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Elaboration and characterisation of fly ash based mineral supports for microfiltration and ultrafiltration membranes

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Abstract

The development and the characterisation of a new support for microfiltration and ultrafiltration membranes from fly ash applied to filtration are presented. The choice of this material is based primarily on its low cost (as fly ash is produced abundantly as a solid waste by coal fired power plants in many parts of the world).

The support, with tubular configuration, was prepared from fly ash which was obtained by the sintering of non-grinded mineral coal at 800 °C. The resulting powder, mixed with organic additives and water, could be extruded to elaborate a porous structure. The firing temperature of the support is 1125 °C. The morphology of the surface and the cross-section observed on scanning electron microscope (SEM) are homogeneous and do not present any macrodefects (cracks, etc.). The mean pore diameter, measured by mercury porosimetry is 4.5 μm and the pore volume is 51%. The tubes display a good mechanical and chemical resistance that allow to use them as supports for tangential micro- and ultrafiltration processes.

Keywords: Extrusion; Membrane; Porous supports; Fly ash

1. Introduction

Due to their potential application in a wide range of industrial processes, membrane technologies have received an increasing interest. Ultrafiltration and microfiltration are often used to remove particles, micro-organisms, and colloidal materials from solutions and suspensions [1,2]. The use of ceramic membranes has many advantages such as high thermal and chemical stability [3–5], pressure resistance, long lifetime, and catalytic properties from their intrinsic nature [1]. A membrane support provides mechanical strength to a membrane top-layer to withstand the stress induced by the pressure difference applied over the entire membrane and must simultaneously have a low resistance to the filtrate flow.

The marketed supports are generally manufactured from metallic oxides such as alumina (Al_2O_3), titania, which have a relatively elevated cost. For economical considerations, the supports have been manufactured, in this work, from mineral coal fly ash raw material which is a solid waste produced by the coal-fired power stations. The fly ash powder was obtained by burning to a cinder the mineral charcoal at 800 °C leading to 8–13% of fly ash. This quantity depends on the nature of the burnt mineral charcoal.

2. Experimental

2.1. Analysis of the raw material

The starting raw material was the fly ash obtained by burning a mineral coal. The chemical composition of the fly ash powder was determined by spectroscopic techniques, as X-ray fluorescence for metals and by atomic absorption for alkaline earth metals. The powder morphology as well as the microstructure of samples were obtained using a HITASHI scanning electron microscope (SEM). Phases present in the powder compositions were analysed using an X-ray diffractometer (Siemens, Germany) with Cu Kα radiation ($\lambda = 0.154$ nm).

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2.2. Characterisation of powders issued from different thermal and mechanical treatments

The mineral coal was submitted to different mechanical and thermal treatments. Thus, four types of fly ash powders based on particle size distributions are obtained.

- Powder (P_1) obtained by calcination at 800 °C of a non-grinded mineral coal.
- Powder (P_2) obtained by calcination at 800 °C of a finely grinded mineral coal.
- Powder (P_3) obtained by calcination at 700 °C of a finely grinded mineral coal.
- Powder (P_4) obtained by calcination at 600 °C of a finely grinded mineral coal.

The particle size analysis of the powder was done using the Particle Sizing Systems (Inc. Santa Barbara, CA, USA, Model 770 AccuSizer). The grinding of the mineral coal was performed with the assistance of a planetary crusher at 300 rpm.

2.3. Elaboration of porous support

The elaboration of a ceramic macroporous support was achieved as follows:

- preparation of a plastic ceramic paste;
- shaping by extrusion;
- consolidation by thermal treatment.

The process of the ceramic preparation is described in Fig. 1.

Elaboration of a ceramic paste requires a specific ageing and organic additives to favour the powder dispersion and the adjustment of the paste rheology. The paste composition used was chosen based on the previous work done in our laboratory concerning clay supports preparation [7,8] which is

- fly ash powder: 84%;
- organic additives: methocel (The Dow Chemical Company); 4% amijel (Cplus 12076, Cerestar): 4%, porosity agent: starch (RG 03408, Cerestar): 8%.

