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Tape-cast ceramic membranes for microfiltration application

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Alumina membrane filters in the form of thin (0.3–0.8 mm) discs of 25–30 mm diameter suitable for microfiltration application, have been fabricated by the tape-casting technique. Their pore size could be varied in the range 0.1–0.7 μm and porosity in the range 25%–55% through optimization of experimental parameters. The most important factor which determines the pore size, is the initial particle size of ceramic powders used for this purpose. Temperature of firing, and also the soaking time are crucial parameters which determine the porosity. Water permeability under suction conditions varies in the range 110–900 $\mathrm{l\,m^{-2}\,h^{-1}}$ depending on porosity, pore size and thickness of the membrane. Most of these membranes, particularly those with pore sizes less than 0.5 μm, are found to be suitable for complete removal of bacteria from water and are also reusable after cleaning by acid or heat sterilization.

1. Introduction

A membrane is a selective barrier between two homogeneous phases. Transport of a species across the membrane occurs normally under a pressure gradient or sometimes under electrical potential gradient. Membranes are generally classified according to the pore size of the barrier layer or the size of the species retained over the membrane. Membranes used for reverse osmosis or gas separation have pore sizes around 1 nm, whereas ultrafiltration membranes have pore sizes in the range of 0.001–0.02 μm. The pore size of a microfiltration membrane lies in the range 0.02–2 μm. Membranes with pore sizes in the range 2–10 μm are used for fine filtration.

Depending on the field of application, various materials have been used for preparation of membranes. Most of the membranes presently in use are made of polymeric materials, which include cellulose acetate, nylon, polyester, polyamide, polyvinyl chloride, polysulphone, etc. In recent years, ceramic membranes utilizing alumina, cordierite, mullite, silicon carbide, silicon nitride, zirconia, silica, titania, etc., have gained ground, replacing polymeric membranes in several areas of applications owing to many of their advantages over polymeric and metallic membranes. They are resistant to high temperature, abrasion and chemical attack. They are not only suitable for elevated temperature applications but also can be cleaned by high-temperature treatment. Ceramic membranes also tolerate cleaning with alkalis and acids and resist high pressures up to 30 atm required in the back-flushing technique. Besides polymeric and ceramic membranes, porous metallic membranes made of stainless steel, monel metal, nickel, hastalloy, silver, and inconel are also commercially available.

Ceramic membranes have already found application in areas such as food processing [1], biotechnology [2], pharmaceutical and petrochemical industries, particularly for separation of macromolecules of different sizes. In addition to separation, the membranes can also be used as catalytic agents as, for example, in hydrocarbon conversion [3].

The structure of a ceramic membrane is normally multilayered in nature. There is a gradual decrease in pore size and layer thickness starting from the lower layer to the top layer. The lower layer is called the support, with pores 1–15 μm, the middle layer is called the intermediate layer having a pore size of 0.1–1 μm, and the top layer is called the separation layer, with a pore size 3–100 nm. The combination of the lower and the middle layer is called a microfiltration or primary membrane, and that of the three layers is called an ultrafiltration or secondary membrane [4]. The overall thickness of a ceramic membrane is therefore much higher ($>$ 2 mm) compared to its polymeric counterpart.

Considering the fact that the thinner the membrane, the higher is the permeate flux and the lower is the pressure gradient required, an attempt has been made in this investigation to prepare thin ceramic membranes by the tape-casting process which is normally used for the preparation of thin ceramic substrates used in the microelectronic industry [5]. Possibly the technique has not been tried in a regular manner to prepare ceramic membranes with controlled pore structure and porosity.

