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Influence of starch content on the properties of low-cost microfiltration ceramic membranes

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Abstract

The use of starch as pore former is frequent in the fabrication of porous ceramic membranes, since starches are cheap, innocuous and environmentally friendly. A study has been conducted to evaluate the influence of potato starch content (0–30 wt%) and sintering temperature (1100 and 1400 °C) on low-cost ceramic microfiltration membranes. The raw materials were a mixture of kaolin, alumina and starch, from which membrane specimens were shaped by uniaxial dry pressing.

The results indicated that the percentage of potato starch did affect the properties of the membrane. Thus, an increase of starch content provoked a reduction of bulk density (an increase of porosity) a rise of water permeability and a substantial modification (coarsening) of the pore size distribution. This effect deals with the role as pore former of starch, which burns out when fired. More interestingly, it was experimentally observed that the effect of starch was particularly effective for starch percentages higher than 10 wt% once a connected coarse pore network is developed. On the other hand, an increase in sintering temperature from 1100 to 1400 °C also influenced membranes' characteristics but the effect was much less significant than that of starch content.

A percolation analysis based on the Effective Medium Approximation (EMA) contact model allowed to conclude that the critical porosity calculated corresponds to a starch content of 10.2 wt%, which agrees quite well with the estimation from experimental results. Finally, tortuosity was calculated with a simple model derived from the Hagen–Poiseuille equation. The obtained data showed that tortuosity factor decreased as the starch content or sintering temperature increased. These findings are consistent with SEM analysis and pore size determination.

Keywords: A. Precursors: organic; B. Microstructure-final; B. Porosity; E. Membranes

1. Introduction

The interest in low-cost ceramic membranes has recently increased since they combine high performance (as high thermal and mechanical stability, long life and good chemical stability) with economy (compared with habitual ceramic membranes available in market, made of alumina, zirconia or titania) [1,2]. The properties of the ceramic membranes are mainly determined by their composition, the pore-former content and the sintering temperature. The proposed compositions of low-cost ceramic membranes are very wide, depending on the nature of their raw materials: local clays [3–10] and kaolin [11–13], sepiolite [14], apatite [15,16], perlite [17,18], phosphate [19,20] or a mixture of some of them [21–26], among others.

To reach the optimum permeability level, most of the ceramic membranes' compositions include starch as pore former, in a proportion between 2 and 20 wt% [3,5,8–11, 16–19,22,27]. Starch generates pores during its burning out around 500 °C; moreover, it is environmentally friendly, easy to burn out and very cheap [28]. The addition of starch granules to a mixture of inorganic raw materials yields ceramic membranes of greater porosity, tailored pore size and higher permeability. By adjusting the amount of starch added, a ceramic membrane of a specified pore size distribution and permeability can be obtained across a broad range. As reported

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examples, the mean pore sizes for alumina membranes ranged from 1 to 2 μm and apparent porosities increased from 23% to 44% as the added amount of starch rose from 0 wt% to 15 wt% [9], whereas in ball clay membranes the apparent porosity increased from 9% to 32% as the added amount of starch augmented from 0 wt% to 35 wt% (no data about pore sizes were published) [10].

Changes in maximum temperature of thermal cycle modify the properties of the ceramic membranes through its affect over sintering. The variations are reflected in porosity, which usually decreases when temperature increases, and pore size distribution, which shifts towards coarser pore sizes. Some studies about those phenomena have been previously reported. Membranes derived from ball clays showed a reduction in apparent porosity from 19% to 16% when sintering temperature increased from 1000 to 1300 °C [29]. Other membranes whose composition was based on a mixture of inexpensive raw materials (kaolin, quartz and different carbonates) displayed a similar trend: the porosity decreased from 40% to 22% when the sintering temperature increased from 900 to 1000 °C whereas the average pore size coarsened from 2.6 to 5.5 μm [30]. Similar trend have been found in ceramic membranes developed from a mixture of kaolin, pyrophyllite, feldspar, ball clay, quartz, and calcium carbonate: the porosity initially grew and then decreased in the range of 41–46% and the average pore diameter augmented from 0.87 to 1.10 μm with an increment of sintering temperature from 850 to 1000 °C [31].