For the paste preparation, a quantity of 130 ml of water per 250 g of the mixed powder was added. Before extrusion stage, an ageing stage of the paste is necessary to obtain a good homogeneity and to favour the hydration of the cellulose binders. The time necessary for this stage is 24 h. Shaping is performed by extrusion. The drying of the extruded pieces was conducted in air at room temperature during 24 h. The main steps of the processing route for supports preparation, used in this work, are described in Fig. 1.

Sintering experiments were carried out under air; the temperature and time schedule used are given in Fig. 2. Two steps have been determined: the first one for the elimination of organic additives at 250 °C and the second one for the sintering at different temperatures. The temperature–time schedule not only affects the pore diameters and porous volume of the final product but also allows to obtain the final morphology and mechanical strength. Sintering was performed at a temperature ranging from 1100 to 1130 °C.

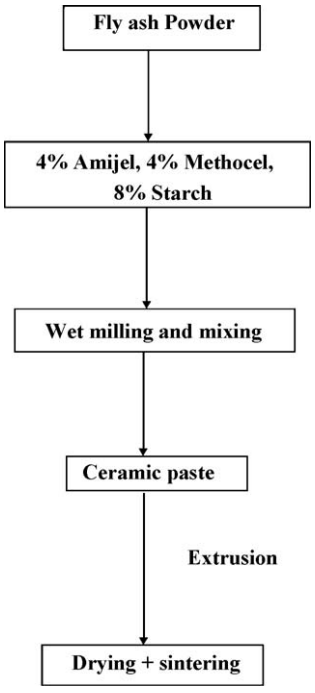

Fig. 1. Main steps of the processing route for supports preparation.

2.4. Support characterisation

The porosity and the average pore diameter of the sintered material were determined using Hg-porosimetry. The presence of possible defects in the prepared supports was checked by using scanning electron microscopy (SEM).

The measurement of the mechanical resistance of the sintered material was carried out by the three point bending method (LLOYD Instrument) applied to sintered parallelepipedic test bars. The size of samples was 32 mm/10 mm/2 mm and the distance separating the two points is 28 mm.

3. Results and discussion

3.1. Fly ash characterisation

The chemical composition of the used fly ash was given in Table 1 and compared to data obtained for other fly ash samples from various countries [6]. It is shown that the major components were SiO_2 (49–58%), Al_2O_3 (23–28%) and Fe_2O_3 (4–16%)

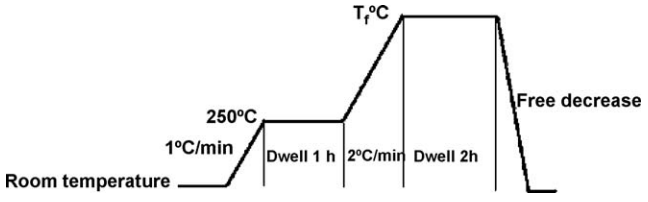

Fig. 2. Temperature–time schedule used.

Table 1
Weight % chemical composition comparison between typical fly ashes given by the literature [6] and the fly ash used in this work.

Fly ash origin	Composition (%)							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	SO_3	LOI[a]
Fly ash used in this work	49.09	24.34	8.93	4.88	3.15	1.74	2.15	1.07
UK	50.09	28.10	11.70	1.62	1.54	0.62	–	1.27
USA	52.24	19.01	15.71	4.48	0.89	2.05	1.34	0.92
Netherlands	50.46	25.74	6.53	4.32	2.24	4.43	–	3.95
Japan	57.50	26.10	4.00	5.10	1.30	1.35	0.4	1.60
Taiwan	48.75	23.21	4.15	3.93	1.00	1.10	–	10.39
Poland	50.80	23.90	8.60	3.60	2.80	2.90	0.80	2.90

[a] Loss on ignition.

independently of the fly ash origin. In addition, in the used fly ash, the percentages of other components such as CaO (4.88%), SO_3 (2.15%) and MgO (3.15%) are relatively high.