Usually tape-casting technique uses polymer-bonded flexible ceramic sheets of thickness 25–1000 μm which are used as a precursor for the fabrication of thin ceramic layers or discs. This is one of the

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low-cost processes for the manufacture of thin ceramic sheets of controlled thickness and very good surface smoothness. In this method, ceramic powder of sufficient fineness is suspended in an organic solvent to which a binder, a plasticizer and a dispersant are added to make the suspension homogeneous, well-dispersed and stable. The dispersant used depends on the nature of the ceramic powder and that of the solvent. For the alumina–MEK–EtOH system, the most widely used dispersant is phosphate ester [6]. Most binders require the addition of a plasticizer to improve the flexibility of the tape. Polyethylene glycol (PEG) and benzyl butyl phthalate (BBP) act as plasticizers for the binder polyvinylbutyral [7]. The most commonly used binder for alumina powder is polyvinylbutyral and the corresponding solvent is either an azeotropic mixture of methyl ethyl ketone (MEK) and ethylalcohol (EtOH), or trichloroethylene (TCE) and ethyl alcohol [8–10].

2. Experimental procedure

2.1. Membrane material

Alumina powders from different sources having different mean particle sizes have been used to prepare the membranes. The average particle size as well as the size distribution were determined using a Micrometrics (USA) Sedigraph 5100. The D_{50} values obtained for each of the powders and also the sources of these powders are presented in Table I. Their size distribution may be seen from Fig. 1.

TABLE I Mean particle size (D_{50}) and sources of different alumina powders used in this investigation

Sample code	Average particle size (μm)	Source
A3	0.3	ACC, Bombay
A6	0.6	Indal, Calcutta
A10	1.0	Indal, Calcutta
A12	1.2	Alcoa, USA
A15	1.5	Indal, Calcutta

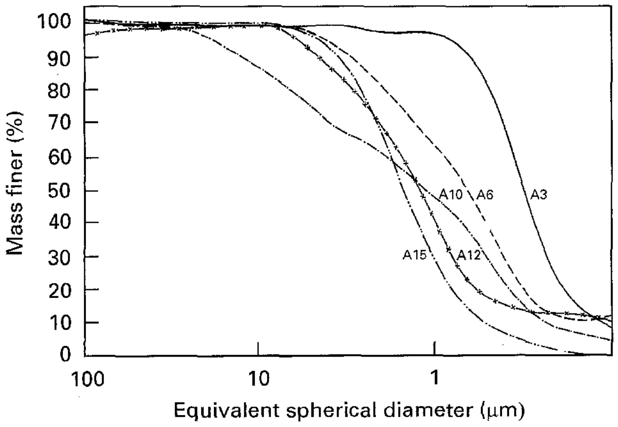

Figure 1 Particle-size distribution of different alumina powders used in this investigation.

2.2. Membrane preparation

Flexible tapes were prepared with each of the alumina powders. For this purpose, they were suspended in MEK–EtOH azeotropic mixture using Emphos 2A (phosphate ester) as dispersant. The suspension was milled for 4 h for deflocculation. In the second milling step, PVB as binder and a mixture of PEG and BBP as plasticizer were added to the suspension and milled for another 20 h. The suspension after 24 h milling was degassed and spread on a flat glass bed as a thin layer using a doctor blade. It was allowed to dry overnight. A thin sheet with very high uniformity and surface smoothness was formed. Powder loading of the green tapes was varied in the range 71%–83%, organic content 17%–29%, and the binder to plasticiser ratio used was 1:1 (dry basis). Dried tapes with sufficient strength and flexibility were cut into small pieces in the form of circular discs with diameter ranging from 25–50 mm and fired at different temperatures ranging from 1200–1500 °C for different lengths of time (2–12 h). Both heating and cooling rates were carefully controlled in order to avoid warpage or cracking of the fired discs. The complete firing schedule is as given below.

Heating: 30 °C h^{-1} (up to 800 °C) then 60 °C h^{-1} (up to the soaking temperature)
Cooling: 60 °C h^{-1} (down to 1000 °C) then 100 °C h^{-1} (to room temperature).

2.3. Characterization

The powder loading was determined from the loss of weight between green and fired tapes. Pore-size distribution and porosity of the fired samples were determined using mercury porosometry. Microstructures of fired samples were analysed by scanning electron microscopy. The permeability and permeate flux were measured under suction pressure (rotary vacuum pump) using a specially designed permeability cell.

