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Permeability of diatomite layers processed by different colloidal techniques

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Abstract

Recently, efforts have been directed towards the development of ceramic filters for water treatment systems in which the microstructure is tailored to the application, is well characterised and is reproducible. This work reports on the use of slip and tape casting techniques, as well as a new "direct consolidation technique", to obtain porous diatomite layers for filtration purposes. Diatomite has been chosen because of its low price, abundance, and intrinsic properties such as high porosity and small grain size. Layers prepared by tape casting and lamination, with a bending strength of 57 MPa, were almost 3 times stronger but less permeable than those produced by slip casting, due to the presence of binders and to the lamination step that promoted particle rearrangement. However, both forming techniques gave relatively low permeable layers due to fine (0.25–0.6 μm) and monomodal pore size distributions. The use of starch granules (30–50 wt%) as pore former and consolidator agents enabled to increase the permeability of sintered bodies for almost one order of magnitude as a result of the increasing amount and average size of pores. As expected, porosity and average pore size values show a direct dependence on the starch content. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Membranes; Diatomite; Filtration; Slip casting; Tape casting; Porosity

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1. Introduction

A membrane is a thin selective barrier between two homogeneous phases that allows preferential passage of certain substances across its structure.[1] It can be a solid, a solvent-swollen gel or even a liquid. The applicability of a membrane for separation depends on differences in its permeability to different compounds. Separation occurs under a pressure gradient or sometimes under an electrical potential gradient. In membrane separation applications the aims are high permeability and high selectivity values. The different types of filtration are dependent on the size of particles retained, changing from microfiltration to hyperfiltration or gas separation.[2–4]

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.[5–7] Assuming a laminar flow through a bundle of cylindrical capillaries, the system can be described by the Poiseuille equation.[7] In a simplified manner, the dependence of volumetric flow, J, on the relevant microstructural parameters is given by the equation:

$$J\alpha \text{ porosity} \times (\text{pore diameter})^2/\text{ filter thickness} \qquad (1)$$

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

Ceramic membranes comprise an important membrane classification mainly because of their thermally and chemically stable structure.[8] 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.[1,4] In parallel with this work, microporous membranes have been considered as catalysts or supports for chemical reactions.[9] In water and wastewater purification

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processes, the use of membrane filtration technologies is becoming more frequent.[10] The use of common raw materials, such as clays[11] and diatomite[12,13] as filtration media is favourable, due to their abundance, low price, and intrinsic properties like high porosity and small grain size. However, the ability to produce porous ceramics with controlled pore size and porosity is somewhat difficult. Recently, efforts have been directed towards the development of ceramic filter systems in which the microstructure is tailored to application, is well characterised and is reproducible.[14–16]

A gain in selectivity and mechanical stability of the whole filter is frequently obtained by creating asymmetric structures, where the average pore size changes through the thickness of the membrane. Keizer et al.[9] described synthesis methods commonly used to fabricate this type of filter. In a cylindrical configuration, the porous support tube is normally prepared by extrusion, and slip casting or other film-coating techniques[17–19] are then used to deposit finer-grained layers. Processing from colloidal suspensions is also a promising method for obtaining bodies with low microstructural heterogeneities. The easy control of the relevant morphological parameters, like the size and volume of pores is another advantage of this technique.

In previous works[20,21] porous diatomite layers were produced from colloidal suspensions in water, by using slip and tape casting techniques. The rheological behaviour, the selection of additives and the optimised specific processing conditions for each technique were detailed in those papers. Only very thin layers were obtained by tape casting, which are unusable in filtration devices due to their low mechanical strength. For this reason, thicker compacts made by several sheets were then produced by thermocompression at 40°C.[21] Final properties of the membranes, including mechanical resistance and permeability, typical thickness, and other relevant morphological aspects, are presented in this paper.

In order to increase the permeability of the membranes, starch granules were used as pore formers. Starches are usually used as processing aids in the manufacture of adhesives, textiles, paper, food, pharmaceuticals and building materials due to its thickening, gelling, adhesive and film-forming capabilities. Most starches consist of mixtures of two polysaccharides, a linear type (amylose) and a branched type (amylopectin).[22] The glucose units expose a large number of hydroxyl groups that confer a strong hydrophilic character to the starch, facilitating the dispersion of the granules in aqueous media.[23] Starch granules are insoluble in water below 50°C. Above this temperature the intermolecular bonds within the granules are weakened and the granules undergo a rapid and irreversible swelling by water uptake.[22] The amount of water available for flowing the starting suspension gradually decreases, causing the ceramic particles to stick together and consequently, consolidate into a solid body. In this way a fluid suspension is transformed into a rigid body without liquid removal ("direct consolidation"). After burning off of the starch and sintering of the ceramic matrix, a material is obtained with porosity corresponding to the original amount, shape and size of the swelled starch particles. [23–24]

Final characteristics of sintered bodies produced by this technique are compared with those obtained by slip and tape casting. Advantages and limitations of each technique will be discussed.

