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Porosity Development of Diatomite Layers Processed by Tape Casting

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Abstract: The processing from colloidal suspensions is a good method to obtain bodies with low microstructural heterogeneities, by careful control of the interfacial stresses. In previous papers we described the use of slip and tape casting techniques to obtain diatomite porous layers, having controlled morphology such as the amount and size of pores. The present work reports the use of tape casting bodies for filtration purposes. As the maximum thickness of the layers produced by tape casting is about 0.3 mm, their mechanical resistance is very low. It was necessary to produce thicker compacts made by several single layers (up to 20), obtained by thermocompression at different temperatures between 20 and 90°C followed by sintering at 1200°C. By selecting a careful heating programme, final bodies with 0.6–1.3 mm thickness were obtained, having porosity levels of about 44% and pore sizes between 0.1 and 1 μm. High bending strength values (57 MPa) were obtained, enough to support mechanical stresses in use as a membrane. Permeability to an air flux was evaluated as a function of relevant morphological parameters (porosity, thickness, etc.).

1 INTRODUCTION

1.1 Ceramic membranes and porous beds

The art of making dense ceramics has been practised and developed for decades. Efforts have been made to increase density, for instance by using smaller and more active particles, and by employing higher pressures or novel processing techniques such as hot isostatic pressing. The ability to produce porous ceramics with controlled pore size and porosity is less well documented. Recently, efforts have been directed towards the development of ceramic filter systems in which the microstructure is tailored to the application.[1–3] This objective requires a careful characterisation of processing parameters, in order to achieve reproducible porous structures. Compared with other materials, like polymers or metals, the ceramic-based systems have higher chemical resistance and refractoriness, but require higher temperature processing conditions to get enough mechanical resistance and show brightly-type fracture.[4] Engineering research on ceramic membranes has had two primary objectives. The first and by far the more extensively investigated is the development of membranes for separation processes.[5,6] In parallel with this work, microporous membranes have been considered as catalysts or supports for chemical reactions.[7] Different materials like alumina, mulite, zirconia, SiC, etc., have been tested for these purposes, and many are now commercially available.[4,8,9]

Membranes are defined as thin selective barriers between two homogeneous phases that allow preferential passage of certain substances across their structure.[5] Separation occurs under a pressure gradient or sometimes under an electrical potential gradient. Systems to separate are solid particles in liquid systems, larger molecules (proteins) from liquid systems, liquid/liquid separation and gas separations with or without catalytic reactions.[8] In membrane separation applications the aims are high permeability and selectivity values. This is normally realised in an asymmetric structure, as

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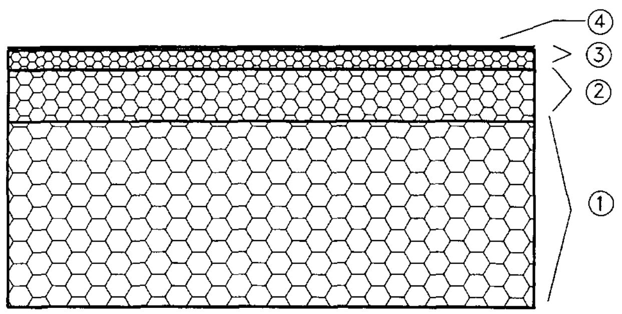
shown in Fig. 1. In this layered shape there is a gradual decrease in pore size and layer thickness starting from layer 1 to layer 4. Generally, layer 1 is called "support", with pores between 1 and 15 μm; 2 is the intermediate layer, and is made by pores between 0.1 and 1.5 μm; layer 3 is the separation layer with pores of 3–100 nm, which can be chemically modified in layer 4. The combination of different layers gives several types of filtration, from microfiltration (primary layer) to hyperfiltration and gas separation, depending on the size of particles retained.[8,10,11]