3.2. Thermal analysis

The DSC–TGA data of the mineral coal powder is represented in Fig. 3. It can be seen that the fly ash represents around 8% of the total weight. The oxidation of the carbon, contained in the coal, starts at around 550 °C. The firing temperature on the particle size of the fly ash obtained will be discussed when studying the difference between powders P_2, P_3 and P_4.

The DSC–TGA data of the fly ash powder P_1 is represented in Fig. 4. The mass loss is very low (1.5%) which may be caused by some impurities or a small percentage of unburned mineral coal powder, since the phenomenon started at 250 °C and continued to 800 °C.

3.3. Phase identification

XRD data for the fly ash samples sintered at different temperatures are shown in Fig. 5. The major crystalline phases identified were quartz (SiO_2), anorthite ($CaAl_2Si_2O_8$), gehlenite ($Ca_2Al_2SiO_7$), hematite (Fe_2O_3) and mullite ($3Al_2O_3{\cdot}2SiO_2$). A minority of anhydrite ($CaSO_4$) can be seen also on the spectrum.

This result is in concordance with the work done by Ilic et al. [6] in which they report that ''the ash forming from coal combustion originates from clays incorporated into the coal seam''.

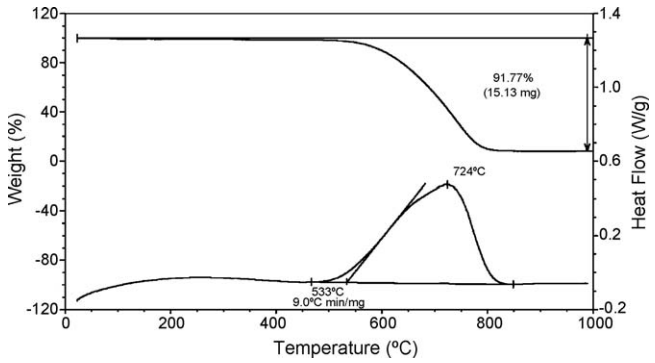

Fig. 3. The DSC–TGA data of the mineral coal powder.

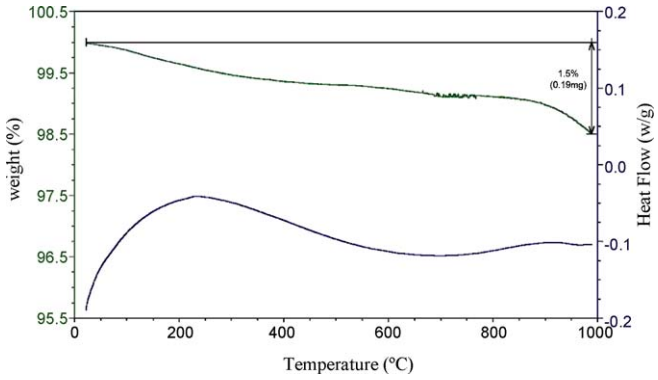

Fig. 4. The DSC–TGA data of the fly ash powder P_1.

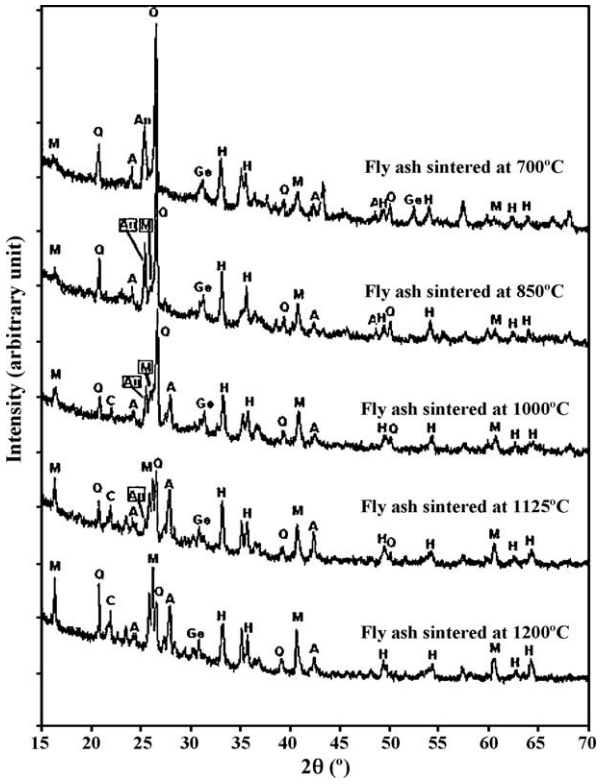

Fig. 5. XRD data for fly ash sintered at different temperatures. Quartz (Q), anorthite (A), mullite (M), hematite (H), cristobalite (C), gehlenite (Ge), and anhydrite (An).

