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Fabrication of glassy membrane filters and characterization of its hydrophilic nature by thin layer wicking approach

Osman Şan [a,*], Cem Özgür [a], Cengiz Karagüzel [b]

[a] Dumlupinar University, Department of Ceramic Engineering, Kütahya 43100, Turkey
[b] Dumlupinar University, Department of Mining Engineering, Kütahya, Turkey

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Abstract

Contact angle measurement of porous ceramics is difficult by goniometry application and it is impossible to determine where the water drops are immediately absorbed by the filter pores if the porous sample is of capillary type. The dynamic wicking approach is a potential technique for the contact angle measurement of capillary materials. In this study, different microstructures of glassy membrane filters were prepared and the water contact angle was determined by using thin layer wicking approach. The success of wicking results was examined. The glassy filters were shaped by two techniques (slip casting and pressing) and they were sintered at different temperatures (900, 950, 1000 and 1050 °C). Results indicated that both the shaping techniques and sintering temperature produced different microstructures and the contact angles obtained by the wicking approach were consistent with the hydrophilic nature of the filter materials. Low temperature sintering did not produce a sufficiently good glassy dispersion and high temperature led to crystallization. The best glassy filter was obtained at moderate temperatures: the sintering temperature being at 900 °C and 1000 °C for the material shaped by pressing and slip casting, respectively. At these temperatures, the glassy pore wall microstructure without crystallization could be obtained. The wicking results have been correlated with the hydrophilic nature of the filters so that the measured water contact angle was equal to or lower than 11°. Normally, the crystallization of the glassy material decreases the hydrophilic nature of the filters and the obtained wicking results are consistent with the phenomena and indicated higher contact angles.

Keywords: B. Microstructure-final; D. Glass; D. SiO_2; E. Membranes; Hydrophilic

1. Introduction

Capillary filters with micropores and hydrophilic properties makes the filters advantageous during filtration where most of the liquid in the slurry is absorbed into the filter bodies via capillary action and by this mechanism the filtering time can be reduced [1–4]. Recently, the author fabricated the capillary filter as glassy pore walls microstructure. High silica-content ceramic powder has been used for the fabrication in which the filter matrix was prepared from quartz particles and sintering was provided with the mixture of frit glass with some additives (i.e., clay, Na–feldspar, pigment type zinc oxide and natural zeolite). The sintering temperature was applied above the fusion temperature of the glassy composition and the obtained homogenous porosities and the filter matrix acquired a glassy nature [5–8]. The fabrication of glassy filters required great attention where less spreading of the glass through the microstructure and crystallization of the glass during sintering decreased the hydrophilic nature of the filter material [9,10]. These filters need a correct characterization regarding their hydrophilic nature.

The water contact angle of materials directly indicates the hydrophilic nature; a contact angle of about 10° indicates a filter material named as super hydrophilic [11–13]. Glassy filters are super hydrophilic materials. Less dispersion of the glassy through the microstructure and crystallization of the glassy material after the well dispersion make the material less hydrophilic and a water contact angle is obtained. Thus, the true sintering temperature has to be determined for the fabrication of the glassy membrane filters. It is obvious that the sintering temperature was influenced by the particle compaction during

* Corresponding author. Tel.: +90 274 265 20 31/4302; fax: +90 274 265 20 66.
E-mail address: osmansan@dumlupinar.edu.tr (O. Şan).

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shaping. On the liquid phase sintering, the high compaction produces fine capillary pores and thus well dispersion of melted glass was obtained through the microstructure. Subsequently, sintering temperature was decreased. In light of this, the true sintering temperature for glassy filters has to be investigated with respect to the particle compaction during shaping.

Contact angle measurement has been operated easily by goniometry. But this technique truly determined the contact angle of flat and nonporous materials. This technique can be slightly applicable for high hydrophobic-microporous materials. The use of this technique is impossible if the porous sample is of the capillary type where the water drop is immediately absorbed by the filter pores. Dynamic wicking approach is a potential technique for measurement of contact angle of the capillary materials. Dynamic wicking approach has been widely used for the determination of contact angle of ceramic powders (Table 1 [14–18]) and this technique has been so far quite popular in studying the porous ceramic structure [19]. It is believed that this technique has potential for the determination of pore wall properties of porous membrane filters: the measurement is based on the wettability of filter surface. It is an easy to perform technique that requires no expensive equipment or particular expertise; these properties also make it advantageous.