Keizer *et al.*[8] described synthesis methods commonly used to fabricate this type of membrane. In a cylindrical configuration, the porous support tube is normally prepared by extrusion, and further coating steps of finer-grained layers are done by slip casting or other filmcoating techniques.[12–14]

Membrane filtration technologies are being applied with increasing frequency to treat water for potable use and to treat industrial and domestic wastewater, due to requirements of faster and more efficient cleaning operations.[15] Different materials have been tested for these applications, including ceramics like alumina,[16] clays,[17] etc., and other kind of materials like activated carbon.[18] The use of diatomite has been suggested by different authors,[19,20] due to its low price, abundance, and intrinsic properties like high porosity and small grain size.

1.2 Membrane permeability

The flow of a fluid through the pores in a filter is determined by several parameters including the flow regime, the pressure gradient, the porosity and size of pores, etc.[21–23] Assuming a laminar flow through a bundle of cylindrical capillaries,



1 - Porous Support (pore size: 1-15 μm)
2 - Intermediate Layer(s) (pore size: 0.1-1.5 μm)
3 - Separation Layer (pore size: 3-100 μm)
4 - Modification of Separation Layer

Membrane Types | (1+2) Microfiltration Membrane
| (1+2+3) Ultrafiltration Membrane
| (1+2+3+4) Hyperfiltration or / and Gas Separation Membranes

Fig. 1. Schematic representation of an asymmetric multilayer membrane.

the system can be described by the Poiseuille equation:[23]

$$J = (fd^2_{pore}A\Delta P)/(32\eta\tau l) \qquad (1)$$

where J represents the volumetric flow, f is the fraction of open pores, A is the cross-sectional area of the filter, τ is the pore tortuosity factor,[24] η is the viscosity of the water, l is the thickness of the filter, and ΔP is the pressure gradient across the capillaries. Most approaches to characterising flow through porous media have described deviations from ideality, in terms of changes in the viscosity of the permeating fluid near the capillary walls. However, empirically modified models for systems of less uniformity did not change the relations between the essential constituent parameters:

$$J \,\alpha\, \text{porosity} \times (\text{pore diameter})^2/\text{filter thickness} \qquad (2)$$

For a given porosity and pore size, it is clear that the filter thickness should be minimised in order to maximise the flow rate of fluid through the filter. However, a minimum mechanical resistance should be assured in order to provide a long lifetime in good working conditions, and this factor tends to decrease with decreasing thickness.

2 EXPERIMENTAL

2.1 Preparation of multilayer compacts (MCs)

Pre-calcined diatomite powder (Sociedade Anglo-Portuguesa de Diatomite, Óbidos) was used to produce multilayer compacts (MCs) from films obtained by tape casting (prepared from suspensions with 25 vol% Mowilith60P), as described elsewhere.[25] Small rectangular plates (50×50 mm) were cut from the tapes and then stacked together by pressing in hot metallic plates (between 20 and 90°C). This procedure was done very carefully to try to minimise thickness variations and avoiding the incorporation of impurities. Figure 2 gives a schematic view of the apparatus used for this purpose. The use of a polypropylene film coated with a thin vaseline layer was found relevant to avoid the stick of the tapes on the metallic plates. Figure 3 shows the experimental procedure used to produce MCs. The best sintering process was found assuming previous information on the materials behaviour during heating,[26] and involved the following steps: (i) 1°C min^{-1} heating rate up to 500°C; (ii) 3°C min^{-1} between 500–800°C; (iii) 2°C min^{-1}

