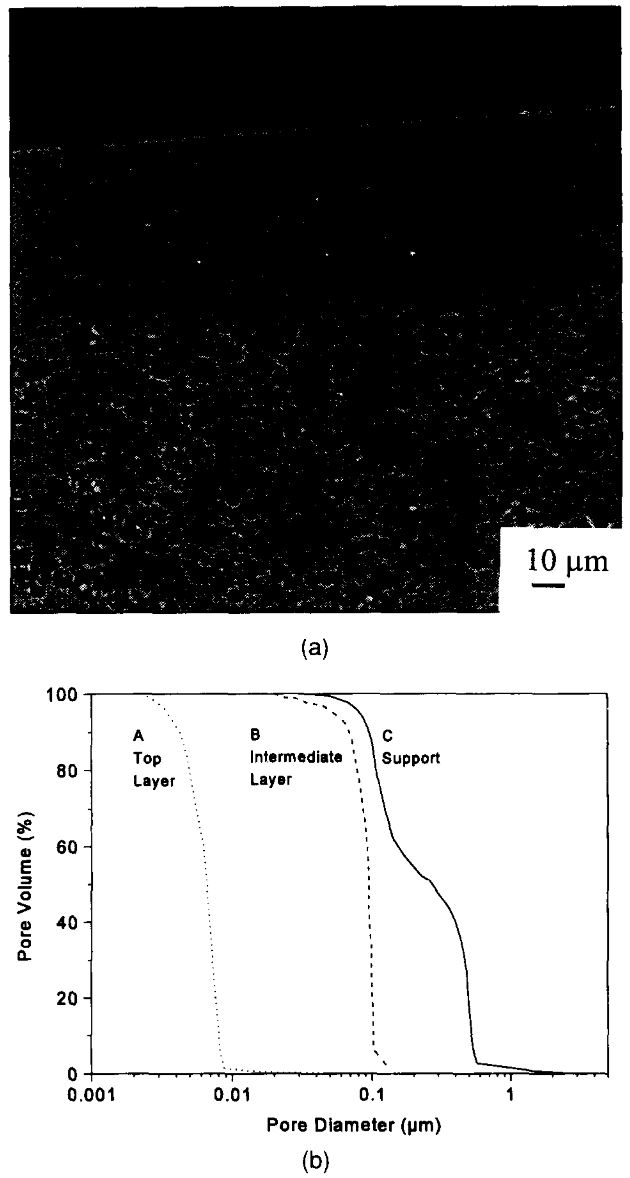


Fig. 3. Laminated support and intermediate layer sintered at 1300°C with dip-coated top layer (prepared by the alternative process).



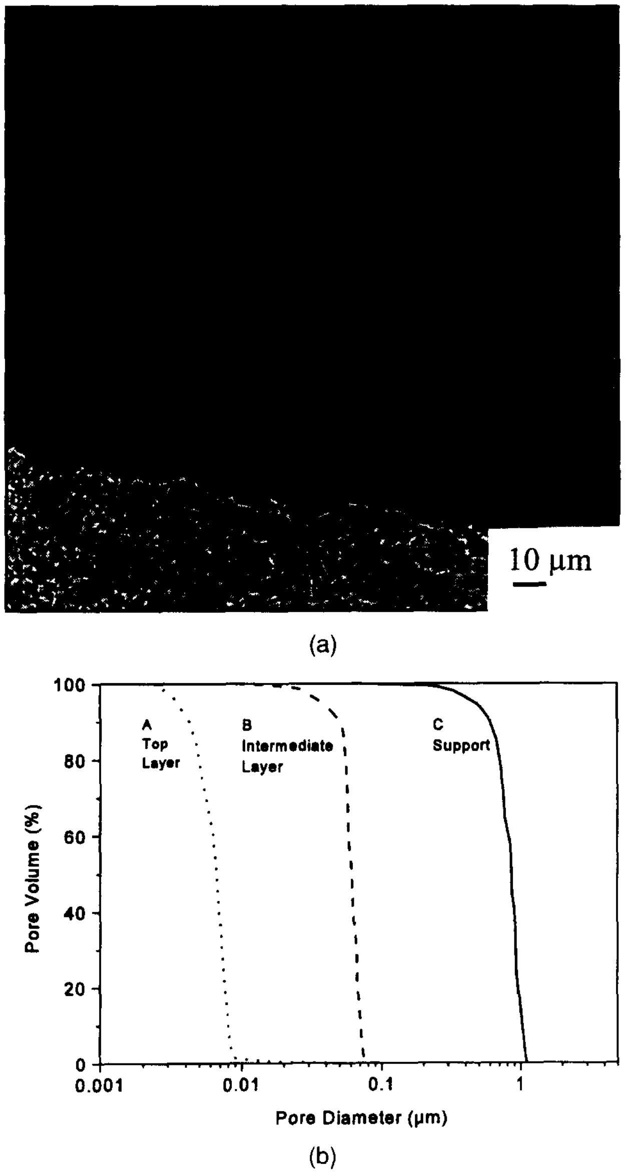
(a)