Water contact angles for some silica and glass materials determined by thin layer wicking and goniometry techniques are shown in Table 1. Glass materials indicate super hydrophilic natures (contact angles: $\sim 10^{\circ}$), determined only via the goniometry technique. However, glassy materials are not only nonporous; recent studies have focused on the fabrication of glassy porous materials for use in membrane technology [5–8] and they need characterization regarding with respect to their hydrophilic nature. In light of these, this study focused on (i) the influence of shaping technique on the glass dispersion and crystallization with respect to sintering temperature and (ii) the success measurement of water contact angle for the glassy membrane filters by thin layer wicking approach.

1.1. Thin layer wicking measurement

Thin layer wicking measurement is the determination of the rate of liquid penetration into the pores of solid surface and such a liquid penetration requires wettability of solid surface with the used liquid and that the pores be small enough to enable capillarities. The capillary rise of the liquid is greatly determined by the contact angle between the liquid and the hydrophilic surface of the material. The other parameter is the effective 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 [20]:

$$\frac{h^2}{t} = \frac{r\gamma_L \cos\theta}{2_\eta} \tag{1}$$

where h is the rise of the liquid in a 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 the Poiseuille's law for viscous flow and the Young–Laplace equation for capillarity.

The wicking measurement for contact angle measurement consists of three steps (i) capillary rise (h^2/t) experiments with different molecular weight of apolar liquids (having different surface tension: see Table 2) are studies in which the contact angle of the liquids are close to zero, and thus the $\cos\theta = 1$, (ii) drawing of the previously determined rate of capillary rise (h^2/t) with respect to surface tensions of the liquids (γ). This plotting leads to the calculation of effective capillary pore radius for the porous materials and (iii) the same capillary rise experiment produced with the polar liquids (i.e., water). In such cases, the effective capillary pore radius is known and the other unknown parameter (contact angle) could be calculated from the Eq. (1).

2. Experimental

2.1. 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

Table 1
The water contact angles determined for some silica materials.

Material types	Materials	Water contact angle (°)	Technique	Reference number
Natural silicate	Diatomitic silica	41.3	Thin layer Wicking	[14]
	Silica Particle coarse powder	34.9	Thin layer Wicking	[13]
	Ground silica fine powder	59.6	Thin layer Wicking	[13]
	Quartz	44.1	Thin layer Wicking	[16]
	Albite	43	Thin layer Wicking	[17]
	Orthoclase	45	Thin layer Wicking	[17]
	Kaoline	47.4	Thin layer Wicking	[14]
	Kaoline	46.1	Thin layer Wicking	[15]
Glass	Glass slide	9	Goniometry	[13]
	Glass slide	9	Goniometry	[11]
	Glass microscope slides	10–15	Goniometry	[12]

Table 2
Surface tensions of the liquids and their viscosities used in the experiments [16].

Wicking liquids	Surface tension, γ_L (dyn/cm) (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

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).

The slurry was dried at 105 °C for 24 h, then the powder was passed through 45 μm with sieve, and finally the agglomerates were wetted by tap water. Uniaxial pressing at 9.1 MPa was used to form ceramic plates (0.4 cm × 12 cm × 7 cm). The samples were sintered in air atmosphere at 900, 950, 1000 and 1050 °C for 20 min with a heating and cooling rate of 5 °C/min. The sintered specimens were cut into 0.2 cm × 1 cm × 7 cm for wicking measurements. The cutting was applied only one surface of the membrane and the free surface was used for the observation of capillary rise during the wicking experiments.

The phases in the bulk materials were identified by X-ray diffraction (XRD) (Rigaku Miniflex). The phases were determined in the 2θ range of 10(70° operating at 40 kV and 30 mA using Cu Kα radiation with Ni filter; a scanning speed of 2° min^{-1} was adopted.

