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Effect of Size Distribution of the Starting Powder on the Pore Size and its Distribution of Tape Cast Alumina Microporous Membranes

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Abstract

Thin disc type pure alumina membranes have been prepared by tape casting technique. Pore size distribution and pore volume have been determined by mercury porosimetry. Initial particle size of the alumina powder and the size distribution are found to have a strong influence on the ultimate median pore size and pore size distribution of the fired membranes. The spread of the particle size distribution of the powders is expressed by 'quartile ratio' which represents the size ratio corresponding to the cummulative finer percentages of 75 and 25 in the particle size distribution curve. With higher quartile ratio (wider particle size distribution) not only the median pore size increases but also the distribution tends to be bimodal. This is explained on the basis of certain basic sintering behaviors of the fine powders in general. © 1999 Elsevier Science Limited. All rights reserved

Keywords: membranes, Al_2O_3, tape casting, porosity, microstructure – final.

1 Introduction

For many years porous materials have been used for the separation of fluids in a number of industrial processes. Filter papers or cloths have been the traditional materials used for separation of solids from the liquids or gases. With the advancement of this physical separation technology, much finer filters or membranes have found their places in several industries such as biotechnological, phar-maceutical etc. Until very recently polymeric materials dominated the scene so far as the preparation of membranes is concerned. However, in recent times, ceramic membranes have been used in a growing number of areas in different industries such as water purification or filtration, clarification and sterilisation of beverages, concentration of proteins in food and dairy industries, purification and recovery of lignin in paper industries and many others.[1,2] A possible new application is the separation of high molecular hydrocarbons at elevated temperatures (a few hundred degrees celcius) in the petrochemical industry.[1] A rapid growth of their use in recent years is due to their inherent chemical, physical, thermal and microbial stability and improvement in their fabrication techniques. Among different types of ceramics used to prepare the porous membranes alumina is used most widely.[3] There are different methods of manufacturing the porous ceramics, e.g. by using burnout additives,[4,5] sublimable compounds etc.[5] Recently, the present authors prepared a very thin disc type ceramic membrane made of pure alumina by tape casting (doctor blade) process,[6] which is normally used for the preparation of thin ceramic substrates used in the microelectronic industry.[7,8] Membranes with a narrow pore size distribution are necessary to obtain a high degree of separation. The important controlling factors in the production of porous materials by the tape casting process is the average particle size of the starting powders and their size distribution, polymeric binder content in tape casting slurry as also the final firing condition of the tapes. In a previous paper we have reported the effect of several of these factors on the development of pore structure and porosity of the fired membranes.[9] Here we report particularly the relationship between the particle size distribution of the starting powder and the resulting pore size distribution of the tape cast and fired membrane.

2 Experimental Procedure

2.1 Membrane material

Alumina powders with different median particle sizes (D_{50}) ranging from 0·22 to 1·50 μm (obtained

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from M/S ACC, India; Indal, India; Alcoa, USA and Condea, Germany) were used in ‘as received’ condition to prepare the membranes. Only the powder A63 (Table 1) was prepared by grinding A108 powder in a Planetary mill for 4 h. The median (D_{50}) and modal particle sizes and also the size distribution were determined using a Sedigraph 5100 (Micromeritrics, USA) particle size analyzer. The surface area of the powders was measured by N_2 adsorption method using BET equation. The results are presented in Table 1.

2.2 Membrane preparation

Flexible tapes were prepared with each of the alumina powders separately. For this purpose they were suspended in an azeotropic mixture of methyl ethyl ketone (MEK) and ethyl alcohol (EtOH) using Emphos 2A (Witco chemicals, USA) as the dispersant. The suspension was milled for 4 h for deflocculation. In the second milling step, polyvinyl butyral (PVB) as binder and a mixture of benzyl butyl phthalate (BBP) and polyethylene glycol (PEG) as plasticisers were added to the suspension and milled for another 20 h. Then the suspension 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 of good uniformity and surface smoothness was formed. Dried tapes with sufficient strength and flexibility were cut into small pieces in the form of circular discs and fired at different temperatures in the range 800–1600°C for a constant soaking time of 4 h. Figure 1 shows the flow chart for the complete process of tape casting technique. After drying the circular discs were punched out from the tapes and fired at high temperature as per the schedule given below.