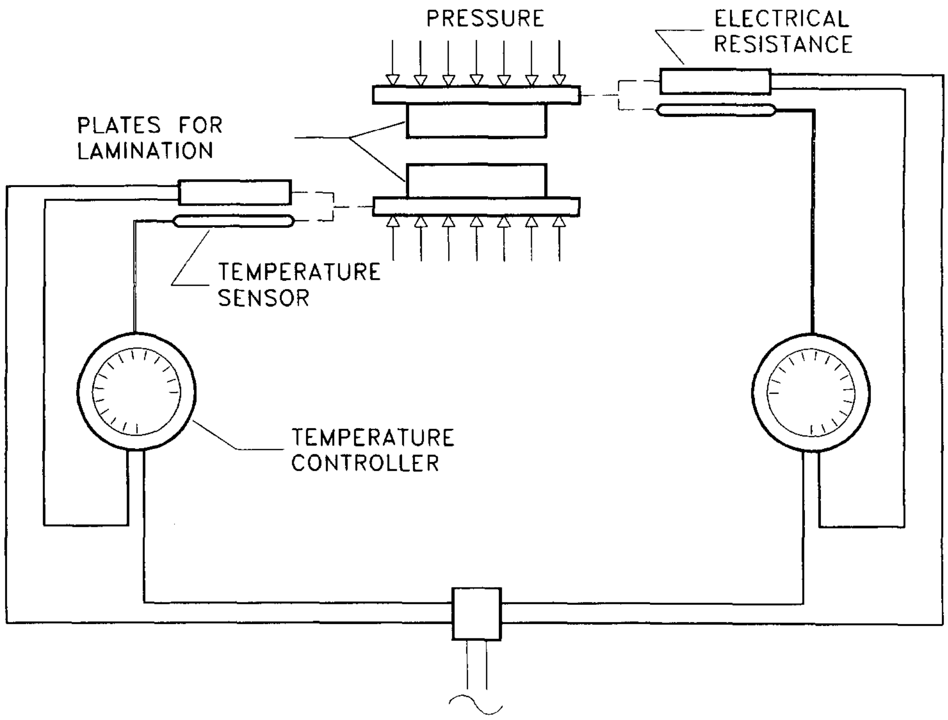


Fig. 2. Schematic representation of the apparatus used for lamination of multilayer compacts.

between 800–1200°C; (iv) 1 h plateau at maximum temperature; (v) cooling (5°C min^{-1}). Following this procedure and using two porous and flat refractory blocks on bottom and top of samples seem essential to avoid the degradation of MCs and formation of cracks or warps. These defects are more critical for thinner compacts.

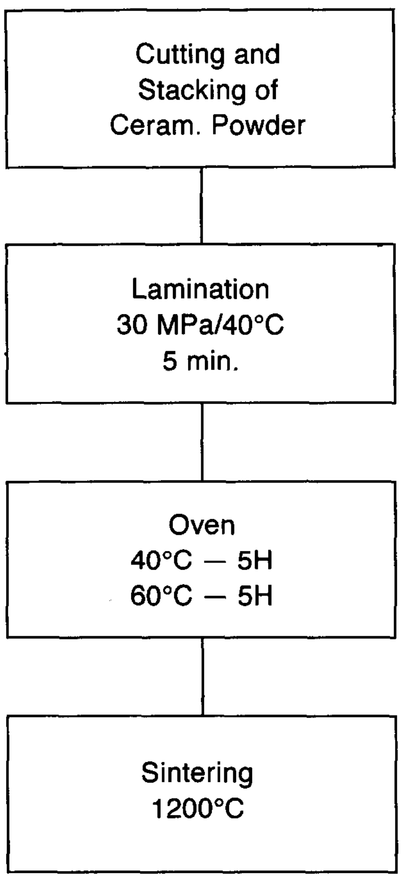


Fig. 3. Flow-chart of the experimental procedure used to produce multilayer compacts from diatomite tapes.

2.2 Characterization of MCs

The processing variables under study are: (i) temperature (20–90°C), pressure (30 and 50 MPa), and pressing time (1–20 min); (ii) the number of individual tapes stacked (5–20), which controls the thickness; (iii) the sintering temperature (1000–1200°C).