2.2. Wicking experiments

The prepared filter plates required additional study for wicking measurements during which the membrane filters were cleaned in an ultrasonic bath for 2 min and dried in an oven at 105 °C for 24 h to remove any residual pore water. It is important for the dynamic wicking measurement because that might have interfered with the measurements as the residual water can dilute the wicking liquids and change their surface tensions and viscosities. The plates were then stored in desiccators.

Wicking experiments were performed by immersing the plates in the vertical position to a depth of about 5 mm in a test liquid 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 come to equilibrium with the vapor of the wicking liquid. This procedure was carried out to equalize the spreading pressure which can disturb the measurements. The plate was then immersed into the liquid, and the vertical movement of the liquid through the filter plate was observed. After the liquid had traveled to the required distance (e.g. between 1 and 3 cm, yet short enough to avoid gravity effect), the experiment was stopped by removing the filter plate from the glass container. The effective pore radius of the membranes were investigated using the following apolar liquids: *n*-heptane (J.T. Baker, >99%), *n*-octane (J.T. Baker, >99%), *n*-decane (Sigma, >99%), *n*-dodecane (Sigma, >99%). Later, the contact angle of membrane surface with water was investigated by the wicking experiments in which distilled water was used. Data reduction was performed using literature values for the viscosity (η), molecular weight and surface tension (γ) of the wicking liquids (see Table 2). At least three tests with different samples from the same membrane were conducted. All experiments were performed at room temperature of 20 ± 1 °C.

3. Results and discussions

3.1. The microstructure of glassy filters

Filters obtained by slip casting were from earlier studies [9]. The sintering temperature slightly decreased the apparent porosities of the filter material; the apparent porosities were obtained as 48.48 and 44.62% by sintering at 900 and 1000 °C, respectively. Here, the same material was shaped by applying uniaxial pressing and significantly lower porosities were obtained: the porosities being 45.02%, 43.42% and 40.02% for the sintering applied at 900 °C, 950 °C and 1000 °C, respectively. These results indicated that the press shaping produced less porosity. This is the indication of high sinterability where small pore sizes between the grains occurred by the high compaction and thus well spreading of the glass through the microstructure could be obtained. The increase of sinterability not only decreased the porosities but also influenced the glass crystallization was expected.

The glass frit used in the filter composition was of lead borosilicate. The lead content facilitated observation of the glassy dispersion through the microstructure where the white grains having high atomic numbers are the leaded glass frit. The microstructure of glassy filters obtained by slip casting had been studied via the sintering temperature and glass dispersion within the filter matrix was determined and it was observed that its crystallization is greatly temperature dependent [9]. The sample sintered at 1000 °C displayed good dispersion of PbO-rich glass (Fig. 1) and the sample indicated the lowest water contact angle. Here, the press shaped samples were investigated with respect of the microstructure evaluation due to the applied sintering temperature. Fig. 2a–c shows the back-scattered SEM micrograph of the fracture surface of the filters sintered at low (900 °C), moderate (950 °C), and high (1000 °C) temperatures, respectively. The white grains with high atomic number consist of lead containing glass by even dispersed through the microstructure are observed at the moderate and high temperatures (see Fig. 2b and c) but the PbO-rich areas are still localized at the low temperature (see Fig. 2a) which indicates a poor sintering. These results show that the press shaped filters require a sintering temperature of about 950 °C for the presence of substantive liquid phase for good dispersion. The good glassy dispersion observed at high temperature leading to the glassy crystallization can only be determined by X-ray analysis.