Heating : 300°C h^{-1} (up to 80°C) then 60°C h^{-1} (up to soaking temperature) Cooling 60°C h^{-1} (down to 1000°C) then 100°C h^{-1} (to room temperature).

Porous properties of the fired membrane such as porosity, pore size, and its distribution were evaluated by mercury porosimetry (Quantachrome Autoscan mercury porosimetry).

3 Resuts and Discussion

Experiments have been carried out to understand the influence of various experimental parameters on the membrane properties such as porosity, pore size distribution, median pore size etc. First of all, the particle size and its, distribution are found to have important effects on the pore size and its distribution in the membrane. Figure 2 shows that the median pore size of the membranes are directly proportional to the initial particle size (D_{50}) of the raw material. It may be noted that within the range of particle size used in this investigation there is nearly a straight line relationship between the mean particle size (D_{50}) and the median pore size of the fired membrane. As expected, finer the particle size, smaller is the pore size. This provides a very simple and effective means of controlling the pore size of the membrane at any desired value,

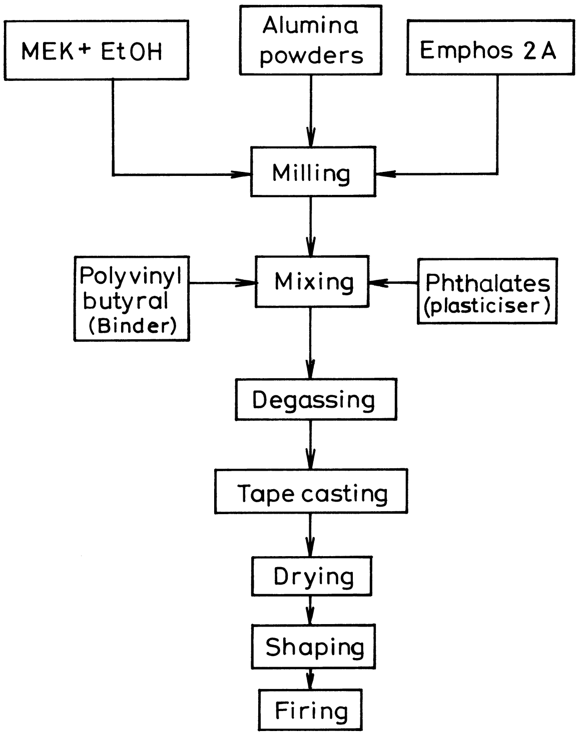

Fig. 1. Flow sheet for preparation of the membrane.

Table 1. Characteristics of the starting alumina powders

Sample code	*Source*	*Median particle size* D_{50} (μm)	*Modal particle size* (μm)	*Surface area* ($m^2 g^{-1}$)
A22	Condea, Germany	0·22	0·24	15·7
A31	ACC, India	0·31	0·33	25·4
A33	Alcoa, USA	0·33	0·44	—
A51	ACC India	0·51	0·47	20·0
A52	Indal, India	0·52	0·44	8·6
A63	Indal, India	0·63	0·47	9·1
A108	Indal, India	1·08	0·50	7·8
A121	Indal, India	1·21	1·06	3·6
A128	Indal, India	1·28	1·32	3·3
A150	Indal, India	1·50	1·53	2·8