Table 2
XRD peak intensities of the major peaks of crystalline phases found in the fly ash after sintering at different temperatures.

Fly ash (heated at)	Quartz $2\theta = 26.6^\circ$	Anorthite $2\theta = 27.9^\circ$	Mullite $2\theta = 26.2^\circ$	Hematite $2\theta = 33.3^\circ$	Cristobalite $2\theta = 21.7^\circ$	Gehlenite $2\theta = 31.3^\circ$	Anhydrite $2\theta = 25.5^\circ$
700 °C	3001	–	574	198	–	359	801
850 °C	3464	–	461	385	–	411	754
1000 °C	1451	392	637	705	216	796	701
1125 °C	1170	802	1034	672	213	221	200
1200 °C	869	878	1501	777	245	–	65

The changes in the XRD intensities of the major peak associated with the different phases are summarised in Table 2. Gehlenite and anhydrite intensity decreases in the fly ash with the increase of the sintering temperature until almost disappearing at 1200 °C in the anhydride case and effectively disappeared in the Gehlenite case. Cristobalite which is obtained at the high temperature of quartz is formed during sintering. However, the amount of quartz decreases during sintering. In fact, the intensity of the major peak decreases as the sintering temperature increases. In comparison, the intensities of the peaks associated with mullite and anorthite increase significantly as a result of rise of the sintering temperature. These results are in accordance with the Ilic et al. studies who found the same results [7].

3.4. Determination of the appropriate powder for the support elaboration

Generally, membrane supports should have a porosity of at least 40%. A preliminary work carried out on the sintering of the fly ash issued from the burning of a finely grinded mineral coal showed a porosity value around 52%. However, the average pore size obtained was too low: of about 0.34 μm, in comparison to the commercial supports which have an average pore volume in the range of 4–10 μm. In fact, a particle of the mineral coal used when burning loses 92% of its weight. Thus, a study of the effect of the thermal and the mechanical treatments of the mineral coal on the particle size of the fly ash must be given.

The powder P_1 related to not grinded coal and the powder P_2 related to finely grinded coal, were obtained by a heat treatment of the mineral coal at 800 °C. Fig. 6 shows that the particle size distribution of powder P_2 is narrower than that of powder P_1. The average particle size of the powder P_1 is higher than that of the powder P_2, this result shows clearly that the grinding of the coal have an important effect on the obtained fly ash powder.

The effect of the temperature on ash fly particle size distribution was studied for powders P_2, P_3 and P_4. All these powders were obtained from the firing of the same finely grinded mineral coal powder. The higher is the firing temperature, the