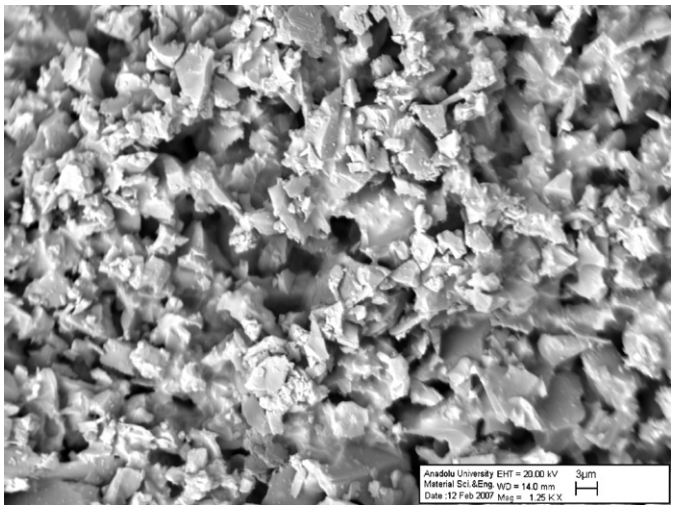

Fig. 1. SEM micrograph of the slip cast shaped-membrane filter sintered at 1000 °C [9] (backscattered mode).

3.2. Crystallization of the glassy pore wall

Fig. 3 shows XRD patterns of the porous ceramics sintered at different temperatures for the samples shaped by slip casting (Fig. 3a [9]) and by uniaxial pressing (Fig. 3b). For the sample shaped by slip casting, the sintering up to 1000 °C show only one crystalline phase (α-quartz). The sample on heating to 1050 °C indicates the formation of alpha-cristobalite. However the sample shaped by uniaxial press, the cristobalite crystallization occurred at 1000 °C (see Fig. 3b). The change of crystalline temperature was attributed the compaction efficiency of particles with respect to shaping technique. It is obvious that high compaction decreased pore sizes between the grains and thus increased the liquid phase sinterability as well as decreasing crystallization temperature.

3.3. The capillary rise experimental results

Capillary rise experiments with different apolar liquids, such as heptane, octane, decane and dodecane make it possible to calculate the effective capillary pore radius (r) of the membrane filters. Later, the same filters with a polar liquid are studied for contact angles measurement. The slip cast shaped samples were studied in an earlier study [9]. Here, the experimental results for the press shaped samples will be given and the results compared with the microstructure findings.

Fig. 4a–c shows a representative wicking plot for the press shaped samples where h^2 versus t curves are displayed for the wicking liquids tested with filters sintered at a low (900 °C), moderate (950 °C) and high temperature (1000 °C), respectively. The good linear dependence of h^2 on t is in agreement with the Washburn equation (see Eq. (1)). The linearity indicates that there is no gravity effect during the measurements. The effective pore radius for the filters is then determined from the slope of $2\eta h^2/t$ versus γ_L plotting (see Fig. 5).

Once the value of r is obtained, it is then possible to calculate the value of contact angles for a given polar liquid. In our studies, the same capillary rise experiments were conducted by water as a wetting liquid. Fig. 6 shows the wicking plots where h^2 versus rt curves are displayed for the water tested with filters sintered at the different temperatures. The linear relationship obtained for the contact angles of the membranes have resulted in a good distribution and the values we obtained were 40.71°,