(b)

Fig. 4. (a) Laminated support and intermediate layer sintered at 1200°C with dip-coated top layer (prepared by the alternative process). (b) Pore size distributions for top layer, intermediate layer and support in a membrane prepared by the alternative process.

layer. Sintering of the laminated membrane in one step at 1200°C, however, resulted in a defect-free intermediate layer [Fig. 4(a)]. An excellent linkage between the support and the intermediate layer was obtained as the same alumina powder was used in the two parts. The tape-cast intermediate layer had a very uniform and controlled thickness which was a great advantage when applying the top layer. The thickness could be measured and varied during preparation. The thickness of the intermediate layer was 50 μm and the top layer was 3 μm thick. The pore size distributions for the individual layers and the support in a membrane prepared by the alternative process are shown in Fig. 4(b).

The thickness of dip-coated intermediate layers on supports with corn starch varied as the particles were partially sucked into the pores of the support. A coarser powder would have to be used when preparing the intermediate layer to solve this problem. The dip-coated intermediate layer on a support with rice starch was 110 μm, which is too thick. The dipping time should be reduced in this case. However, the layer was uniform and the particles did not penetrate into the pore structure of the support, see Fig. 5(a). The pore size distributions for the individual parts of a membrane prepared by the conventional process are shown in Fig. 5(b).



(a)

(b)

Fig. 5. (a) Slip-cast support and dip-coated intermediate layer with dip-coated top layer (prepared by the conventional process). (b) Pore size distributions for top layer, intermediate layer and support in a membrane prepared by the conventional process.

The results from the study of the influence of calcination temperature on the pore size distribution of unsupported top layers are shown in Fig. 6. The values are calculated from the nitrogen desorption branch. There is a broadening of the pore size distribution with increasing calcination temperature as the large pores grow at the expense of the smaller ones at high temperatures. Table 4 shows the increase in the average pore diameter for supported and unsupported top layers. The results from measurements performed on supported top layers were evaluated quantitatively on a diagram that revealed the pores in the top layer and in the intermediate layer as separate peaks. The average pore diameters are larger for the supported top layers than for the unsupported ones. The reason is that the support somewhat hinders the shrinkage of the top layer during calcination. The decrease in the specific surface area for unsupported top layers with increasing temperature is shown in the same table and indicates the degree of densification which takes place at increasing temperatures. Measurements of the total porosity do not necessarily reveal this phenomenon because large pores grow while small pores are eliminated, and the value of the total porosity can remain constant.[10] As mentioned above, the values of the specific surface area of supported top layers include the intermediate layer and the resulting figures do not accurately reveal the processes taking place in the top layer. The study showed that a calcination temperature of 600°C was suitable because the average pore diameter was still small, the specific surface area high and the binder was completely burned out. The highest application temperature possible for the prepared ultrafiltration membrane will be 500–550°C when the calcination temperature is 600°C unless any stabilization of the top layer is made.