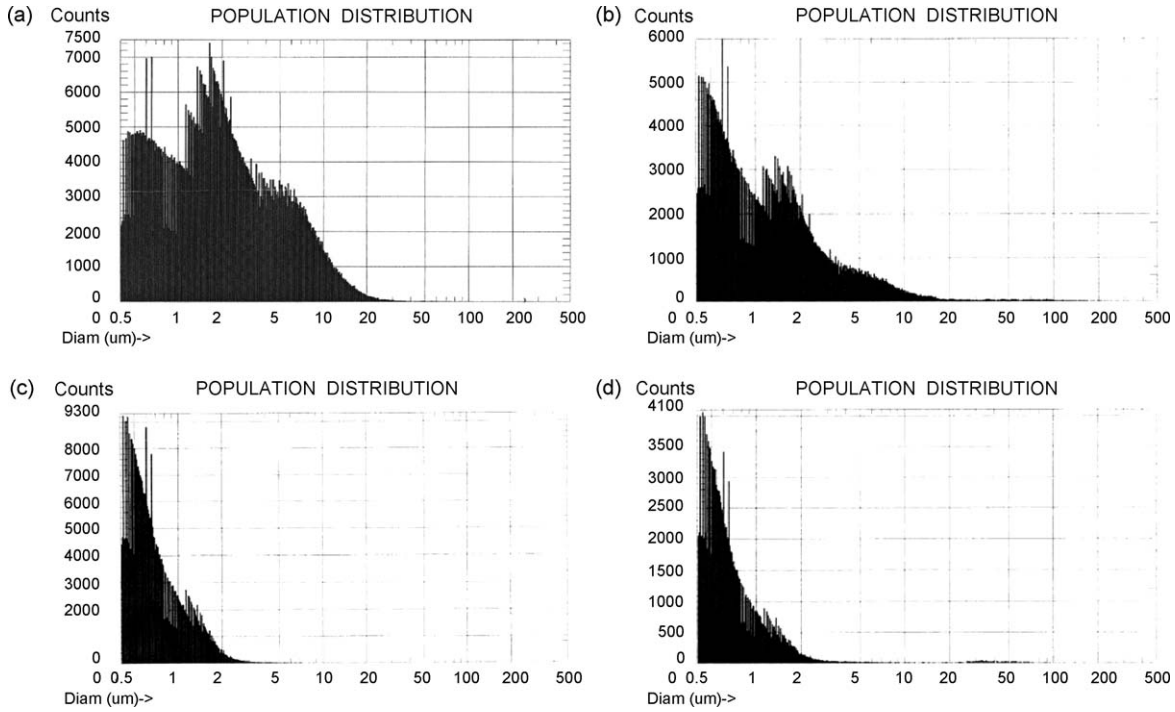

Fig. 6. Effect of the thermal and mechanical treatments of the mineral coal on the particle size distribution of the fly ash powder: (a) powder P_1, (b) powder P_2, (c) powder P_3, and (d) powder P_4.

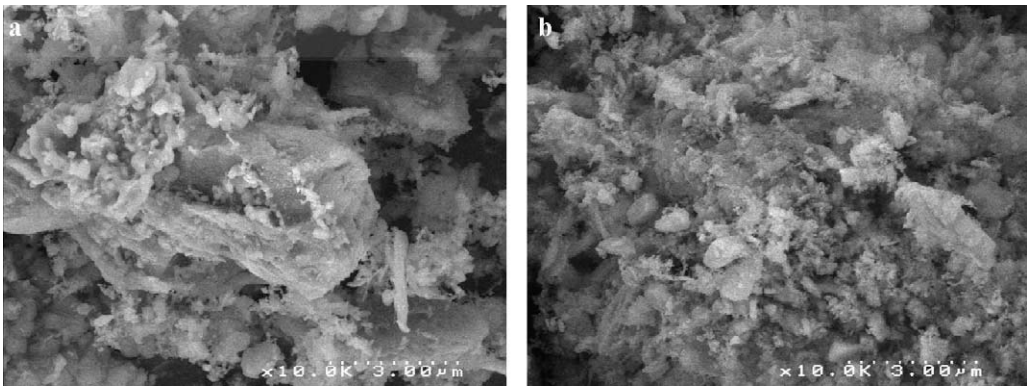

Fig. 7. SEM images of (a) fly ash powder P_2 and (b) fly ash powder P_3.