2. Experimental

2.1. Materials

Pre-calcined (600°C) diatomite powder (from Sociedade Anglo-Portuguesa de Diatomites, Óbidos) was used. Its fully characterisation is given elsewhere.[20] Water-based slurries containing 50 wt% of solids were stabilised with a fixed amount (0.7 wt%) of a suitable dispersing agent (Dolapix CE 64, from Zschimmer and Schwarz, Germany). This slurry was then used in the slip casting process. The complete formulation for tape casting is more complex, and includes binder (Mowilith DM60, from Hoechst), thickening (Mowilith VDM 7000, also from Hoechst), and defoamer (Byk 036, from Chemie) agents. The optimum formulation is described elsewhere.[21] Considering results reported in a previous work[23] the pore former and consolidator agent (etherificated potato starch Trecomex AET1, from Lyckeby Starkelsen AB) was selected for the direct consolidation of diatomite bodies. The average grain size of starch particles is about 55 μm, suitable to improve the average pore size of the bodies. When compared with the native product (without any chemical modification), this starch presents a lower gelification temperature and promotes a better adhesion through the ceramic particles, enabling ceramic parts with more reproducible properties.[23]

The required amounts of starch were added to diatomite slurries already prepared for the slip casting process. The optimal formulation is given in Table 1. The slurries were then poured into plastic bags, which were pressed between two metallic plates to form sheets of about 3-mm thickness and put in an oven at 80°C for 1 h to consolidate. The plastic sheets were then removed and the samples allowed drying at the same temperature for one night. Complete drying was performed in a ventilated oven at 120°C for 12 h. The resultant green samples were sintered in a kiln in which air was pumped during the burning off of the organic matter up to 500°C. The heating schedule used was the following: 1°C/min from 120 to 500°C, followed by a ramp of 5°C/min up to the sintering temperature (1200°C), with

Table 1
Optimal formulation of pore former-containing slurries for DCL fabrication

Component	Function	Weight %
Diatomite	Ceramic matrix	31.5
Water	Solvent	31.5
Starch	Pore former/consolidator	21.0
Mowilith DM 60P	Binder	15.7
Dolapix CE 64	Deflocculant	0.2
Byk 036	Defoamer	0.1

holdings at 200, 300, 500 and 1300°C for 1 h; the samples were then furnace-cooled to less than 100°C.

2.2. Preparation and characterisation of samples

A detailed description of the optimal preparation conditions of slurries for slip and tape casting processing is given in previous works.[20,21] In the present paper, only the new preparation route of direct consolidation is described. Fig. 1 shows the sequence of experimental steps used. Two main steps might be distinguished: (1) mixture of dispersant + water + diatomite powder, with a permanent stirring action; (2) addition of binder + starch. Several starch concentrations (referred to the weight of solids) were tested (30:70, 40:60, and 50:50). Drying and sintering steps are even more critical than for bodies produced by tape casting, due to the larger amount of burning additives. For this reason the heating rate was only 0.75°C/min, up to 500°C, and then increased to 2.5°C/min. The sintering temperature was 1200°C, which proved to be the optimum value for multilayer compacts produced from tape-casting samples.[23] A fixed holding time of 1 h at the sintering temperature was used for all samples. As a preliminary attempt to produce asymmetric membranes, some green plates were covered with a sheet of diatomite, previously prepared by tape casting, and laminated (40°C, 30 Mpa).