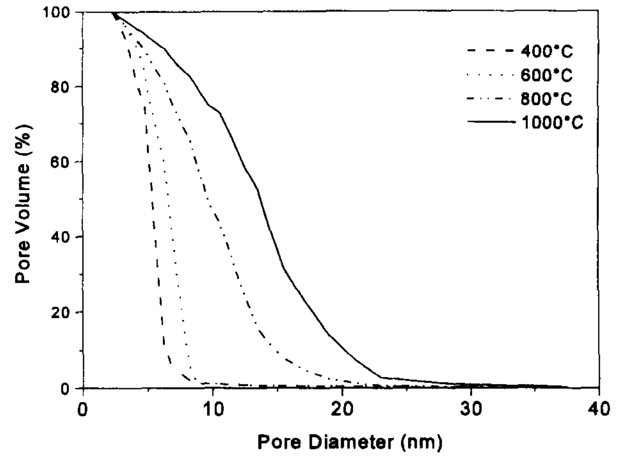


Fig. 6. Cumulative pore volume versus pore diameter for unsupported top layers at increasing calcination temperatures.

The results from the gas and liquid permeability measurements are summarized in Table 5. The permeability unit Darcy is derived according to the standard DIN 51058 from Darcy's law. The permeability of the support with corn starch is larger than that of the support with rice, which shows the influence of the pore sizes (See also Table 3). The permeability decreases, however, when an intermediate and a top layer are applied and the permeability is thus dominated by the small pores in the top layer. Tranto[8] obtained gas permeabilities of the same magnitude on extruded alumina supports and on supports with dip-coated intermediate layers applied. The fluxes were calculated from the results of liquid permeabilities and can be compared with values found in the literature. Fluxes for ultrafiltration membranes are

Table 4. Specific surface area (SSA) and pore diameters of unsupported top layers and pore diameters of supported top layers

Temperature (°C)	*Unsupported top layers*		*Supported top layers*
	SSA ^{1} *(m^2/g^{-1})*	*Pore diameter (nm)*	*Pore diameter (nm)*
400	223·1	4·4	6·5
600	195·2	5·4	6·5
800	146·6	6	9
1000	104·5	8	20

Table 5. Results from permeability measurements

	Pore size	*Permeability (mD)*		*Flux (l m^{-2} h^{-1} bar^{-1})*
		Gas	*Liquid*	
Support 35 vol% corn starch	1–5 μm	13·4	5·5	405·9
UF membrane (35 vol% corn)	~ 6 nm	3·1	0·5	23·2
Support 40 vol% rice starch	0·8–1·5 μm	5·6	2·3	108·1
UF membrane (40 vol% rice)	~ 6 nm	4·2	0·5	24·2

commonly in the range 10–1000 l m^{-2} h^{-1} bar^{-1}; depending on the pore sizes.[11] The conclusion concerning the permeability measurements is that the method to create porosity in the support by addition of starch particles does not negatively influence the results which are governed by the applied top layer.

The conventional and the alternative method to prepare ultrafiltration membranes have different advantages. The conventional method offers the advantage of supports with high strength and a narrow pore size distribution. The alternative method, on the other hand, has the advantage of being shorter and faster. The possibility of easily controlling the thickness of the intermediate layer and the good linkage between the intermediate layer and the support have several applications, among others in the field of catalytic membranes.[12] The pore size in the intermediate layer can also be varied using powders with different particle size distributions provided that sintering can be performed at the same temperature as the support.

4 Conclusions

An alternative process to prepare flat ceramic membranes was developed. The tape-cast support and tape-cast intermediate layer were laminated together before sintering. One advantage of the alternative process is that a drying and a sintering step is eliminated, resulting in a faster and cheaper preparation. Another benefit of this process is the excellent linkage between the support and the intermediate layer, as well as the uniform and controlled thickness of the intermediate layer.

The porosity in the support could be carefully controlled by the choice of starch particles. The desired pore sizes of the intermediate layer (60–100 nm) and the top layer (<<50 nm) were achieved by optimization of the calcination temperatures. Ultrafiltration membranes of alumina with pore sizes as small as 6.5 nm could be produced.

Acknowledgements

The authors would like to acknowledge the assistance of Ms Janne Tranto at the Institute of Mineral Industry, The Technical University of Denmark, Mr Niels Springer at the Geological Survey of Denmark, and Dr Hans Theliander at Chemical Engineering Design, Chalmers University of Technology. The Swedish National Board for Industrial and Technical Development (NUTEK) and the member companies in the Foundation for Silicate Research are thanked for financial support.

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