3. Results and discussion

3.1. Binder burn-out from the green tapes

Green tapes contain a considerable amount of organic material as binder. So the firing conditions need to be controlled with precision to avoid deformation of the fired membranes. To determine the best possible firing schedule of the tapes, we performed thermogravimetric analysis of the samples. The results are presented in Fig. 2. It may be noted from this figure that decomposition of green tape takes place in three major steps. The first step, which continues up to 80 °C, indicates the evaporation of solvent from the green tape. Weight-loss data show that the solvent content of the green tape is around 2%. The second step of decomposition, between 170 and 330 °C, shows the maximum weight loss of 17%. Another 5% weight loss takes place between 350 and 600 °C. The weight becomes stable beyond about 650 °C. These temperatures may vary slightly depending on particle size of the powder, heating rate, etc. Total weight loss during the burn-out process is around 24%, which includes

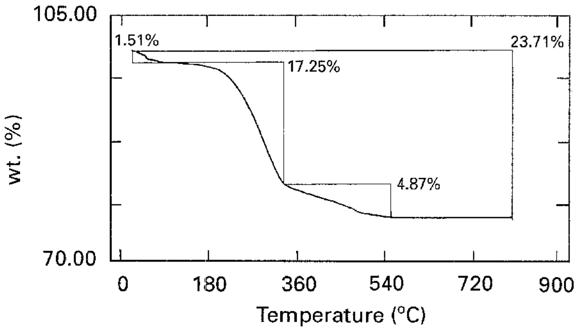

Figure 2 Thermogravimetric analysis of the green tape.

the losses primarily from the binder, plasticizer, dispersant, and the residual solvent. During the burnout, large quantities of gases evolve which may cause the warpage of the membranes. It was therefore necessary to use very slow heating rates, particularly in the temperature range where major decomposition steps occur. As the samples were very thin (0.3–0.5 mm) it was also necessary to maintain a slow cooling rate, particularly to avoid cracking or breakage. In addition, it was also necessary to apply some weight on the tapes during firing to avoid warpage of the fired membranes. All these aspects were considered in choosing the heating and cooling schedule given above.

3.2. Variation of pore size and porosity with different experimental parameters

Experiments have been carried out to understand the influence of various experimental parameters on the pore size, its distribution and the overall porosity of the fired membranes. The results have indicated that the most important parameter which controls the pore size, is the initial particle size of the alumina powder used to prepare the membranes. Fig. 3. shows the change of pore size with particle size of the starting powder. It may be noted that within the range of particle sizes used in this investigation there is nearly a straight line relationship between the mean particle size (D_{50}) and the mean pore size of the fired membranes. As expected, the finer the particle size, the smaller is the pore size. This provides a very simple and effective means of controlling the mean pore size of the membrane at any desired value, especially within the range studied. The pore-size distribution of the membranes also has a strong correlation to the particle-size distribution of the starting powders. For a narrower particle-size distribution, pore-size distribution is also relatively narrow. From Fig. 1 it is seen that particle-size distributions of A3 and A15 powders are narrower than that of A6. Accordingly, the pore-size distributions of the membranes prepared from A3 and A15 powders are narrower than that prepared from A6 powder (Fig. 4). It is interesting to note that the firing temperature and time have only a small effect on the mean pore size (Fig. 5) and pore-size distribution (Figs 6 and 7) of the fired membranes.

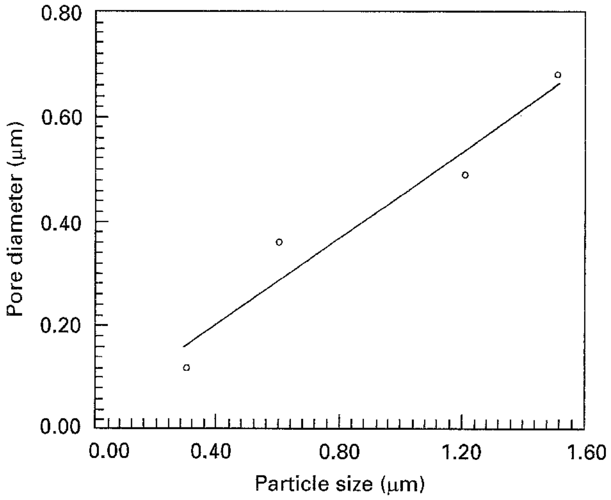

Figure 3 Change of pore size with initial particle size of thin alumina membranes sintered at 1350 °C for 4 h.