The characterisation of green tapes, and green and sintered MCs involved Hg intrusion for pore size determinations (Hg poresizer, Micromeritics 9320), real density (He pycnometer, Quantachrome), apparent density (Archimedes immersion in Hg), thickness determinations, and morphological observations (SEM, Hitachi). Permeability tests performed under an air flux were done by using the apparatus described in Fig. 4. The permeability coefficient (α) was estimated by rearranging eqn (1) and considering $\tau = 1$:

$$\alpha = (J\mu l)/(A.\Delta P) = (1 - f)d_{pore}^2/32 \qquad (3)$$

The mechanical characterisation of sintered MCs involved measurements of 4 points bending strength (Autograph AG-A, Shimadzu) on samples with dimensions of 3.5×3.5×40 mm, and under a charge velocity of 0.5 mm min^{-1}.

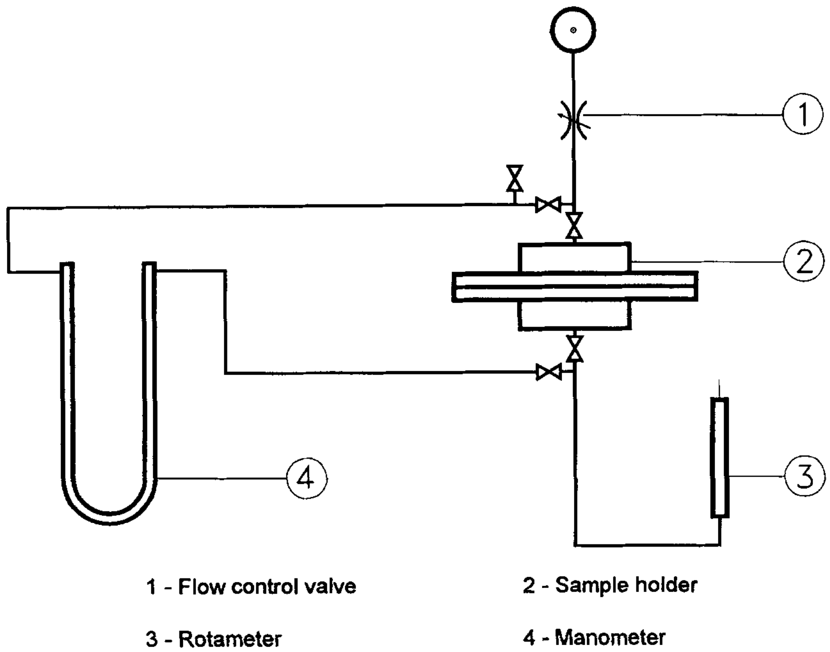


Fig. 4. Schematic representation of the apparatus used for permeability measurements.

3 RESULTS

3.1 Packing density

Pressing of multilayer compacts causes differential shrinkages that depend on the direction of the samples. In planes parallel to the surface the shrinkage is low, but on thickness direction it can reach very high values ($\approx$26%), as a probable result of binder diffusion to the voids of the structure promoted by pressing. Maximum shrinkage is achieved when diatomite particles are in contact and seems to be favoured by pressing at higher temperatures (Fig. 5). When compared with green tapes, an increase of about 10% on packing density was observed by pressing. Higher values were obtained by using higher temperature and pressure levels. However, the use of higher temperatures tends to decrease the warping effects on further sintering steps, probably due to a more effective

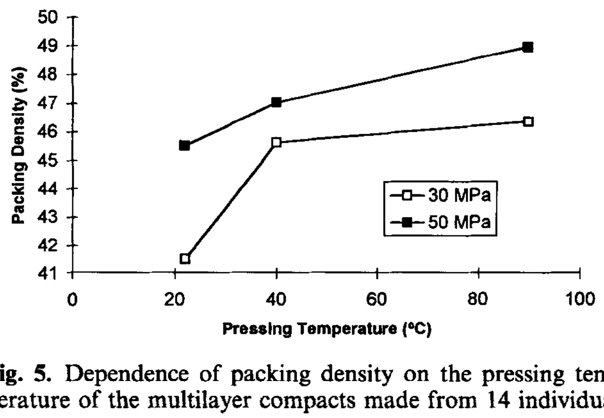


Fig. 5. Dependence of packing density on the pressing temperature of the multilayer compacts made from 14 individual tapes.

stress relaxation process. The combination 30 MPa/22°C seems to be the minimum limit to obtain a mechanically stable body. As a rule, the increasing number of layers causes a decrease on packing densities. This effect is related with discontinuous character of interface contact between two consecutive layers.