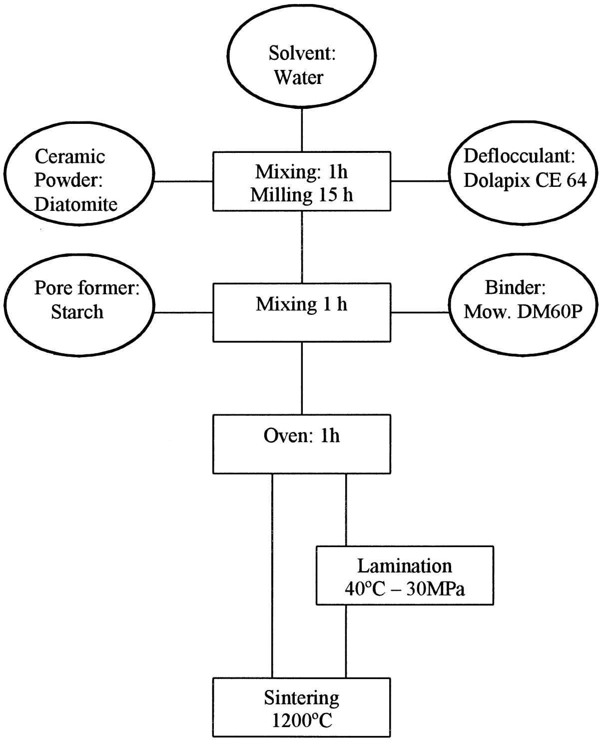

Fig. 1. Flow-chart of direct consolidation processing used to produce diatomite porous layers.

2.3. Characterisation of membranes

A simplified notation will be used to describe the samples prepared by different manners: SC — slip casting; TC — tape casting + lamination (multilayered compacts normally produced from 5 individual layers); DC — direct consolidation with starch; DCL — direct consolidation + lamination. When present, the number denotes the (weight) fraction of the relevant additive (for example the starch), used to produce the bodies.

The characterisation of green and sintered bodies involved Hg intrusion for pore size determinations (PoreSizer 9320, Micromeritics, USA), real density (He pycnometer, Model MVP-1, Quantachrome, USA), apparent density (Archimedes immersion in Hg), and morphological observations (SEM, Hitachi Model S4100-1, Japan). Permeability measurements under an air flux were performed as described elsewhere.[23] The permeability coefficient (α in m^2) was estimated as:[7]

$$\alpha = (J\mu L)/(A.\Delta P)$$

where J represents the volumetric flow, μ is the viscosity of the fluid (air), L is the thickness of the filter, A is its cross-sectional area, and ΔP is the pressure gradient across the capillaries. The mechanical characterisation of sintered bodies involved measurements of 4-points bending strength (Autograph AG-A, Shimadzu, Japan) under a displacement velocity of 0.5 mm/min.

3. Results

3.1. Direct consolidated samples

Due to the large amount of burning agents, shrinkage during firing of the starch-containing samples is always relevant. Starting from a green plate having a typical thickness of about 2.7-mm, the simple lamination process reduced that value to 1.9 mm. After sintering, the thickness of both DC and DCL samples were, respectively, 2.2 and 1.6 mm. This indicates that the lamination process induced the most significant dimensional changes (about 30% shrinkage). Upon sintering, the additional shrinkage values were about 16 and 18.5%

for DCL and DC samples, respectively. These variations can be related to a low-density diatomite matrix (the maximum workable solid loading was 50 wt%), in combination with a large quantity of shrinking starch granules during sintering. A matrix with low density has a tendency to shrink during firing due to the empty space existing between the matrix particles. Furthermore, if the matrix is weak the starch shrinking can cause a local breakdown by removing adhered matrix particles and leaving more open space.[23] This partially explains why the lamination process induces a significant part of the total shrinkage.

Table 2 gives the evolution of relevant morphological parameters, such as the total Hg intrusion volume (porosity) and average size of interconnecting pores, e.g. the pore necks between the large ones left by the starch particles, of samples with starch contents changing from 30 to 50 wt%. As expected, porosity and average pore size values show a direct dependence on the starch content. However, the increase of porosity is less pronounced in laminated samples (DCL), as shown in Fig. 2. Direct comparison of samples having similar starch contents, denotes an increase of packing density of about 50% for DCL bodies. The lamination step promotes a better accommodation of particles and inhibits the enlargement (coalescence) of pores during sintering, in comparison with DC bodies. A near linear dependence of density on starch content (from 30 to 50 wt%) was obtained in the case of DC samples, while DCL bodies denote a stronger dependence when starch content varies from 30 to 40%. However, in both types of samples the dependence of average pore size on starch content is more pronounced between 40 and 50 wt% (Table 2). This result can be explained as follows. In the green bodies, the packing of diatomite particles is disrupted by the much larger starch particles. This disruption can be of two types, the wall effect and the contact effect, and is confined to the first layer of diatomite particles around each starch granule.[24] The increasing population of starch particles tends to increase the average distance between diatomite particles on starting green bodies, and diffusion mechanism during sintering is less effective. After sintering, the starch particles leave behind the corresponding hollow ceramic shells.[22] If the starch content is low, isolated shells can be found throughout the microstructure (no contact effect). However, as the concentration of starch increases, individual shells start interacting and an open structure interconnecting the coarse pores is being gradually established. This interpretation is supported by the results showed in Figs. 3, 4 and 5.