Water permeability is the most used parameter to characterise a ceramic membrane. Viscous flow of a Newtonian fluid through a porous medium can be described by Darcy's law, which relates the specific permeability to water (K_p, m^2) with the slope of the straight line obtained graphing the volume flux versus the pressure gradient (Eq. (1)):

$$K_p = \frac{b \cdot \eta \cdot e}{S_0} \tag{1}$$

where η is the water viscosity, e the membrane's thickness, b the value of the slope and S_0 the specific surface [32]. In addition, the best-known equation for describing the specific permeability of a medium (K_p, m^2) in terms of its structural properties is the Kozeny–Carman equation (Eq. (2)):

$$K_p = \frac{1}{K_0 S_0^2} \frac{\varepsilon^3}{(1-\varepsilon)^2} \tag{2}$$

where K_0 is the Kozeny constant, S_0 the specific surface, and ε the porosity of the membrane [33]. Assuming that the product $[K_0 \bullet S_0^2]$ varies little in a set of microfiltration membranes obtained with a similar process, the model predicts an approximately linear relationship between K_p and the porosity term $[\varepsilon^3/(1-\varepsilon)^2]$. The permeability coefficient (K_p) can also be related with the pore diameter (d) though the Hagen–Poiseuille equation:

$$K_p = \frac{\varepsilon_{sf} d^2}{32 \eta \tau} \tag{3}$$

being the water viscosity (η), the surface porosity (ε_{sf}) and the tortuosity factor (τ).

Assuming that the tortuosity can keep constant in a set of microfiltration membranes, the model prognosticates an approximately linear relationship between K_p and $[\varepsilon_{sf} \bullet d^2]$.

On the other hand the Effective Medium Approximation (EMA) contact model has also been employed to explain the permeability behaviour [34–36]. This model is based on the similitude between Darcy's law and the equation to calculate the current flow in electricity. At certain porosity (a critical porosity, ε_c), a network of connected pores appears, resulting in a sudden increase in the permeability. At porosities around the critical porosity (which corresponds to the percolation threshold of porosity) the permeability (k) satisfies a scaling relation (Eq. (4)):

$$k \propto (\varepsilon - \varepsilon_c)^t \tag{4}$$

where t is the critical exponent.

Finally, the tortuosity factor of a membrane can be calculated using a simple model based on the Hagen–Poiseuille equation [Eq. (3)] and the pore size distributions measured by mercury intrusion [37–39], as shown in Eq. (5).

$$\tau = \sqrt{\frac{\sum_{i=1}^{m} \left[\frac{a_i}{2} \left(r_{i_{max}}^4 - r_{i_{min}}^4 \right) + \frac{b_i}{3} \left(r_{i_{max}}^3 - r_{i_{min}}^3 \right) \right]}{8 \cdot \eta \cdot e^2 \cdot \text{slp}}} \tag{5}$$

Where a_i and b_i are constants calculated from every interval i of the pore size distribution, $r_{i_{max}}$ and $r_{i_{min}}$ represent the maximum and minimum pore radius of every interval and slp the straight line's slope obtained in the water permeability test.

Although the research activity on low-cost microfiltration membranes has been very intense in the last years due to the many potential industrial applications of these materials very few papers have intended to model microstructural features of sintered membranes with functional properties of the membranes [40–42]. This is because the use of natural minerals (ball clays, kaolin, etc.) as raw materials makes it harder to model the intricate microstructure of these ceramic membranes.

As a consequence of the above, this research focuses on the relationship between microstructure and properties of low-cost ceramic microfiltration membranes. Hence, potato starch has been used as pore former and a mixture of kaolin and alumina as base composition. The objective was to determine the effect of starch addition at different weight percentages on the ceramic composition processing (by pressing) as well as on microstructure and permeation characteristics of the ceramic membranes. In addition, the effect of sintering temperature on the microstructure and performance of sintered membranes has been also addressed. Some equations have been assessed to model the permeability in function of structural parameters of the membranes.

2. Experimental

2.1. Membrane preparation

The raw materials used to prepare the ceramic membranes were alumina (AR12B5, Pechiney, France; D_{50}=5 μm, S_e=12 m^2/g) and kaolin (ER/N, Caobar, Spain; D_{50}=4.2 μm). Potato