ACOUSTIC CHARACTERIZATION OF MICROPOROUS MEMBRANES.

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ABSTRACT.

This work presents an investigation carried out to apply an air-coupled broadband ultrasonic spectroscopy technique to the study of membrane filters. The technique is based on the analysis of the amplitude spectra of broadband ultrasonic pulses transmitted through the membranes. Density of the membrane and velocity and attenuation of sound waves are obtained. These magnitudes are correlated to other properties of the membrane like porosity, pore size, water flow and bubble point. Observed relations suggest that this technique can be used as a filter integrity test and as a non-invasive characterization procedured.

INTRODUCTION.

Broadband ultrasonic spectroscopy is a well known technique used to measure velocity and attenuation of ultrasonic waves in materials. The technique is based on the frequency-domain analysis, by using the Fourier transform, of broadband pulses transmitted through a sample, or reflected from it. Density, velocity (or thickness) and attenuation of sound waves and the frequency dependence of these variables can be obtained. In 1978, Sachse and Pao presented an ultrasonic spectroscopy technique, or broadband pulse technique, based on a phase spectral analysis from which phase and group velocity of longitudinal waves can be obtained.[1] Simultaneously, Haines et al. applied broadband ultrasonic spectroscopy to thin layered media.[2] Later, the technique has been improved to measure attenuation,[3] and velocity and attenuation of shear waves.[4] Alternatively, Pialucha et al developed a method to measure the phase velocity in plate samples based on the amplitude spectrum instead of phase-spectrum.[5]

Velocity and attenuation of sound in porous materials are closely related to parameters like: pore size, porosity, tortuousity, permeability, and flux resistivity. For example, it is well known that for porous materials like acoustic absorbents flux resistivity can be related to the attenuation of sound waves.[6, 7] For some others porous materials, velocity of slow longitudinal sound waves has been related to pore tortuosity and difusion and transport properties. [8, 9, 10, 11] Attenuation of sound is very sensitive to the appearance of any external agent in the pore space as moisture, and can be used to monitor wetting and drying processes.[12],[13] Nevertheles there is no study about the acoustics of membrane filters and the relationship between acoustic and filtration properties. The purpose of this work is to present the application of an air-coupled ultrasonic broadband spectroscopy technique to the characterization of filtration membranes. In particular, the technique is based on the analysis of the amplitude spectra of broadband ultrasonic pulses transmitted through the membranes. Air-coupled piezoelectric transducers that generate ultrasonic broadband pulses at an amplitude high enough to overcome the problem of the attenuation in the gas at the megahertz frequency range and ambient pressure are used.[14, 15, 16] Ultrasonic spectroscopy using airborne through transmitted ultrasonic pulses has been successfully applied in the past to the characterization of other porous materials like paper,[17, 18] and silica aerogels.[19]

MATERIALS.

A large number of different commercial microporous membranes (20) were used for this study. Different manufacturers, materials, pore sizes, and other filtration properties were selected to have a wide collection of samples. Information is gathered in table I.

Table I. Materials and properties of the studied membranes

Membrane code	Material	Bubble point (bar)	Water flux @0.7 bar (mL/min/cm^2)
P-11	Polypropylene	1.38	28
P-12	Polypropylene	2.9	17
P-2	PVDF	1.1	9.6
P-3	Nylon	3.8	8
M-11	PVDF	n.a.	15
M-12	PVDF	n.a.	6.9
M-13	PVDF	n.a.	2.5
M-2	PTFE	0.63	40
M-31	Mixed cellulose esters	21.1	0.15
M-32	Mixed cellulose esters	14.1	1.5
M-33	Mixed cellulose esters	3.52	18
M-34	Mixed cellulose esters	2.11	60
M-35	Mixed cellulose esters	1.2	190
M-36	Mixed cellulose esters	0.77	270
M-37	Mixed cellulose esters	0.7	320
M-38	Mixed cellulose esters	0.42	580
W-11	Cellulose Nitrate	n.a.	n.a.
W-12	Cellulose Nitrate	n.a.	n.a.
W-13	Cellulose Nitrate	n.a.	n.a.
W-14	Cellulose Nitrate	n.a.	n.a.