The final thickness of pressed compacts is not uniform along the body and tends to change up to a limit of about 10%, depending on pressing alignment conditions.

During sintering the shrinkage is more uniform in all directions (8% in the surface plane against 12% on thickness direction), and is partially determined by the number of contacts between particles obtained by pressing. Figure 6 shows the effect of sintering temperature on density of compacts processed from 10 layers. The increasing bulk density with increasing temperature is a combined result of ignition and decomposition reactions of impurities (organic matter) and components (water removal from diatomite), and sintering process. However, the relative density tends to remain constant above 1100°C and reaches a maximum value of 56%. Porosimetry tests clearly show that remaining porosity is mainly open. Sintering of compacts tends to decrease the morphological differences created by using different pressing conditions. At the end, the effects of temperature and pressing time were found irrelevant for the final density of sintered bodies. For example, the use of pressing times of 1 and 20 min on compacts made from 10 individual layers and sintered at 1050°C, gives bulk densities of 1.17 and 1.22, respectively.

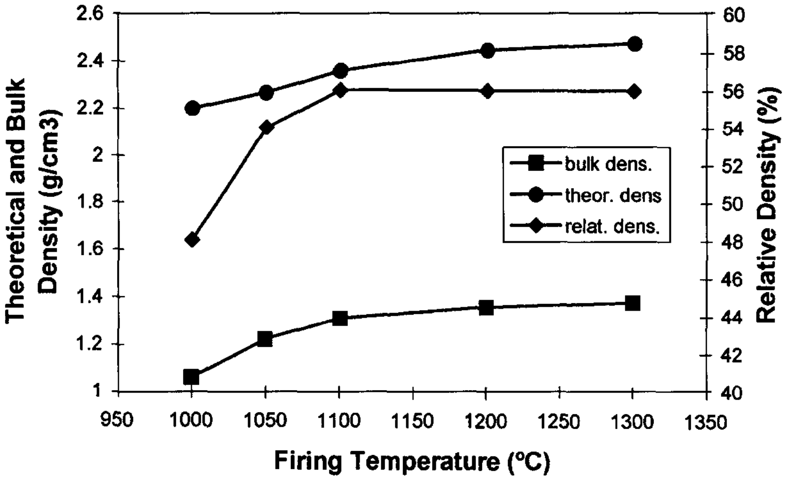


Fig. 6. Effect of sintering temperature on densification of compacts prepared from 10 individual layers.

3.2 Microstructural evolution during compaction

Hg porosimetry and SEM analyses were performed to evaluate the microstructural evolution during different processing steps: (i) as-cast layers; (ii) after pressing of compacts; (iii) after sintering. This evolution is given in Table 1 and Fig. 7 for bodies prepared from a suspension containing 25% binder (Mowilith 60P). It is interesting to notice that the green compacts (as-pressed) present lower volume fraction of pores than the cast layers, despite the similar values of the total pore areas. The difference in the volume of pores is related with a significant decrease of average pore size. By pressing, the large pores almost disappeared, and a large amount of small pores was created.

The further sintering step causes an enlargement of grain and pore sizes and a continuous decrease of porosity, as expected from the coalescence of grains and pores. Figure 8 gives a picture about the pore size evolution during the processing steps already described.