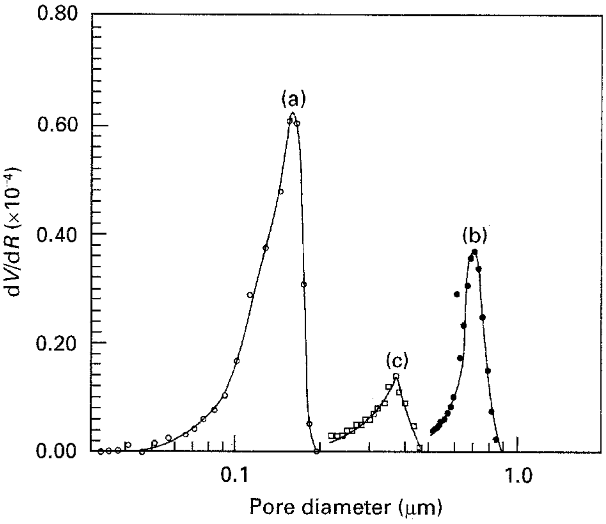

Figure 4 Pore-size distribution of membranes prepared from powders of different particle sizes sintered at 1350 °C for 4 h. (a) A3 alumina, pore diameter 0.12 μm (peak), (b) A15 alumina, pore diameter 0.68 μm (peak), (c) A6 alumina, pore diameter 0.32 μm (peak).

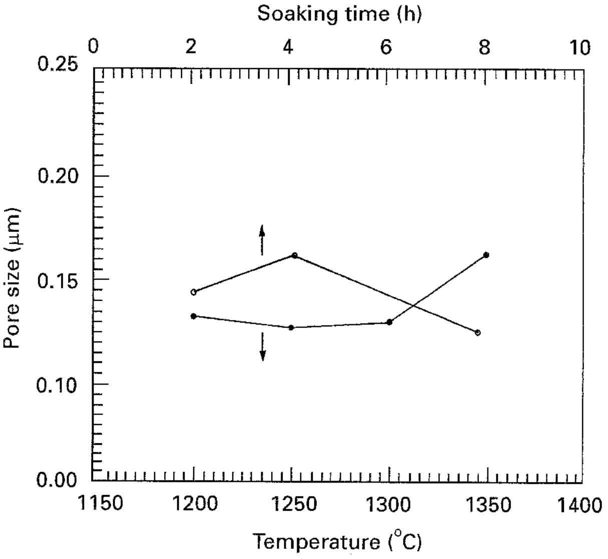

Figure 5 Change of pore size of alumina membranes with sintering temperature (for a fixed soaking time of 4 h) and soaking time (at a fixed temperature of 1350 °C).

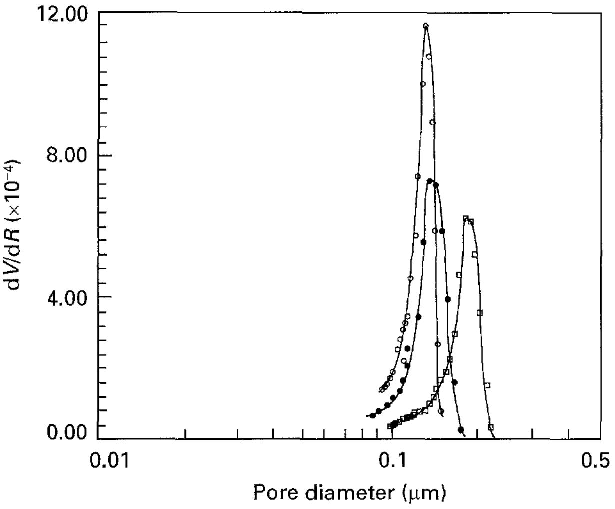

Figure 6 Pore-size distribution of alumina membranes prepared at different sintering temperatures with a constant soaking time (4 h): (□) 1350 °C, (○) 1250 °C, (●) 1200 °C.