THEORETICAL BACKGROUND.

The technique is based on the spectral analysis of broadband ultrasonic pulses transmitted through the samples, specially for the frequency range where, at least, one thickness resonance of the membrane appears, and the solution of the so called inverse problem.[20] Theoretical modelling of the problem of the transmission of ultrasonic waves through a membrane separating two media (1 and 3) is carried out considering plane longitudinal waves, normal incidence, and, therefore, a one dimensional model. Displacement vector potential can be written in the three space regions (*m*) denoted as (1: medium 1, 2: membrane, 3: medium 3):[21]

$$\begin{gathered}\varphi_m = \varphi_m^1 \exp\left[ik_m z\right] + \varphi_m^2 \exp\left[-ik_m z\right] \\ m = 1,\ 2,\ 3\end{gathered} \tag{1}$$

where k_m is the wavenumber in each region of the space, and t is the thickness of the membrane. Faces of the membrane are located at $z = 0$ and $z = t$ .Displacement vector u is calculated from the scalar potential j by:

$$u_m = grad\, \boldsymbol{j}_m \tag{2}$$

Stress (s) is calculated from the constitutive equations in each region of the space.

$$s^m_{33} = c^m_{33} \frac{\partial u^m_3}{\partial z}, \quad \mathrm{m} = 1, 2, 3 \tag{3}$$

where c^m_{ij} are the elastic constants of space region m. Stress and displacement must be continuous across membrane surfaces ($z = 0$, $z = t$). These boundary conditions along with Eqs.(1)-(3) provide a linear system of four equations that can be analitically solved for the coefficients $\boldsymbol{j}^i_m$. From these coefficients, displacements, stress, and energy flux in any point of the space can be derived. The transmission coefficient (T) is defined as the ratio of transmitted to incident energy fluxes. A simple analytical expresion for T is obtained:

$$T = \frac{4Z_3 \left(Z_2 Z_3\right)^2}{Z_1 \left[\left(Z_1 Z_2 + Z_3 Z_2\right)^2 \cos^2 \tilde{k}_l t + \left(Z_2^2 + Z_1 Z_3\right)^2 \sin^2 \tilde{k}_l t \right]} \tag{4}$$

where t is the thickness of the membrane, $\tilde{k}_l = k_l - i\boldsymbol{a}_l = \boldsymbol{w}/c_l - i\boldsymbol{a}_l$, where k_l is the wave vector, $\boldsymbol{a}_l$ the longitudinal wave attenuation, c_l the longitudinal phase-velocity, and $\boldsymbol{w}$ is the angular frequency. Z is the specific acoustic impedance, the subindex 1,2 and 3 refers to media 1, membrane filter, and 3 respectively.

The employed technique to characterise the membranes is based on experimental measurement and theoretical calculation of the transmission coefficient of ultrasonic waves through membranes. This is done for the frequency range where one or several resonances of the membrane appear. Fitting calculated values of T from equation (4) to measured ones provides the velocity of sound in the membrane, the attenuation of sound in the membrane, and the density of the membrane.

EXPERIMENTAL SET-UP.

For the experimental work two pairs of specially designed air-coupled piezoelectric transducers were used. They provide enough sensitivity for air-coupled operation and efficient transmission through membranes. They have an operation frequency band that permits the observation of, at least, one resonance for each membranes (this is the frequency range 0.3-2.5 MHz). These transducers are described in detail in Refs. [14]-[16]. Figure 1 shows the scheme of the experimental set-up.

First, the signal received through the airgap without the membrane in between is digitized by the oscilloscope and transferred to the computer; its frequency spectrum is calculated (Fast Fourier Transform *FFT*). Then the membrane is put in between the transducers, parallel to transducers faces. The received signal through the airgap and the membrane is again recorded and *FFT* calculated. The Insertion Loss (*IL*) for the membrane is defined as $IL = 20 \log_{10} \left(A_{sample} / A_{ref} \right)$ where A_{sample} and A_{ref} are the amplitudes of the FFT (Fast Fourier Transform) of recorded waves with and without the membrane in between the transducers respectively. In addition, it can be demonstrated that in this case *IL* and *T* follow a simple relation: $A_{sample}/A_{ref} = |T|^{1/2}$.