3.3 Effects of sintering on porosity, permeability and mechanical resistance of MCs

As previously mentioned, sintering process tends to increase both pore and grain sizes, and this effect was found more pronounced with increasing temperature (Fig. 9). At the same time, the pore size distributions tend to be narrower with rising temperatures. Above 1200°C the pore sizes change from 0.2 to 1 μm, and the microstructure involves rounded grains that resulted from the significant formation of liquid phase. The increasing uniformity of pore size distribution is an interesting feature for filtration applications.

Table 2 summarizes the evolution of porosity, permeability and average pore size with sintering temperature, for compacts prepared from five tape casting layers having a thickness of about 0.6 mm. The expected densification of the matrix with increasing sintering temperature is responsible for

Table 1. Porosity evolution of the compacts during different processing stages, starting from a suspension having 25% binder

	Green tape casting	Green MCs laminated at 40°C	Sintered MCs (1200°C)
Total Int. Vol. (ml gr^{-1})	0.55	0.36	0.36
Total pore area (m2 gr^{-1})	14.7	14.5	8.7
Average pore size (μm)	0.52	0.10	0.46

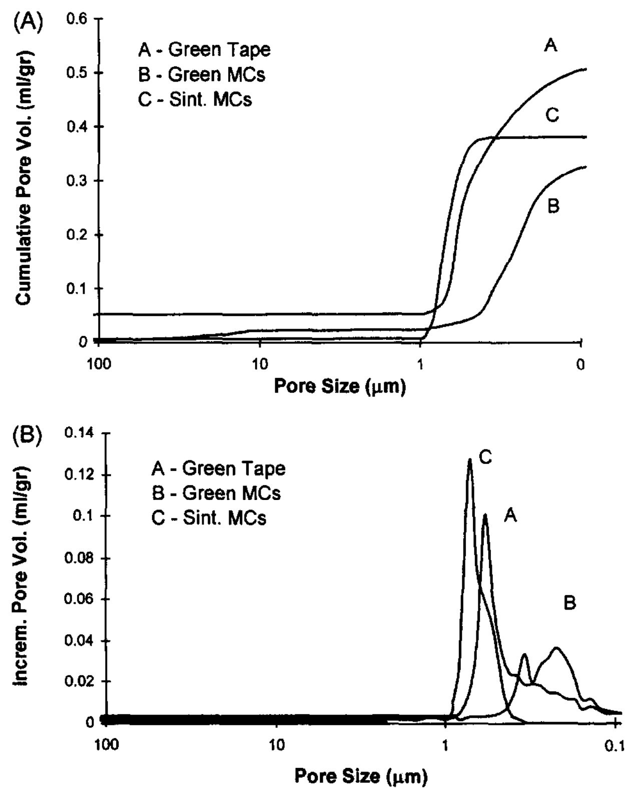


Fig. 7. Evolution of porosity with processing conditions for compacts prepared from suspension having 25% binder.(A) Cumulative curves; (B) Incremental curves.