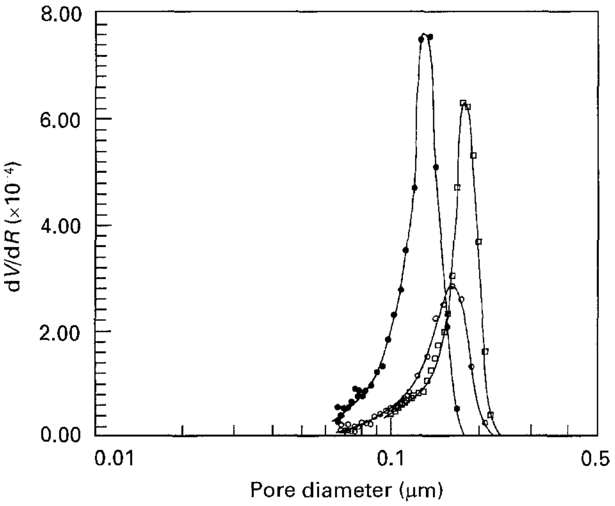

Figure 7 Pore-size distribution of alumina membranes sintered for different soaking times at a given temperature (1350 °C): (○) 2 h, (□) 4 h, (●) 8 h.

With increasing firing temperature, the pores become finer and their distribution also becomes narrower. A very similar effect is also observed with the variation in soaking time at any particular firing temperature. These effects are the direct consequence of the sintering phenomenon during which the interparticle pores are slowly filled up due to mass transport. As expected, increase of temperature has a stronger influence than increasing the soaking time. In addition to pore size and its distribution, both of which determine the range of application of a membrane, another most important parameter which determines the efficiency of a membrane is the overall porosity which, in turn, determines its permeability. As shown in Fig. 8, both the firing temperature and soaking time have significant effects on the ultimate porosity which, as expected, decreases with time as well as temperature. This is the direct consequence of the sintering phenomenon in which neck growth followed by pore closure takes place to greater extents as the sintering temperature or soaking time is increased. Fig. 9 shows the typical microstructures of the membranes prepared from two different starting powders. It may be noted that in either case the grains as well as the pores are of slightly elongated shapes. However, in accordance with the porosometric data, the pores of Fig. 9a are relatively more uniform than those of Fig. 9b.

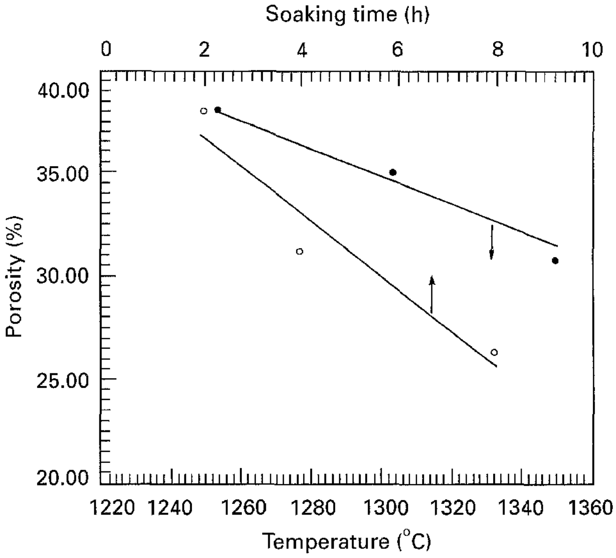

Figure 8 Change of porosity of alumina membranes with firing temperature (for a fixed soaking time of 4 h) and soaking time (at a fixed temperature of 1350 °C).

