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Preparation and characterization of a highly hydrophilic glassy pore wall membrane filter

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A highly hydrophilic glassy pore wall membrane filter, whose ceramic powder consisted of quartz with glassy additives (lead borosilicate glass and natural zeolite), was studied by sintering at different temperatures (900-1100 °C) and determining the apparent water contact angles using a thin-layer wicking approach. The filter sintered at 1000 °C had the lowest contact angle (11°), which increased with an increase in the sintering temperature. The contact angles were also investigated by goniometry measurements for the case of sintering of the glassy additives above their fusion temperatures (> 940 °C) and a similar result (10°) was obtained. Crystallization and an increase in the apparent water contact angle occurred at the same sintering temperature; both crystallization and contact angle increased with an increase in temperature. The contact angles obtained by the wicking approach are consistent with the microstructural findings. Thus, the lowest contact angle condition indicates a way fabricating a highly hydrophilic glassy pore wall ceramic membrane.

Key words: A. microporous materials, D. microstructure, D. surface properties.

Introduction

Microporous ceramics have become increasingly popular in manufacturing filters for large-volume solid/liquid separation purposes, such as drinking, agricultural and waste water treatment, which require low-cost mass production of microporous ceramic filters with the desirable properties. The ceramic filter medium must have a high porosity, a narrow pore size range, and high bend strength, as well as high performance for the chemical nature of the filtered water.

Moreover, the filters have to be hydrophilic to serve the intended function during the operation process. Highly hydrophilic filters can be produced with ceramic powder of a special composition or by giving a coating to the porous wall of a polymeric substance. Recently, a glassy pore wall membrane filter has been produced using a mixture of quartz and a glassy composite consisting of glass frit and zeolite [1-4]. The hydrophilic nature of this membrane has not yet been shown. The objective of this study is to determine the hydrophilic nature of filters using the thin-layer wicking measurements and water dropped goniometry approaches. The results of the study will enable fabrication of filters with high hydrophilicities and thus high performance capillary membrane filters will be obtained that can be widely used in solid/water separation.

Generally, the hydrophilic nature of ceramic membranes is investigated from the water contact angle [5, 6]. Goniometry measurements by the sessile water drop technique are also useful for determining water contact angles, as well as the hydrophilic nature of the material. But, this technique is not convenient for hydrophilic porous material in which the water drop will be immediately absorbed by the sample and no observation will be possible. Recently, goniometric measurements have been applied indirectly [4] in which the glassy composite of the filter material was sintered above its fusion temperature and a nonporous glassy plate obtained for successful measurements. This technique enabled measurement of the contact angle only where the glassy dispersion occurred sufficiently within the filter matrix. The authors were looking for a technique to study the hydrophilic nature of a filter material that has changed by sintering due to the glassy dispersion through the filter matrix and its crystallization. In this regard, the thin-layer wicking approach is chosen for the measurements.

The dynamic wicking approach for contact angle measurement

The dynamic wicking approach, widely used for the contact angle measurement of ceramic powders, is also referred to as thin-layer wicking [7-11] and column wicking [12-15]. This technique has been quite popular so far for studying porous ceramic structures [16]. It is believed that this technique has potential for determining pore wall properties of porous membrane filters. The measurement is based on the wettability of the filter surface. The technique is easy to perform and needs no expensive equipment or expertise.

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The wicking measurement involves determination of the rate of liquid penetration into the pores of the solid surface, and such liquid penetration requires the wettability of a solid surface with the liquid used. The capillary rise of the liquid depends mostly on the contact angle between the liquid and the hydrophilic surface of the material, and also to a significant extent on the capillary pore radius which is measurable by the capillary rise experiments using apolar liquids.

The wicking technique is based on the Washburn equation, which describes capillary rise through a packed colloidal bed thus [17]:

$$\frac{h^2}{t} = \frac{r\gamma_L \cos\theta}{2\eta} \quad (1)$$

where h is the rise of the liquid in time t through the porous medium and γ_L the surface tension of the liquid, θ the liquid-solid contact angle, η the viscosity of the liquid and r the effective capillary pore radius. The Washburn equation is derived by combining Poiseuille's law for viscous flow and the Young-Laplace equation for capillarity.