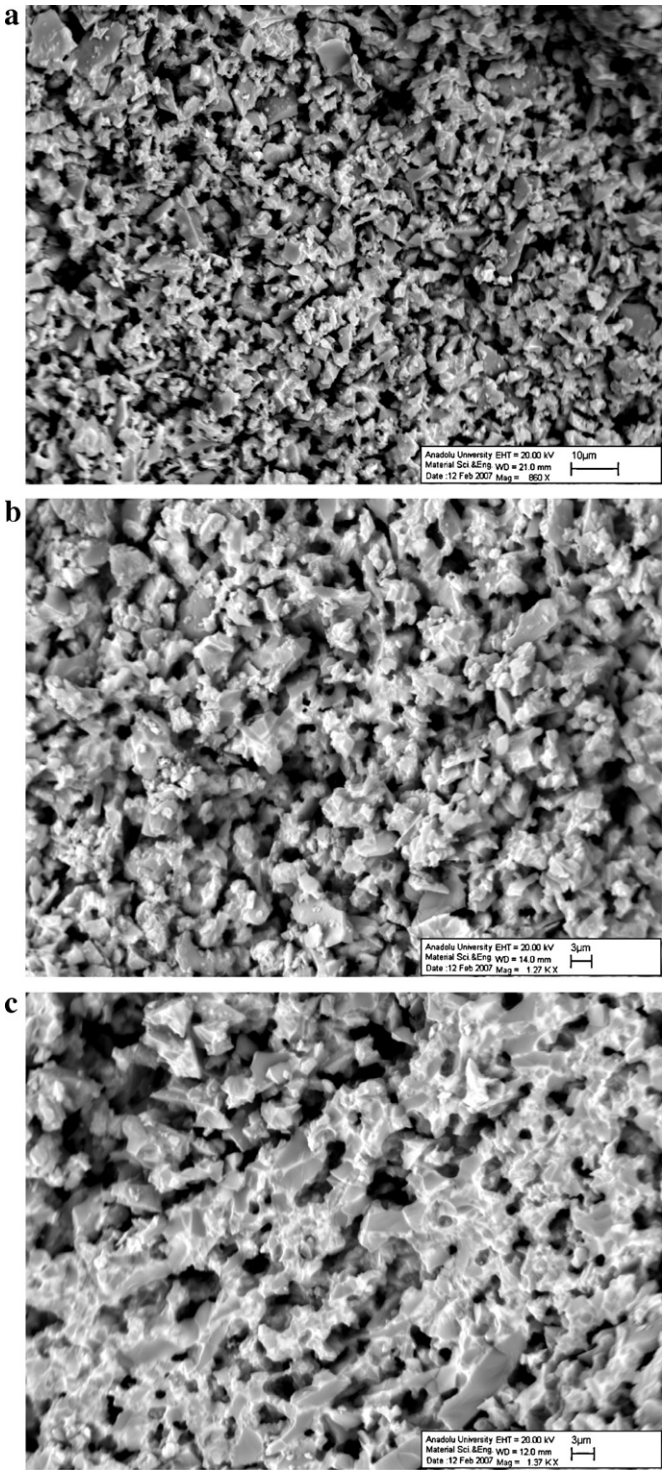

Fig. 2. (a) SEM micrograph of the press shaped-membrane filter sintered at 900 °C (back scattered mode). (b) SEM micrograph of the press shaped-membrane filter sintered at 950 °C (back scattered mode). (c) SEM micrograph of the press shaped-membrane filter sintered at 1000 °C (back scattered mode).

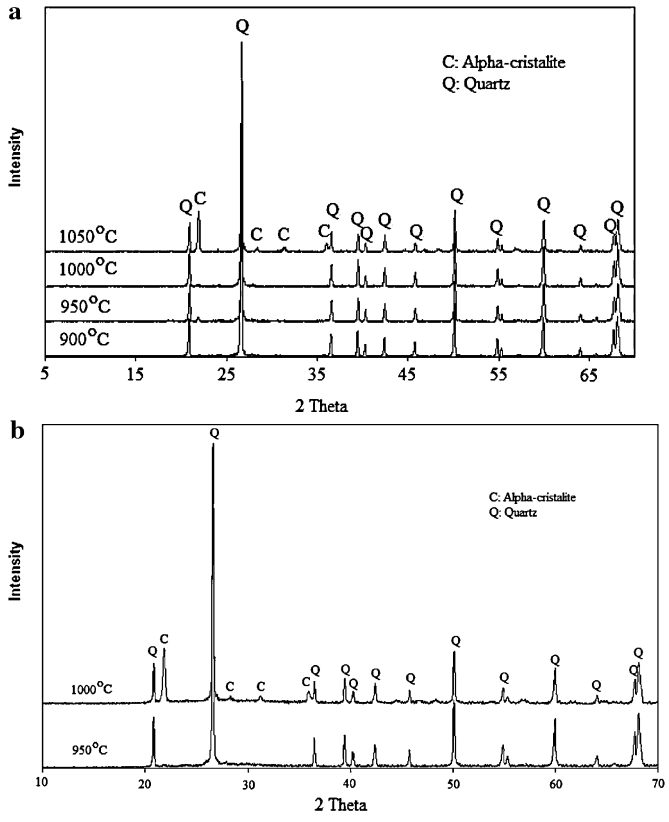

Fig. 3. (a) XRD patterns of the porous ceramics sintered at different temperatures for the samples shaped by slip casting [9]. (b) XRD patterns of the porous ceramics sintered at different temperatures for the samples shaped by uniaxial press.