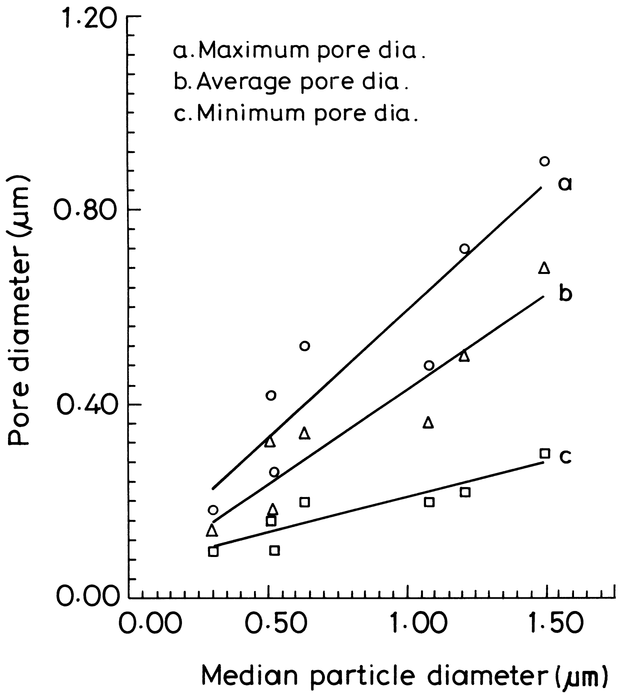

Fig. 2. Effect of particle size on the pore size of the alumina membranes.

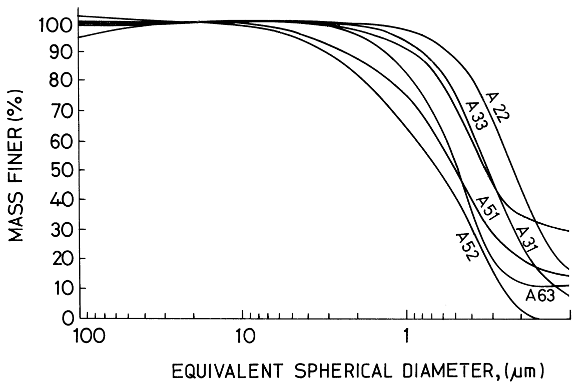

Fig. 3. Graphical representation of particle size distribution of different alumina powders.

especially within the range studied. Not only the initial particle size but also the particle size distribution has a strong influence on the median pore size and the distribution. One of the simple ways to make a comparison between the spread of the particle size distribution data is to measure the difference between the particle sizes corresponding to the cummulative finer percentages of 75% and 25% in the particle size distribution curve. Such a quantity is normally referred to as the quartile range and designated as '$_{25}X_{75}$' in the literature.[10] Figure 3 shows the graphical representation of the particle size distribution of different powders used in this investigation. In this figure it may be noted that the powder A33 contains a large percentage of fines (about 30% below 0·1 µm) compared to A22 and A31 (about 10% below 0·1 µm). It indicates that the size distribution of A33 is much wider than that of the other two. Accordingly the $_{25}X_{75}$ values of A33, A22, and A31 are 7·02, 2·7 and 2·16 respectively. Similarly particle size distribution of A52 is narrower than those of A51 and A63. Quartile ratio values of all the powders used in this study are compared and presented in Table 2.

The pore size distribution of samples from powders having different distribution parameters but with similar median particle sizes of 0·3 to 0·5 µm are shown Figs 4 and 5 respectively. It is interesting to note that the peaks of the distribution curves appear at different values of pore sizes. For the 0·3 µm sized powders the median pore diameter varies between 0·12 and 0·20 µm corresponding to a quartile ratio 2·16 to 7·02. Similarly for 0·5 µm powders (Fig. 5) the pore diameter varies between 0·20 to 0·32 µm corresponding to quartile ratios of 2·42 and 3·42 respectively. It may be noted that wider the particle size distribution of starting powder, the larger is the median pore size of a fired membrane. This may be due to the fact, that a green compact with wide particle size distribution contains a widely distributed pores. During sintering, the smaller pores are eliminated at a much faster rate than the coarser pores, thereby leaving behind a relatively large number of coarser pores, resulting into an increase in the value of median pore size. In addition, there may be a tendency of coalesence of the finer pores to form coarser pores, which also results in a larger median pore size. On the other hand, for the particles have narrow size

Table 2. Relation between the particle size distribution and the pore size distribution of different membranes

Powder code	*Quartile ratio* $_{25}X_{75}$	*Maximum pore dia meter* (µm)	*Median, pore dia meter* (µm)	*Modal pore size* (µm)
A22	2·70	0·16	0·15	0·15
A31	2·16	0·14	0·12	0·10
A33	7·02	0·23	0·20	0·19
A51	4·12	0·38	0·32	0·29
A52	2·42	0·20	0·21	0·22
A63	4·34	0·43	0·33	0·35
A108	11·56	0·48	0·36	0·35
A121	3·72	0·65	0·51	0·48
A128	2·63	0·69	0·61	0·57
A150	2·78	0·82	0·73	0·68