The wicking approach for contact angle measurement is a routine process and involves three steps: (i) capillary rise (h^2/t) experiments with apolar liquids of different molecular weights (having different surface tensions: see Table 1) are carried out in which the contact angle of the liquids is close to zero, and thus $\cos\theta = 1$; (ii) plotting the previously found rate of capillary rise (h^2/t) with respect to the surface tension of the liquid (γ). This plot helps in calculating the effective capillary pore radius of the porous materials; and (iii) capillary rise experiments similar to the one in (i), but with polar liquids (i.e., water). In this experiment, the effective capillary pore radii are known and the unknown parameters (contact angles) can be calculated from Equation 1.

Experimental

Fabrication of ceramic membrane filters

The composition of the ceramic membrane was designed as (weight %): 86.86 SiO_2, 3.47 Al_2O_3, 5.28 PbO, 1.54 B_2O_3, 0.28 Na_2O, 0.71 MgO, 1.11 CaO and 0.11 K_2O. The membrane was prepared by using a mixture of quartz, lead borosilicate glass frit and natural zeolite (clinoptilolite) powders. The mixture was ground for one hour using alumina balls in an aqueous system using attrition milling. The surface-mean diameter of the ground powder was determined by a laser particle size analyzer (Malvern-Mastersizer 2000) as 0.98 μm. The glassy material (glass frit and zeolite) was a low-temperature sintering material, whose fusion point was determined by hot-stage microscopy (Misura ODHT-HSM 1600/80).

A suspension was prepared by adding forty percent by weight solid to distilled water and a plate-like sample (0.2 cm × 1 cm × 7 cm) was shaped by slip casting. The sample was sintered in air at 900 °C, 950 °C, 975 °C, 1000 °C, 1050 °C and 1100 °C for twenty minutes with a heating and cooling rate of 5 °C minute^{-1}.

The phases in the bulk materials were identified by X-ray diffraction (XRD) (Rigaku Miniflex). They were determined in the 2θ range of 10°-70° operating at 40 kV and 30 mA using CuK_α radiation with a Ni filter and adopting a scanning speed of 2° minute^{-1}. The fracture surface of samples was coated with a thin film of gold-palladium and examined using a scanning electron microscope (Zeiss EVO-50 EP). The pore size range of the filters was determined by a mercury porosimetry technique (Quantachrome Poremaster). The apparent porosities of the filtering layers were measured by a water immersion technique following Archimedes' principle.

The water contact angles of the materials were measured by goniometry. For this purpose, a smooth, nonporous surface was obtained from the glassy additive of filter composition. It was shaped and sintered at the same temperatures as that of the filter fabrication. The apparent water contact angles were measured by a water sessile drop method at room temperature with a contact angle goniometer (KSV Cam 100).

Wicking experiments

The plate-like membrane samples were not used directly for the wicking experiments. Those samples that required additional study were cleaned in an ultrasonic bath for two minutes and dried in an oven at 105 °C for twenty-four hours to remove any residual pore water. Such cleaning is important, because the residual water can dilute the wicking liquids and thus change their surface tensions and viscosities. The plates were then stored in a desiccator.

The wicking experiments were performed by immersing the plates vertically in a test liquid to a depth of about five millimeters using a cylindrical glass container. Before actual immersion, the plate was kept inside the closed desiccator for about one hour to allow the material to

Table 1. Surface tension of the liquids and their viscosities used in the experiments

Wicking liquids		Surface tension, γ_L (mJm^{-2}) (at 20 °C)	Viscosity, η (poise) (at 20 °C)
Apolar liquids	Heptane	20.3	0.00409
	Octane	21.6	0.00542
	Decane	23.8	0.00907
	Dodecane	25.35	0.01493
Polar liquid	Water	72.8	0.010

Table 2. Pore sizes and porosities of the membrane filters sintered at different temperatures

Sintering temperature, °C	Apparent porosity, %	Pore size distribution, μm	Median pore size, μm
900	48.48	0.25-4.5	0.91
950	48.03	0.25-4.5	0.99
975	45.40	0.25-4.5	1.01
1000	44.62	0.25-5	1.15
1050	41.16	0.3-5	1.17
1100	37.02	0.3-5.5	1.20

come to equilibrium with the vapor of the wicking liquid. This procedure was followed to equalize the spreading pressure which can disturb the measurements. The plate was then immersed in the liquid, and the vertical movement of the liquid through the filter plate observed. After the liquid had travelled the required distance (e.g. up to three centimeters, no effect of gravity), the experiment was stopped by removing the filter plate from the glass container.