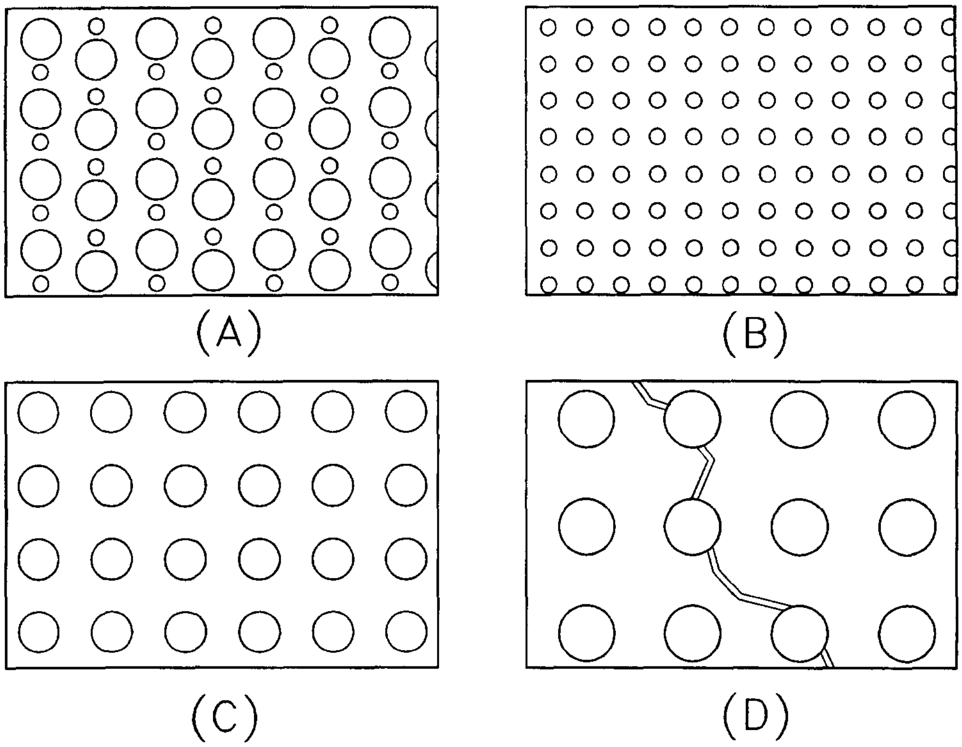


Fig. 8. Schematic representation of the pore size evolution during different steps. (A) green tape; (B) green MCs; (C) MCs sintered at low temperature; (D) MCs sintered at high temperature (p.e. 1300°C).

the decrease of porosity. However, the permeability tends to increase as a result of increasing the average pore size, as predictable by eqn (3). Figure 10 compares the experimental results of permeability as a function of d^2_{pore} with predicted values from Poiseuille model. The similitude between both curves confirms the applicability of the model and the main relevance of pores size on the permeability. A probable explanation for the higher experimental values is given by the effects of heterogeneity and tortuosity of pores, and specially by the strong influence of large pores. The Poiseuille model assumes that all pores have the same size, but this situation is not observed in our compacts. The higher value of the slope determined for the experimental curve suggests an increasing deviation from the model with increasing temperatures. This observation is in accordance with an increasing formation of large pores and gain in pore size uniformity, as mentioned before.

Figure 11 gives the evolution of bending strength of MCs prepared from 30 individual layers (about 4 mm thickness), as a function of sintering temperature. The mechanical resistance increases with increasing sintering temperature, and reaches a maximum at 1200°C (57 MPa). Above this temperature a significant decrease was obtained, as a probable result of excessive formation of glassy phase on the structure, despite the increasing crystallinity of cristobalite. The measured values were found independent on the testing direction, suggesting a homogeneous distribution of stresses on the samples. However, the Weibull modulus tends to decrease with increasing temperature, suggesting

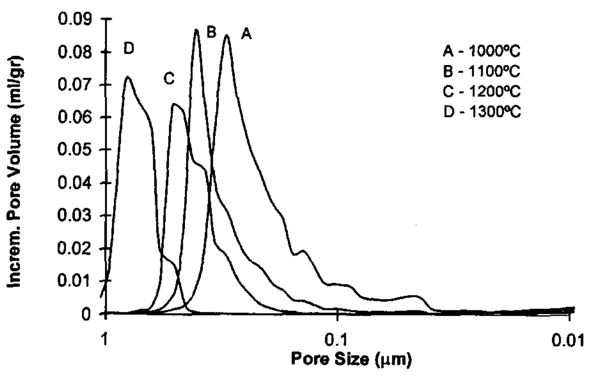


Fig. 9. Incremental evolution of the pores volume as a function of sintering temperature.