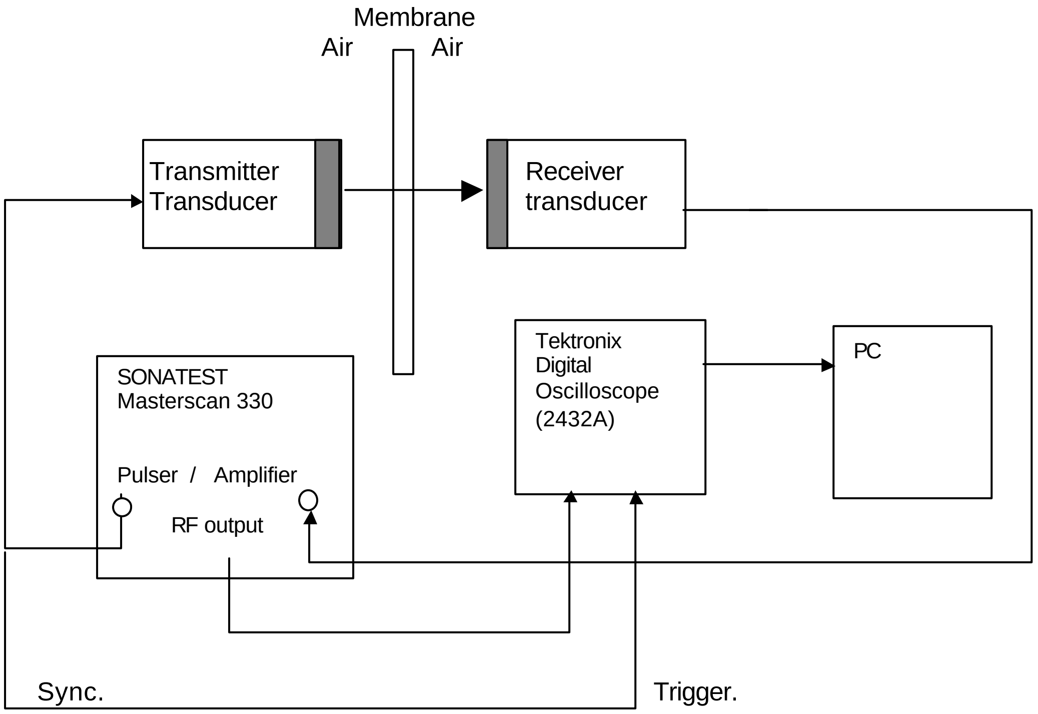

Figure 1. Scheme of the experimental set-up.

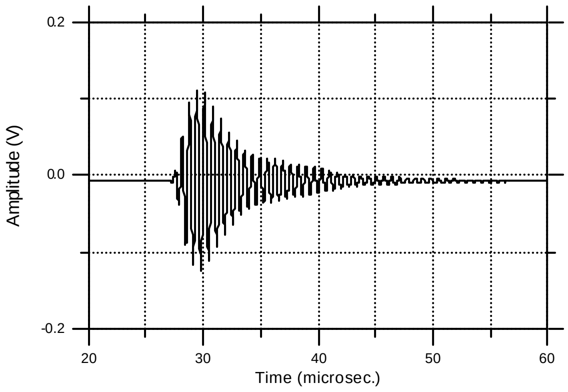

Figure 2. Transmitted signal through membrane P-11

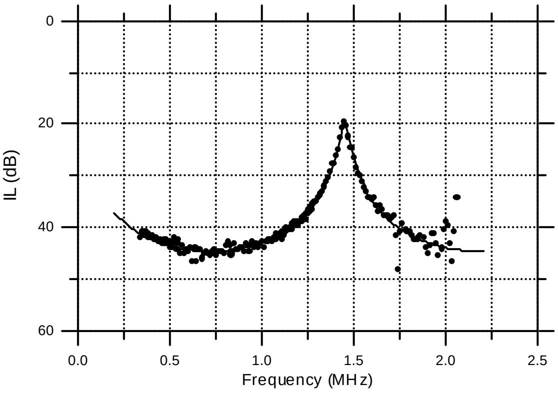

Figure 3. IL for membrane P-11

Figure 2 and 3 show the transmitted ultrasonic pulse and Insertion Loss (*IL*) for a polypropilene membrane (P-11). In figure 3, dots are experimental measurements; solid line is the theoretical prediction obtained from Eq. 4.