Table 2
Porosity evolution of DCL sintered bodies as a function of starch content. For comparison, a TC layer is also given

Starch content (wt%)	Total intrusion volume (ml/g)	Average pore size (μm)
30	0.55	0.92
40	0.76	1.72
50	0.86	6.30

Fig. 3 gives the evolution of porosity of DCL sintered bodies with starch content, expressed as the cumulative amount of pores as a function of the pore size. The bodies prepared from slurries containing higher starch contents show wider distribution of pore sizes, which can be detrimental for the selectivity of the membranes. This is particularly obvious in the case of DC samples. Fig. 4 shows SEM images of DCL and DC samples having a fixed amount (30%) of starch. In DC samples a bimodal distribution of pores is easily noticed [Fig. 4(A)], resulting from the combination of diatomite (having an intrinsic small-sized porosity) with the pore former agent (average grain size of 55 μm). This effect is less pronounced on DCL [Fig. 4(B)], due to the compression exerted during lamination. These membranes show lower permeability and a significant increase of mechanical resistance when compared with DC ones. The higher mechanical strength and selectivity values of DCL bodies make them suitable for filtration purposes.

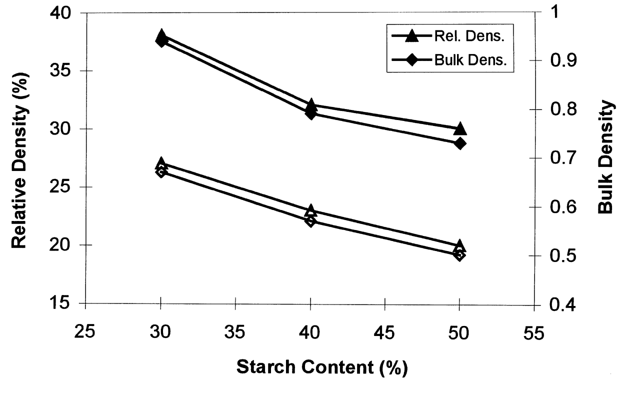

Fig. 2. Density evolution of DC (open symbols) and DCL (closed symbols) sintered layers as a function of starch content.

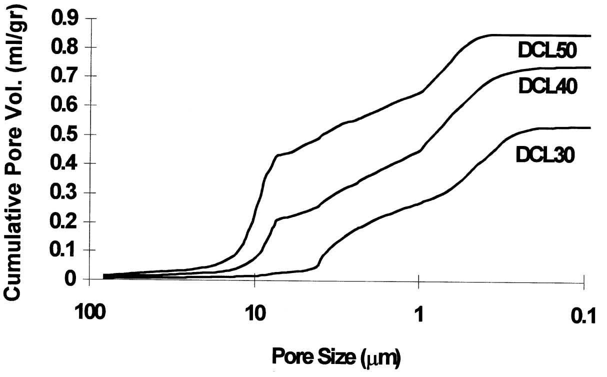

Fig. 3. Porosity evolution of sintered DCL samples with starch content, expressed in cumulative pore size distributions.