4.2° and 55.29° for sintering at low, moderate and high temperatures, respectively. 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 through the glassy pore wall microstructure.

The wicking results for the slip cast samples were slightly different [9]. Those indicated 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 38° at 1050 °C. The high hydrophilic filter could be obtained at the temperature of 1000 °C and this temperature was 50 °C higher than that of the sample shaped by pressing.

It is believed that the contact angles obtained from the wicking measurement are coherent with the pore wall properties of the membrane filters for cases when compactions were carried out by slip casting and pressing: the results for the quartz and glassy filters are comparable with the measurement obtained previously for the silicate and glass type samples (see Table 1). In recent studies [9,21], it has also been reported that glass forming within ceramic materials by vitrification leads to a decrease in contact angles. The crystallization of amorphous phase has been reported as a potential phenomenon for increase of the contact angle [22].

The dynamic wicking approach has been widely used for the determination of contact angle of ceramic powders [14–18] and cotton fabric [23–25]. This technique is also successively

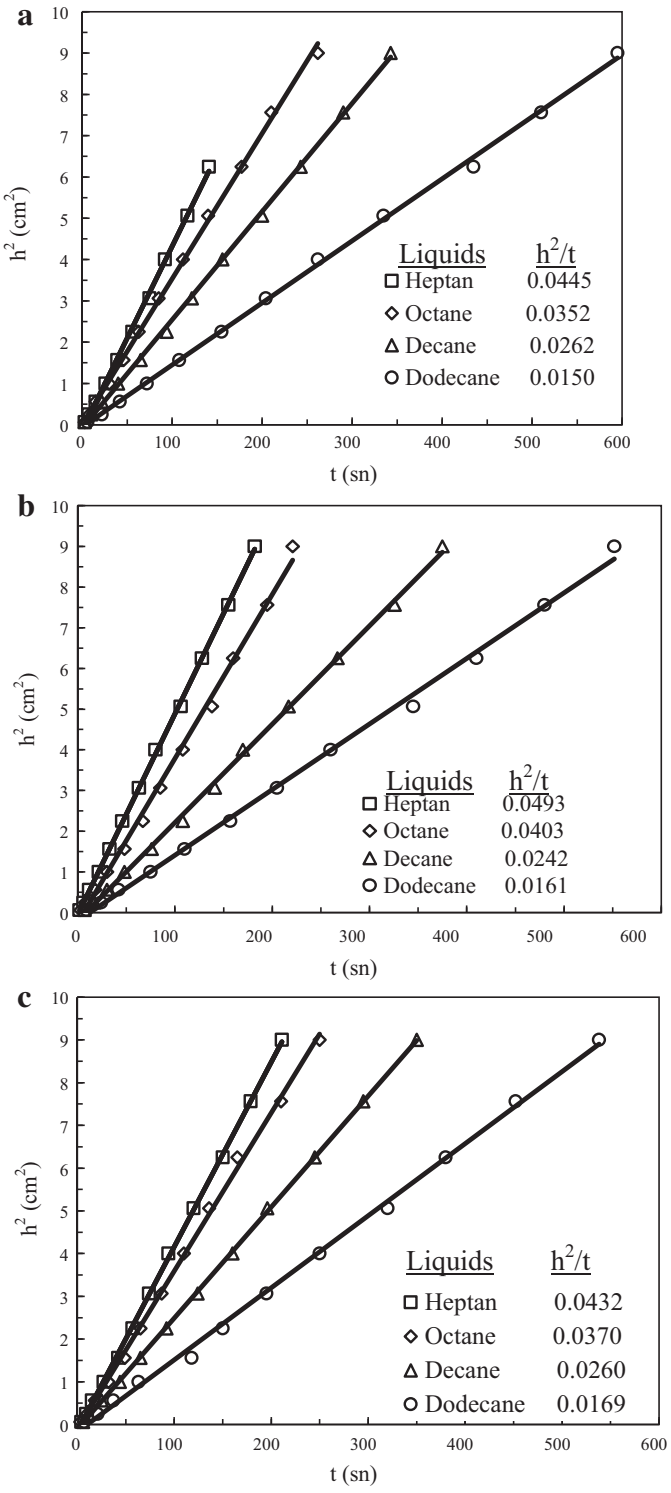

Fig. 4. (a) The capillary rise experiments with the press shaped membrane filter produced at 900 °C. (b) The capillary rise experiments with the press shaped membrane filter produced at 950 °C. (c) The capillary rise experiments with the press shaped membrane filter produced at 1000 °C.