The effective pore radius of the membranes was measured using the following apolar liquids: *n*-heptane (J.T. Baker, > 99%); *n*-octane (J.T. Baker, > 99%); *n*-decane (Sigma, > 99%); and *n*-dodecane (Sigma, > 99%). Then the contact angle of the membrane surface with water was measured by the wicking experiments in which the water used was distilled. Data reduction was performed using literature values for the viscosity (η), molecular weight and surface tension (γ) of the wicking liquids (see Table 1). At least three tests with different samples from the same membrane filter were conducted. All experiments were performed at a room temperature of 20 ± 1 °C.

Results and Discussion

Table 2 shows apparent porosities and pore sizes of membrane filters sintered at different temperatures (900-1100 °C). The sintering temperature changed the porosities and the pore sizes only slightly; the higher temperature decreased the porosities from 48.48 percent to 37.02 percent and increased the median pore sizes from 0.91 μm to 1.2 μm. In one of their earlier studies [3], the authors observed the influence of sintering temperature on porosity and pore size with particles shaped by uniaxial pressing; a temperature of about 960 °C was found good enough for filter fabrication. In the present study, all the fabricated materials (sintered between 900 to 1100 °C) are found useful for filtration applications. This observation is based on considering only the porosities and pore sizes. But, if the hydrophilic nature of the material is also considered, there may be a large difference between the materials sintered at different temperatures.

In the present study, the composition of the filter is so designed such that the glassy additive (glass frit and zeolite mix) is a wetting agent for the quartz matrix, and that it requires sufficient sintering to produce a glassy pore wall microstructure. Sintering is a crucial parameter for successful fabrication. It needs reliable characterization techniques to provide information on the formation of glassy pore walls at the sintering temperature applied. In this way, the best temperature for fabricating the highly hydrophilic filter could be obtained. This study focused on the determination of the sintering temperature for the lowest contact angles which were measured by the thin-layer wicking approach. The reliability of wicking results is tested by goniometry measurements, and X-ray and microscopic studies.

At a low temperature (900 °C), the authors did not expect to produce a glassy pore wall ceramic membrane in which the glassy mix (glass frit and zeolite) had not fused. The sintering behavior of the mixture was investigated by a hot-stage microscope; the softening, half sphere and fusion temperatures were 616 °C, 754 °C and 940 °C, respectively. Normally, glassy pore wall materials can be obtained by sintering just above the fusion temperature of the glassy mix. But, this needs to be investigated, keeping in mind that some other parameters (surface tension of the liquid, contact angle between the liquid and the solid, capillary radius) control sufficient wetting. This was done by producing the materials at different temperatures and determining their hydrophilic nature (water contact angle). A correlation is expected between the water contact angles of the porous materials and their sintering temperatures. If the sintering is poor, the contact angle is greatly controlled

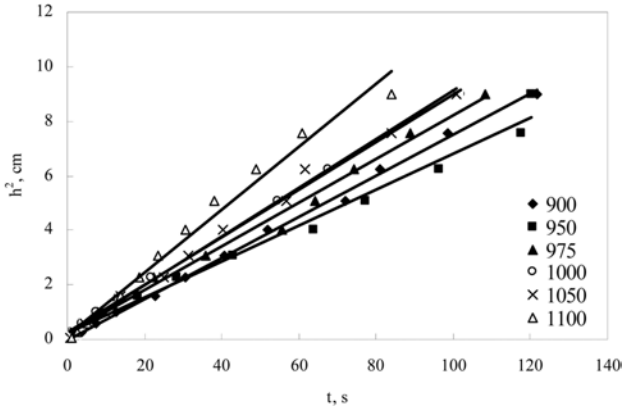

Fig. 1. The capillary rise of water through the membrane filters sintered at different temperatures.

Table 3. The apparent water contact angle of porous materials determined by the thin-layer wicking approach

Sintering temperature, °C	Apparent water contact angle
900	59°
950	62°
975	38°
1000	11°
1050	38°
1100	42°

by the quartz matrix. Glassy material well dispersed through the filter matrix should give the lowest contact angle and it is desirable to have no crystallization.