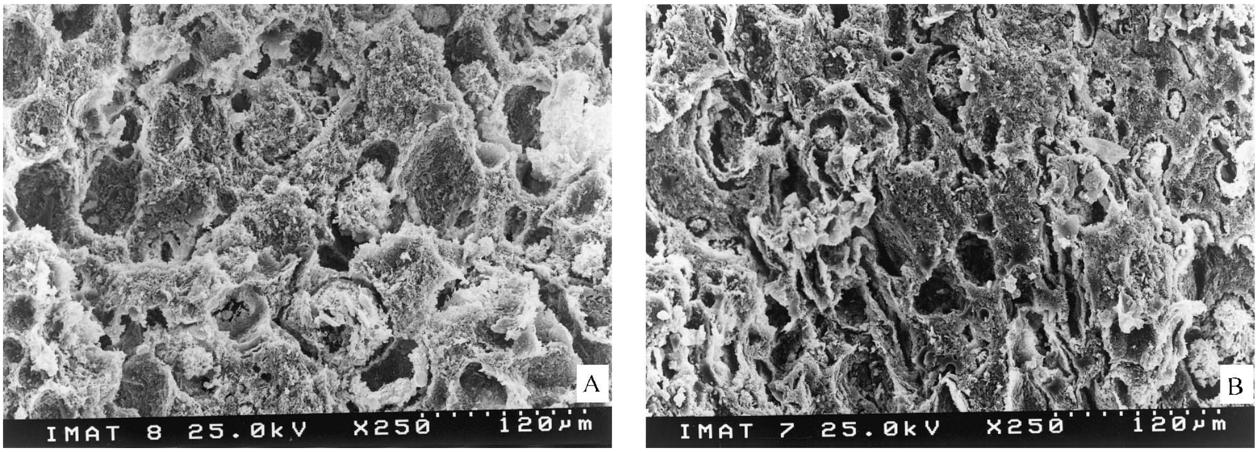

Fig. 4. Scanning electron micrographs of diatomite sintered bodies prepared by direct consolidation from slurries containing 30 wt% of starch: (A) non-laminated body (DC); (B) laminated (DCL).

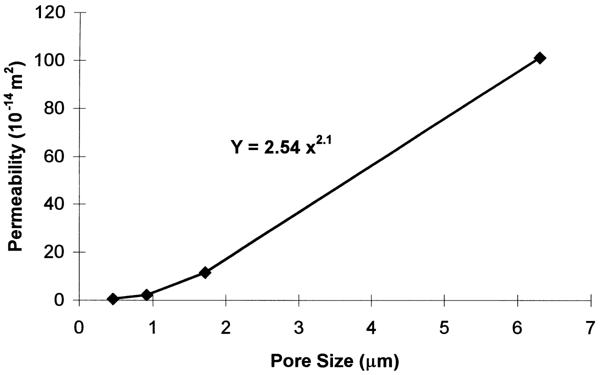

Fig. 5. Dependence of permeability on average pore size of bodies prepared by direct consolidation. Fitting of the curve is given by the inserted equation.

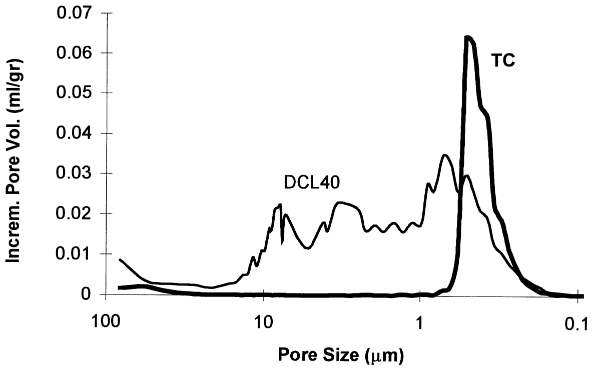

Fig. 6. Incremental pore size distribution of sintered bodies prepared by tape casting (in bold) and direct consolidation techniques. DCL body was obtained from a 40 wt% starch-containing slurry.

Fig. 5 shows the evolution of permeability with average pore size of DCL bodies. Inserted equation gives the dependence between both variables, which is close to that predicted by Poiseuille model.[7] The same law was observed with DC layers. The best compromise between all the relevant characteristics is achieved for a starch content of 40 wt%, which will be assumed constant in the following section.

3.2. Comparison between different processing methods

The bodies prepared from slurries containing starch show a wider (and bimodal) distribution of pore sizes (≈0.3–10 μm) than those obtained by slip and tape casting (0.25–0.6 μm) from slurries without pore former agents (Fig. 6). As a consequence, packing density of direct consolidated samples is smaller (Fig. 7).

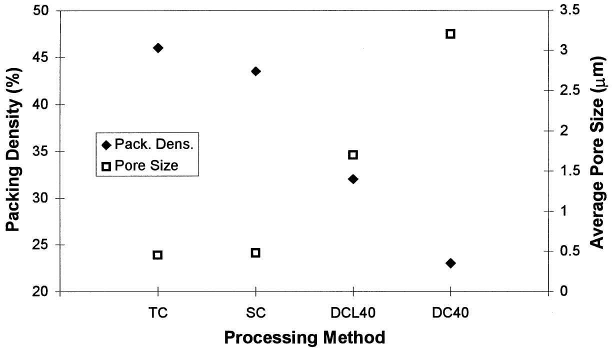

Fig. 7. Values of packing density and average pore size of diatomite sintered bodies prepared by different techniques.