applied for the characterization of composite porous ceramics membrane consists of ca. 64% aluminium oxide (Al_2O_3) ca. 27% titanium dioxide (TiO_2) and ca. 9% silica [26]. The present paper indicated that this technique is also applicable for the

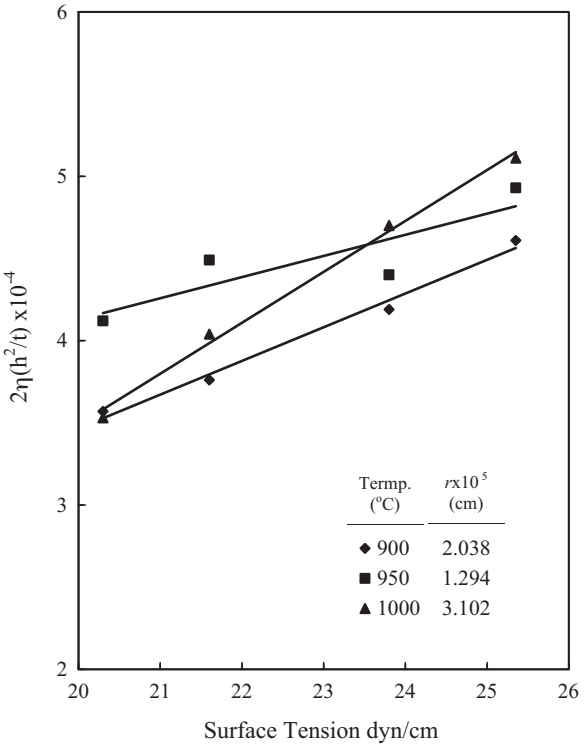

Fig. 5. The calculation of effective pore radius from the slope of $2\eta h^2/t$ versus γ_L plotting.

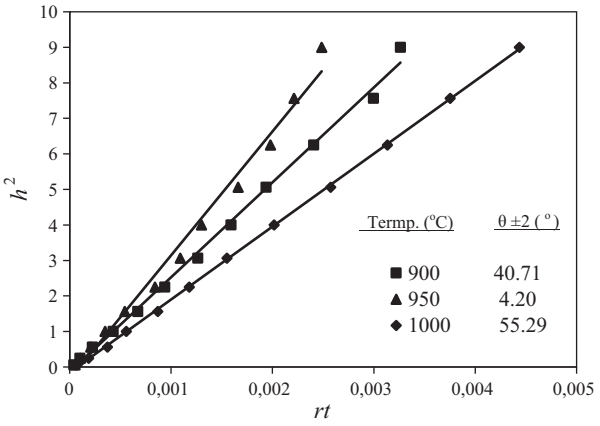

Fig. 6. The calculation of water contact angle from the h^2 versus rt plotting.

glassy porous ceramics either amorphous or crystalline pore wall microstructure.

4. Conclusions

The membrane filter characterization with respect to pore wall properties is an important subject for the determination of material performance and its potential usage area. Wettability of a surface is commonly explained by the contact angle of the filter materials. This study presents contact angles of the ceramic membrane filters determined by the dynamic wicking approach and those accommodations are discussed with the nature of filter pore wall surface.

It is an easy technique and the obtained results are in accordance with pore wall properties: glassy surface shows high hydrophilic surface with low contact angle and crystallization decreases the wettability. Normally, the crystallization temperature is strongly determined by the type of glass and the sintering additives. This study indicates that the crystallization temperature is also influenced by the shaping process Slip cast process produced relatively loose compaction and thus the crystallization temperature increased in comparison with uniaxial pressing. The contact angles obtained by the wicking approach are strongly consistent with microstructural findings of the filter materials.

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