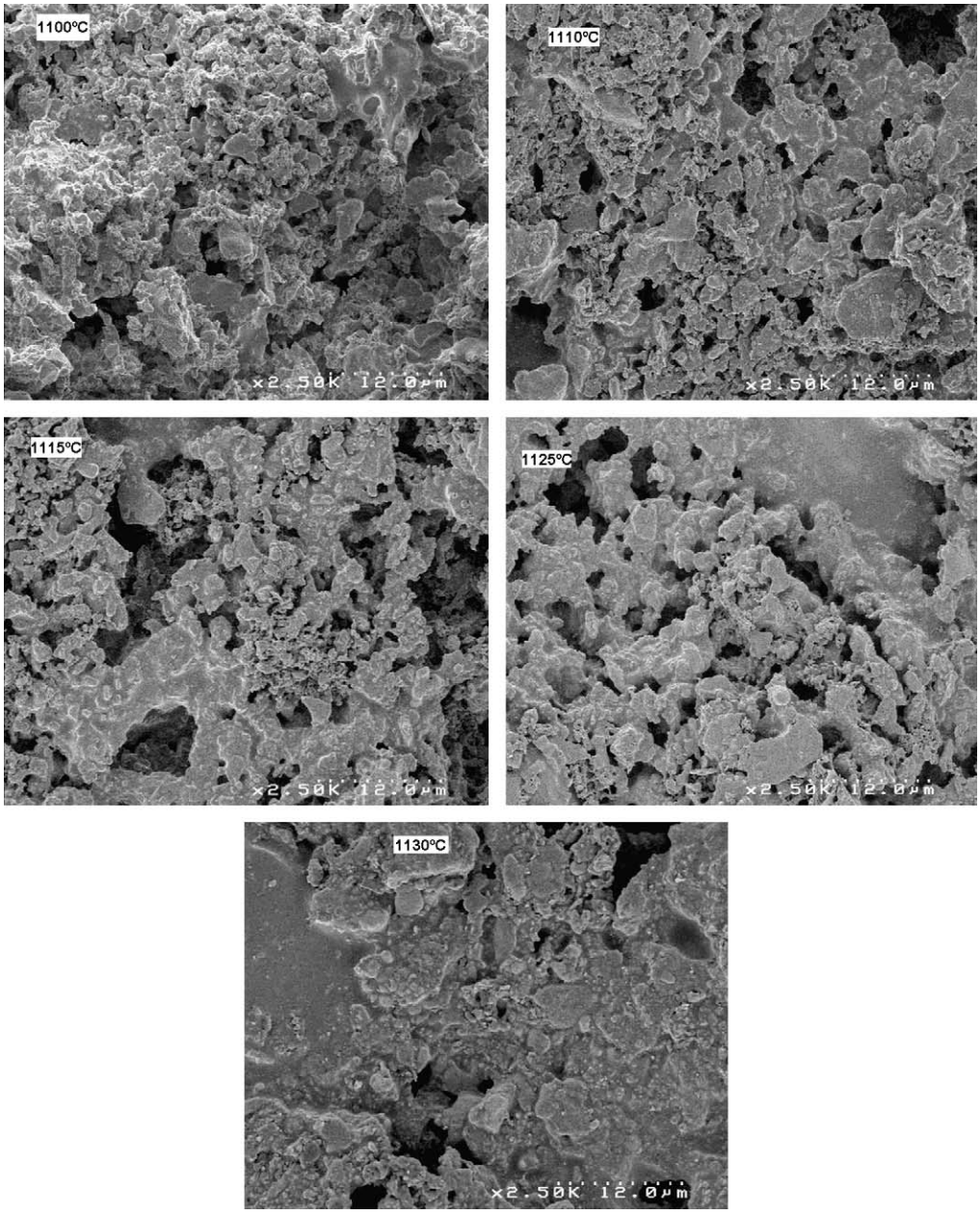

Fig. 8. SEM images of internal surface of tubular supports at various sintering temperatures.

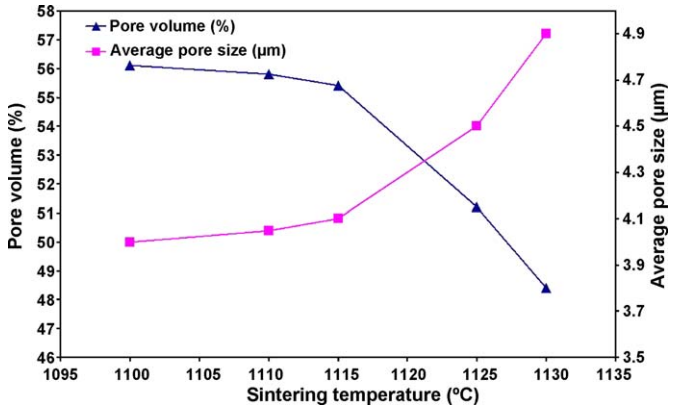

Fig. 9. Variation of pore diameter and pore volume with sintering temperature.