Fig. 8 shows the evolution of some relevant characteristics for filtration applications. As previously described,[21] TC samples are mechanically stronger (almost 3 times) than SC ones, as a result of an increasing accuracy and control of processing parameters observed in the first case, but also as a result of the lamination step used on tapes. At the same time, TC bodies are less permeable, due to the smaller amount and size of pores. The use of pore former agents strongly increases the permeability of sintered bodies, as a result of the increasing amount and average size of pores. For example, DC samples show permeability values almost one order of magnitude higher than those obtained for TC and SC layers. However, the impact of the porosity improvement on mechanical properties is negative, and DC bodies have bending strengths 10 times lower than TC ones. The use of a lamination step on green bodies prepared by direct consolidation (DCL) is somewhat effective in promoting a mechanically stable structure, due to the combined effect of a better packing process and stress relaxation phenomenon. As a result, these bodies have higher bending strength than DC samples. The use of a finer-particle starch (average grain size closer to diatomite) should be also tried, as an attempt to obtain a better compromise between permeability and mechanical resistance.

In the actual conditions, another interesting possibility consists of the fabrication of asymmetric membranes. These can involve a porous DC substrate, where a thin TC layer showing lower permeability and higher selectivity (narrow distribution of pore sizes) is deposited and co-fired. Preliminary attempts to make these bi-layered membranes are now running. Fig. 9 shows the morphological characteristics of one of those membranes, and reveals the potential of the co-firing technique to obtain mechanically stable structures. Permeability values measured with this membrane (1.54×10^{-14} m^2) were similar to those obtained with single TC films, despite the minor total thickness (about 1/5) of the TC layer now used. If we assume that permeability of the bi-layer membrane as a result of a series association of two individual membranes it is obvious that the general behaviour is controlled by the less permeable one. The effect of the interface gap between the two layers might also be neglected as its resistance to a gas or liquid flow is very small. This is in accordance with Eq. (1) that predicts a minor effect of the thickness on permeability, compared with the average pore size dependence. However, the control of processing parameters is still incomplete, and further work is required to adjust all the relevant characteristics for filtration. One possible improvement might be made by the use of a suitable pore former agent in the TC layers.

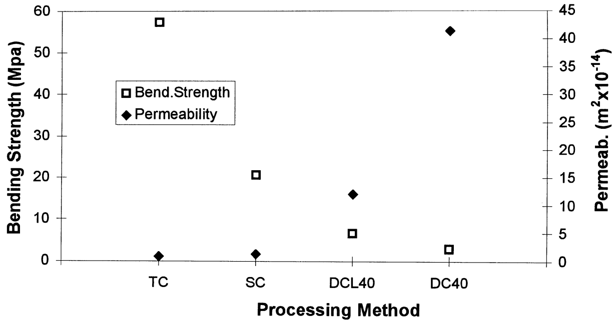

Fig. 8. Evolution of bending strength and permeability (air flux) values of diatomite sintered bodies prepared by different methods.

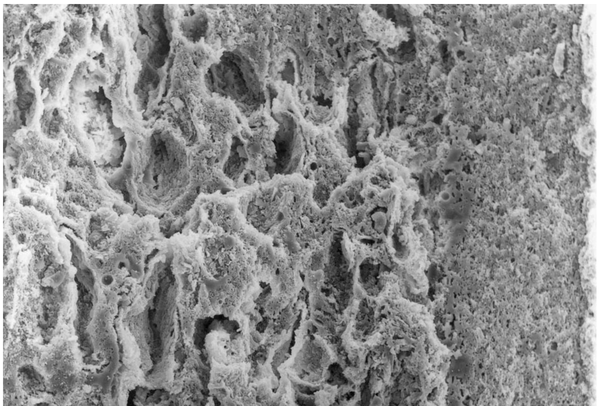

Fig. 9. Microstructure of a double-layered diatomite sintered body, produced by lamination of a porous DCL substrate and a thin TC layer.

4. Conclusions

The combined use of different processing techniques seems to be an interesting way to design the final morphology and physical permeability of diatomite porous layers. A careful control of the relevant processing parameters is always required, but is greatly simplified by the use of a direct consolidation technique. The best compromise between all the relevant characteristics is achieved for a starch content of 40 wt%. The lamination of green consolidated bodies increases the final mechanical strength and improves the control of the relevant morphological parameters. The use of different sized starch particles should be explored in order to adjust the final porosity and permeability of the layers. By exploring all the forming methods that have been already tried, it seems possible to produce multilayered asymmetric membranes for different filtration types.

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