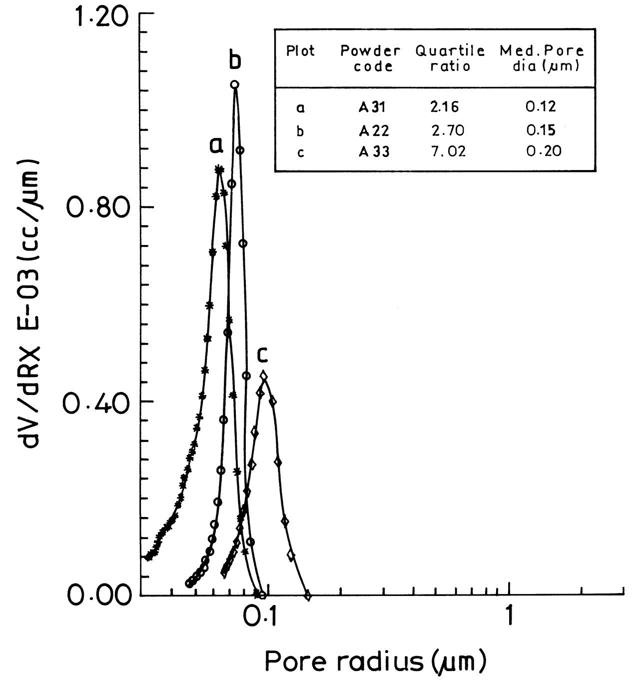

Fig. 4. Pore size distribution of alumina membranes having same particle size (0·3 µm) different distribution.

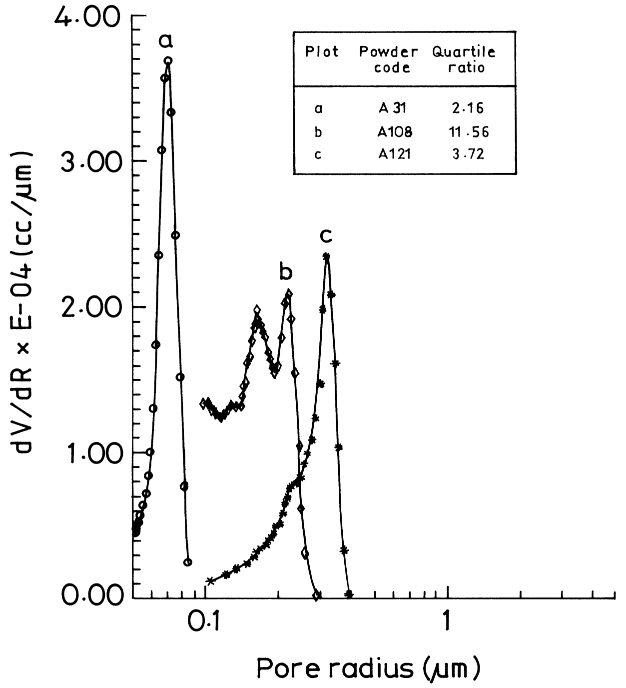

Fig. 6. Pore size distribution of alumina membranes prepared from powders of different quartile ratio.