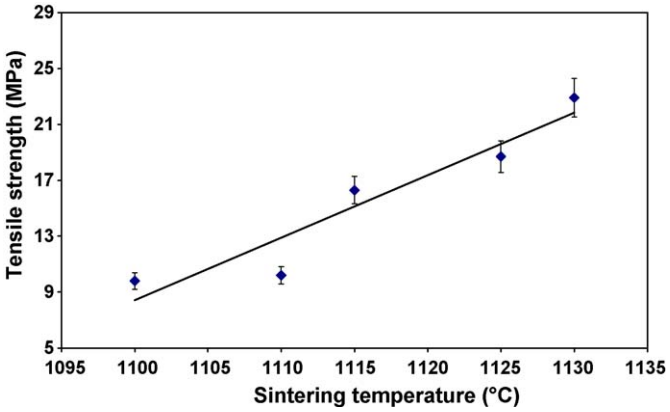

Fig. 10. Variation of tensile strength with sintering temperature.

bigger is the average particle size (Fig. 7). So, powder P_1 was chosen as a raw mineral material for making the support. The other powders might be used to deposit a microfiltration or an ultrafiltration layer.

3.5. Characterisation of the supports

For the development of high-quality supports, the following properties are of major importance: pore size distribution, porosity, surface texture, mechanical properties and chemical stability.

3.5.1. Scanning electron microscopy (SEM)

The micrographs relating to the evolution of the microstructure of fly ash membranes with the increasing sintering temperature (from 1100 to 1130 °C) are shown in Fig. 8. The formation of grain boundaries is achieved within this narrow temperature range. The obtained surface are homogeneous and do not present any macrodefects (cracks, etc.). A smooth inner surface is also observed, which will allow the deposit of a homogeneous membrane layer. The optimal sintering temperature was determined by comparing the texture of samples sintered at the different temperatures.

3.5.2. Mercury porosimetry

The evolution of support characteristics (pore diameter and porosity) with temperature is shown in Fig. 9. As would be expected, there is an increase in average pore size and a decrease in total porosity when the sintering temperature is increased.

The evolution of the average pore diameter and the porosity with the temperature of sintering reveals that the porosity decreases from 56 to 48% between 1100 and 1130 °C, while the pore diameter increased from 4.0 to 4.9 μm. At 1125 °C, the characteristics of the support are an average pore diameter of 4.5 μm and a porosity of 51%.

3.5.3. Mechanical resistance

Fig. 10 shows the variation of tensile strength with sintering temperature of samples prepared using the powder P_1. In accordance with the SEM pictures and the porosity values, the increase of the sintering temperature is accompanied with a densification phenomenon and consequently an increase in the tensile strength (from 9.8 MPa at 1100 °C to 22.9 MPa at 1130 °C).

3.5.4. Chemical resistance

The sintered fly ash presents a chemical resistance towards the acid and basic solutions. In fact the weight loss is negligible when a sample is exposed during 120 h into a soda aqueous solution at 80 °C at a pH of 14 and does not exceed 2% when it is exposed to a nitric acid aqueous solution at a pH of 2 in the same conditions in terms of time and temperature.

4. Conclusion

This study reports the development and the characterisation of new porous tubular supports based on mineral coal fly ash which can be used for microfiltration and ultrafiltration membrane elaboration.

The fly ash powder used to make membrane support heated at 800 °C without prior grinding of the mineral coal show a size distribution which depends on the mechanical and thermal treatments of the mineral coal.

The sintering temperature fixed at 1125 °C provides supports having a good mechanical and chemical resistances and an important porosity of an average value of 51%. The mean pore diameter was of 4.5 μm.

Finally, it appears that mineral coal fly ash materials are appropriate for the development of membrane supports for microfiltration or ultrafiltration membranes.

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