The apparent contact angles of the membrane filters, obtained at different temperatures, were determined by thin-layer wicking measurement. A process route was applied for this purpose; initially, the capillary rise experiments were conducted. They showed a good linearity in the plots of h^2 versus t (a representative plot is given in Fig. 1 for the capillary rise for water). After that, the effective pore sizes were determined with the apolar liquids. Lastly, the water contact angles were calculated from Equation 1. The results, given in Table 3, indicate that the water contact angle of the material reaches its lowest value of 11° at 1000 °C. It then increases with sintering temperature and reaches up to 42° at 1100 °C. The sintering temperature that provides the lowest water contact angle is of great importance, because the material fabricated at this temperature will have high hydrophilicity with a glassy pore wall microstructure.

It is not clear if the contact angles obtained by wicking measurements are the actual values or only the apparent values [18]. Therefore, the reliability of the contact angle measurements was examined by three different characterization techniques. The first one is the water drop measurement by goniometry. For a glassy material with a goniometry measurement it is possible only to determine the lowest contact angle [4]. The glassy additive was sintered above its fusion temperature (> 940 °C) and the contact angle determined from the surface of the glassy plate. For the material sintered at 1000 °C, the water contact angle was determined as 10° which is similar to the one determined with the thin-layer wicking measurement.

The second technique for testing the reliability of the wicking measurement is X-ray studies. Figure 2 shows XRD patterns of the porous ceramics sintered at different temperatures. The samples sintered up to 1000 °C show only one crystalline phase (α-quartz). The sample on heating to 1050 °C indicates the formation of a small quantity of cristobalite. The cristobalite peak height increases at higher temperatures, indicating increasing amounts of crystallization with increasing temperature. The material that showed the high water contact angle at the first crystallization temperature is more significant than the material that showed no crystallization (sintering at

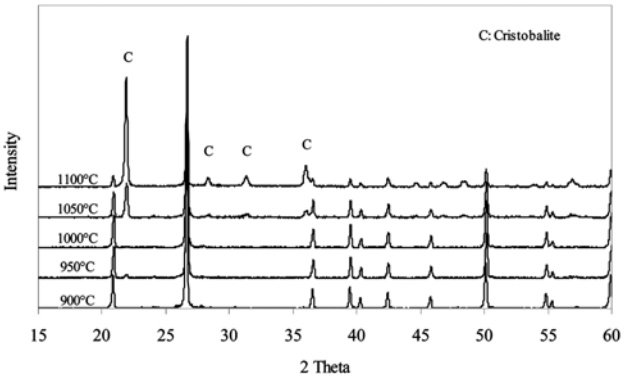

Fig. 2. The crystalline phases of membrane filters sintered at different temperatures.

1000 °C). The contact angle was further increased by increasing the applied crystallization temperature such as by sintering at 1100 °C (see Table 3). The results indicate a correlation between the apparent water contact angles and the amount of crystallization. Using the present results, one can state that the ideal sintering temperature is the one that is slightly below the temperature at which the cristobalite crystallization first appears. This temperature will produce a glassy pore wall filter with high hydrophilicity.

The crystallization temperature of the present mixture is slightly higher than the 1100 °C of the mixture studied earlier for sintering without the fit glass additives [19]. It is thus obvious that the frit glass makes the material crystallize more easily. Therefore, the content of frit glass should be decreased to increase the range of sintering temperature for material to have a high hydrophilicity.

The third investigation for testing the reliability of the wicking measurements was microscopic studies. This technique has been used extensively by the authors in their previous studies [2-4]. The glass frit used in this study was of lead borosilicate. The lead content facilitated observation of the glassy dispersion through the microstructure. Figures 3(a), (d) show back-scattered SEM micrographs of the fracture surfaces. The white grains having high atomic numbers are the leaded glass frit. The difference between the amounts of glass dispersion within the filter matrix of the samples sintered at 950 °C and 1000 °C was large. These observations show that the sample sintered at 950 °C still contained some PbO-rich areas (see Fig. 3(a)), whereas the sample sintered at 1000 °C showed a good dispersion of PbO-rich glass. (see Fig. 3(b)). Sintering at the higher temperatures of 1050 °C and 1100 °C (see Figs 3(c), (d)) gave similar results in relation to those of the sample sintered at 1000 °C. These results suggest that one can use SEM for determining the sintering temperature, but this temperature may not be exactly the same as the one that shows good dispersion in the glassy phase.