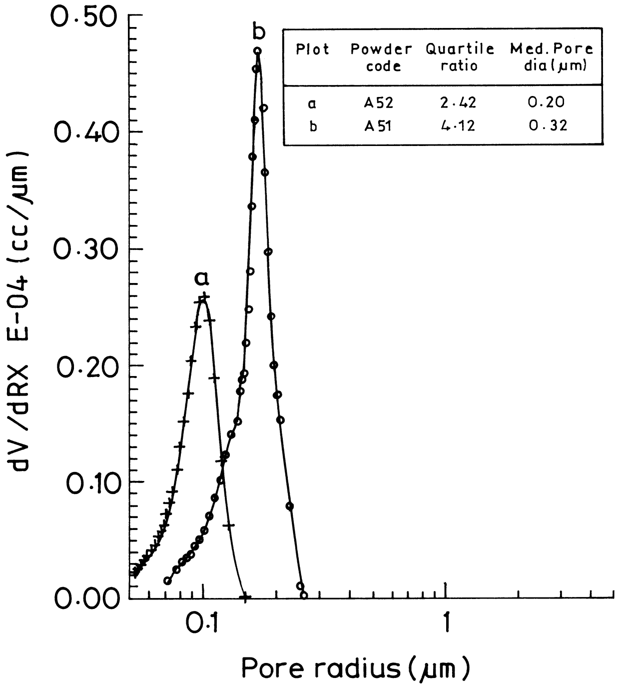

Fig. 5. Pore size distribution of alumina membranes having same particle size (0·5 µm) different distribution.

distribution, this effect is much less, and therefore there is no coarsening in the resulting pore size. Figure 6 depicts the pore size distribution of the membranes prepared from the alumina powders having different median particle sizes and distribution. As expected, narrower the particle size distribution the more uniform is the resulting pore size. As evident from this figure, the mean pore size (peak) of the membrane increases with the mean particle size of the starting powder. In addition, one may also notice that the pore size distribution of the membrane prepared form A108 and A121 powders are bimodal in character compared to a single mode distribution in case of A31 powder. The bimodal nature of the curve is quite distinct in case of A108 but not so clear for the A121 powder. The phenomenon of bimodality is directly related to the particle size distribution or the quartile ratio. It may be noted that A108 powder has a quartile ratio of 11·56 which is the highest among all the powders used in this investigation and consequently we get the most distinct bimodality in pore size distribution. On the other hand the bimodality of the membrane prepared from A121 is relatively less because the quartile ratio in this case is smaller (3.72). Membranes prepared from A31 having a low median particle size (0.31 µm), as also small quartile ratio (2.16) produce a single mode distribution (Fig. 6). A11 these results indicate that the tendency of bimodal distribution of the pores increases as median particle size gets larger together with a wider particle size distribution. This correspondance between the particle size distribution and the resulting pore size distribution of different membranes also may be seen from the data presented in the Table 2.

Particle size distribution also influences the porosity or pore volume of the ultimate membrane. In Figs 4 and 5, the area under the peaks represent the total pore volume per unit weight of the membranes. A comparison of these peaks indicates that the membranes prepared from the powders of nearly the same particle size but different size distribution have different porosity. The measured

Table 3. Comparison of pore volume of membranes with different quartile ratio of the starting powder

Powder code	*Particle size (μm)*	*Quartile ratio* $_{25}X_{75}$	*Pore volume* $cm^3 g^{-1}$
A31	0·31	2·16	0·1581
A33	0·33	7·02	0·1008
A51	0·51	4·12	0·1562
A52	0·52	2·42	0·1581

pore volumes of membranes with different quartile ratios are compared in Table 3. Difference in pore volume arising from size distribution is quite clear from the data of samples A31 and A33, however, it is not so distinct for the samples A51 and A52. It is well-known that the pore volume in a green compact is a function of the size distribution of constituent particles. The wider the distribution the less is the pore volume of the compact. From simple geometry one can calculate that the pore volume in a close packed compact of monosized particles is 26%. Addition of smaller particles to a compact of larger sized powders has the effect of filling the voids without increasing the overall volume of the compact, thus reducing not only the total pore volume but also the size of each pore. During sintering material transport takes place because of the difference in radii of curvature and surface energy, leading to neck formation. The finer the pore, the faster is the neck growth. Therefore, particles with wider size distribution not only produces denser green compacts but also sinter to a greater extent. So the open porosity is less for a widely distributed powder.

4 Conclusion

Porous alumina membrane for microfiltration application can be prepared by the tape casting process. The influence of particle size and its distribution has an important effect on the pore size, pore size distribution and porosity or pore volume of the membrane. Initial particle size of the starting powder is the key factor for controlling the pore size of the membrane. From the range of particle size distribution defined by the term ‘quartile ratio’ uniformity of pore size distribution can be estimated. The lower the value of ‘quartile ratio’ the narrower is the pore size distribution. It becomes bimodal beyond a certain value of this ratio. For powders with the same average particle size but different size distribution, pore volume is lower for a powder of wider distribution.

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