Table 2. Permeability and pore size evolution as a function of sintering temperature for MCs made by five individual tapes

Sintering temperature (°C)–time (h)	Total Int. Vol. (ml gr^{-1})	Average pore size (μm)	Permeability ($cm^2 \times 10^{-11}$)
1000–1	0.52	0.27	3.8
1050–1	0.42	0.31	4.3
1100–1	0.40	0.43	5.1
1200–1	0.36	0.46	7.9
1200–4	0.37	0.52	12.8
1200–8	0.38	0.59	10.6
1300–1	0.31	0.78	*

* The sample broke during sintering.

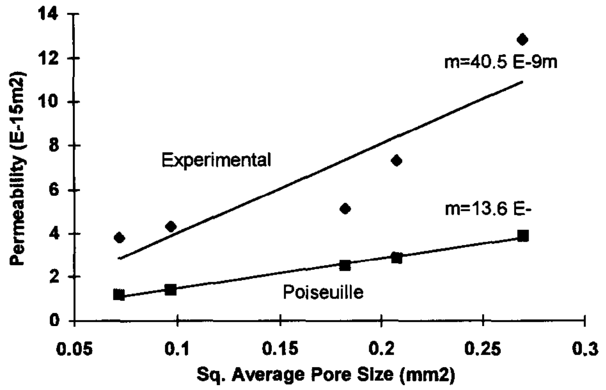


Fig. 10. Comparison of permeability results with Poiseuille model, for MCs made from 5 individual tapes.

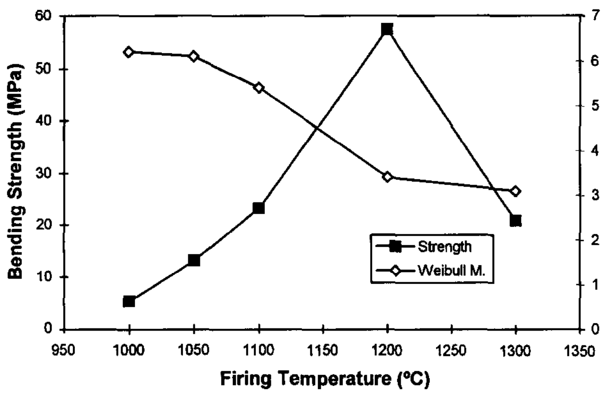


Fig. 11. Dependence of bending stress on sintering temperature, for MCs prepared from 30 individual tapes.

a decrease of feasibility of the measurements probably related with the increasing formation of glassy phase. The mechanical resistance of MCs prepared from tape casting films was found much higher than that of similar bodies prepared by slip casting and pressure slip casting techniques.[27] This is a good indication about the morphological homogeneity of the bodies now processed.

The effect of thickness of MCs on their permeability and mechanical resistance was found relevant, but workability conditions on our filtration setup require: (i) maximum thickness of about 1.5 mm (corresponding to 10 individual layers), to obtain sensitive filtration flows; (ii) minimum thickness higher than 0.5 mm (five individual layers), to get enough mechanical stability.

4 CONCLUSIONS

The use of tape casting layers to produce pressed compacts with enough mechanical resistance to work as filters was found possible. Relevant morphological parameters, including the thickness, porosity, and pore size distribution, were easily controlled by using the proposed technique. Compact layers having 45% of pores with dimensions between 0.2–1 μm were obtained after sintering at 1200°C, which was found to be the optimum firing temperature. The thickness of the compacts varied by simple pressing of several individual layers, and its effect was found relevant to permeability and mechanical resistance of the filters. Workability conditions now tested required the use of compacts with thickness between 0.5 and 1.5 mm. Permeability of the compacts was found strongly dependent on the pore size of the filters, as predicted by Poiseuille model. However, the use of tape casting technique and the singular characteristics of diatomite powders were found restrictive parameters in the attempts to obtain a broad variation of pore size distribution. The use of lower sintering temperatures (under 1200°C), as an attempt to increase the pore sizes, caused a strong decrease of the mechanical resistance of the compacts.

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