Goniometric, X-ray and microscopic investigations were used to verify the results obtained by thin-layer wicking measurements; the sintering temperature which

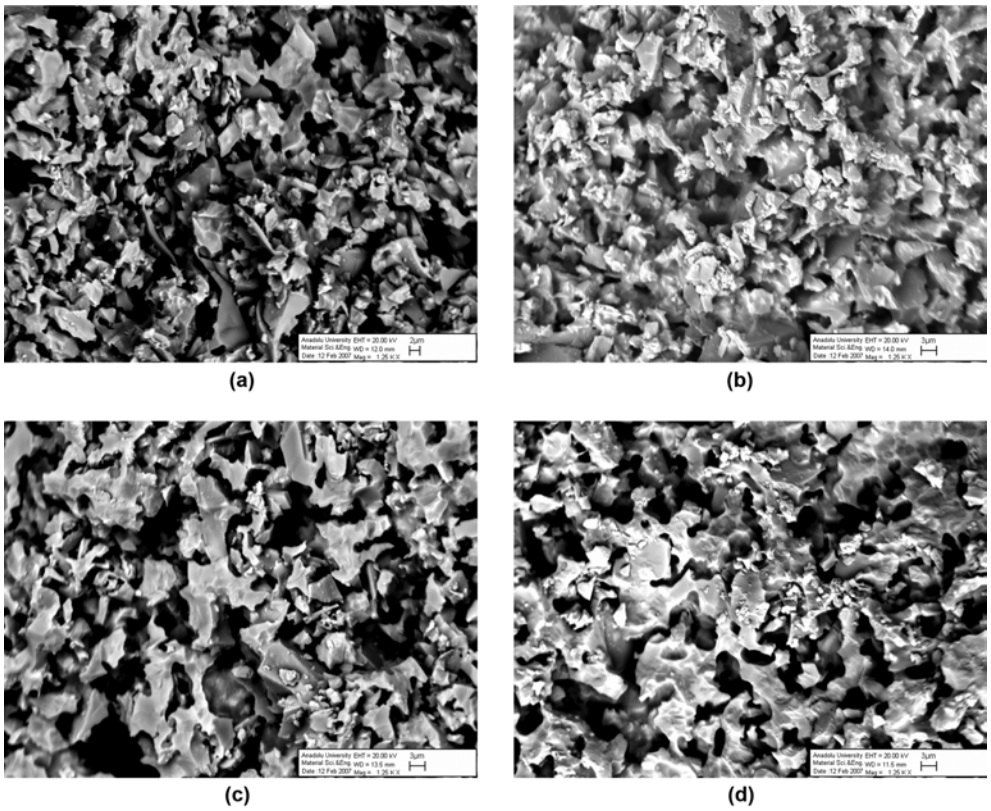

Fig. 3. (a) An SEM micrograph of the membrane filter sintered at 950 °C (backscattered mode) (b) An SEM micrograph of the membrane filter sintered at 1000 °C (backscattered mode) (c) An SEM micrograph of the membrane filter sintered at 1050 °C (backscattered mode) (d) An SEM micrograph of the membrane filter sintered at 1100 °C (backscattered mode).

showed the lowest water contact angle is the right fabrication temperature for obtaining highly hydrophilic glassy pore wall membrane filter. The fabrication temperature should be just below the first crystallization temperature of the material. The low temperature can be determined from the temperature that provided a sufficient glassy dispersion through the filter matrix (which can be detectable by microscopy). The goniometry measurements conducted on the glassy additive can be useful only for the highest hydrophilicity obtainable in filter fabrication.

Conclusions

The thin-layer wicking approach has been applied successfully to determine the water contact angle of glassy pore wall membrane filters. These measurements help in arriving at the best sintering temperature for fabricating a highly hydrophilic glassy pore wall membrane filter. A correlation was observed between the apparent water contact angles and the degree of glassy phase dispersion through the filter matrix and its crystallization. It is clear that the right temperature for fabricating a highly hydrophilic glassy pore wall membrane is between the temperatures that provide a good glassy dispersion and crystallization. The water contact angle of the glassy material (frit glass and zeolite mix) was determined by goniometry. A non-porous glassy plate was prepared by sintering the mixture above its fusion temperature. The results are similar where the contact angle was determined as 11° by the thin-layer wicking approach and 10° by goniometry. These results indicated the reliability of the thin-layer wicking measurements.

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