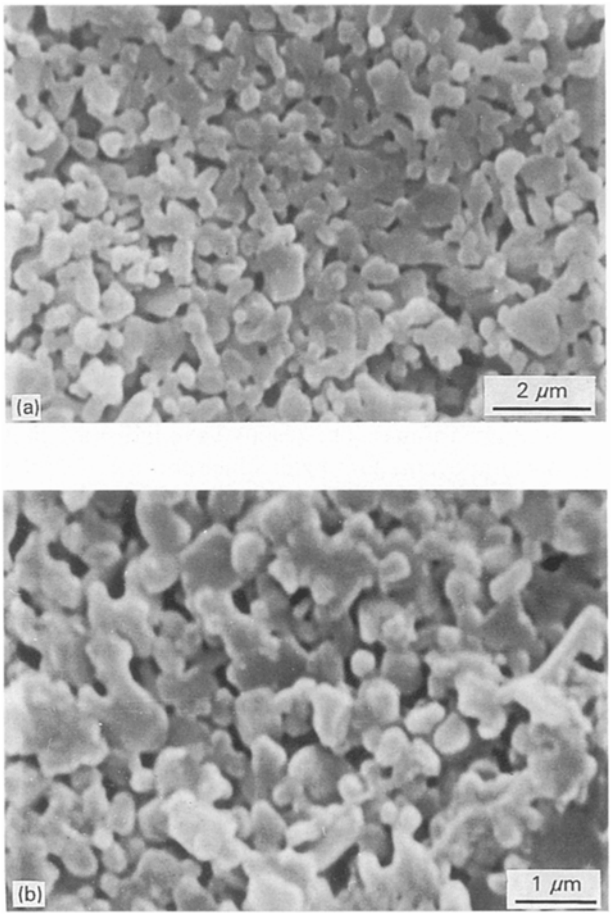

Figure 9 Scanning electron micrographs of membranes prepared from two different sources of alumina powders: (a) A3, (b) A6.

TABLE II Variation of flow rate with pore size and porosity of the membranes

Powder code	Mean pore size (μm)	Porosity (%)	Flow rate ($\mathrm{l\,m^{-2}\,h^{-1}}$)
A3	0.12	31	110
A6	0.28	53	236
A12	0.49	38	552
A15	0.68	42	908

TABLE III Variation of flow rate with sintering temperature and time for membranes prepared with A3 powder

Sintering temp. (°C)	Soaking time (h)	Mean pore size (μm)	Porosity (%)	Flow rate ($\mathrm{l\,m^{-2}\,h^{-1}}$)
1300	4	0.13	35	98
1350	4	0.16	31	81
1350	2	0.15	38	110

The ultimate test of a membrane is its ability to separate the desired species from a liquid medium at a sufficiently high rate. Therefore, the rate of water permeation through the membranes prepared under different conditions has been measured in this investigation using a specially designed sample holder. The measurements were carried out under vacuum of around 0.01 mbar. Thinner samples (less than 0.5 mm thick) did not have sufficient mechanical strength to withstand the suction pressure and therefore required a specially designed support for testing. The results are presented in Table II and III. As expected, both pore size and porosity have strong effects on the flow rate. As these parameters are, in turn, controlled by the sintering temperature and time, in addition to the initial particle size, the formers also have an influence on the flow rate. The observed flow rates are more than sufficient, particularly for laboratory and other low-volume applications. The usefulness of the membranes, as far as biochemical application is concerned, has been tested by their ability to purify water from various sources (tap water as well as sewer water) in terms of bacterial content. It has been noted with interest that the membranes with average pore size of 0.49 μm or less are capable of removing all water-borne bacteria and these membranes can be reused after either acid cleaning or heat sterilization. More detailed investigation is, however, necessary to identify full application potentiality of these membranes.

4. Conclusions

The ceramic tape-casting process can be used to fabricate thin alumina membranes for microfiltration application. Two most important properties of the membrane, namely pore size and porosity, can be controlled to a large extent by two independent experimental parameters such as initial particle size and firing temperature. It is necessary that while the initial particle size needs to be selected by the pore-size requirement of the membrane, the primary factor which would determine the firing temperature is not only the porosity requirement but also the requirement of minimum mechanical strength. It may also be remembered that the finer the pore size, the lower would be the firing temperature to achieve a specified mechanical strength. In addition to the average particle size of the starting powder, its distribution also has an important influence on the membrane characteristics. As expected, the narrower the particle-size distribution, the more uniform is the resulting pore size. Both pore size and porosity influence the permeability of the membranes.

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