Experimental errors are ± 5 KHz and ± 5 µm for the resonant frequency and the membrane thickness respectively. This lead to an uncertainty about 5% and 9% for the determination of velocity and attenuation respectively.

RESULTS.

Table II shows the obtained results for the membranes listed on table I. Thickness of each membrane where independently measured.

Table II. Experimental results.

Membrane code	Density (Kg/m^3).	Velocity (m/s)	Attenuation per wavelength
P-11	230	362.5	0.531
P-12	270	377	0.439
P-2	500	515	0.322
P-3	450	850	0.453
M-11	720	670	0.618
M-12	650	645	0.616
M-13	800	750	0.441
M-2		60	0.600
M-31	700	910	0.200
M-32	700	650	0.229
M-33	440	404	0.202
M-34	370	281	0.216
M-35	370	237	0.212
M-36	490	222	0.249
M-37	470	242	0.198
M-38	460	226	0.249
W-11	360	288	0.195
W-12	440	440	0.209
W-13	470	506	0.206
W-14	520	508	0.222

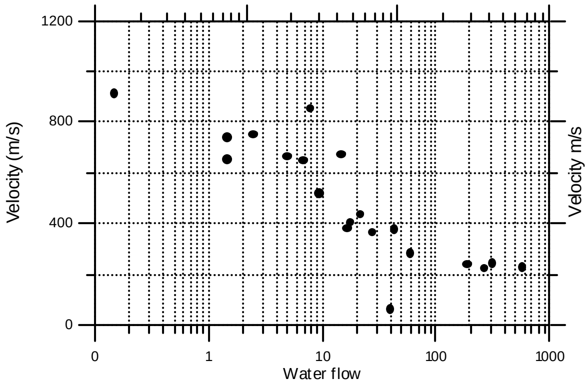

Figure 4. Velocity versus water flow

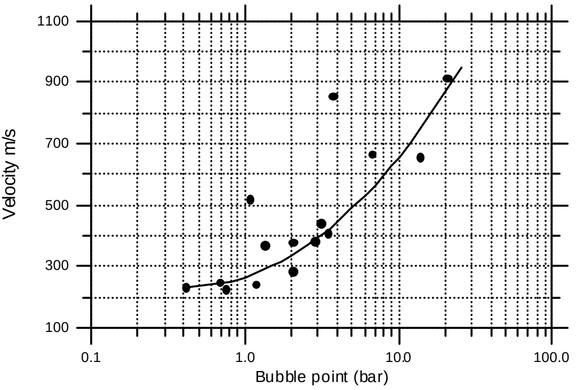

Figure 5. Velocity versus bubble point

Figure 4 shows the plot of the measured velocity of ultrasonic waves versus water flow (mL/min/cm^2 at 0.7 bar). Although data from different membranes made of different materials and by different manufacturers are ploted together, they all seem to follow a common empirical law relating velocity of sound in the membrane and water flow (or flux resistivity). Velocity changes between two bounds. An upper bound, about 900 m/s, for values of water flow approaching to zero, and a lower bound, about 220 m/s, for samples having very high values of water flow. The major sensitivity of the velocity of sound in the membrane to changes of the water flow are obtained for the range 1-100 (mL/min/cm^2 @ 0.7 bar). Figure 5 shows the plot of the measured velocity of ultrasonic waves versus bubble point provided by the manufacturers The close relation between bubble point and the velocity of ultrasonic waves in the membrane sugggests that this technique can be used as an alternative or complementary technique to bubble point tests. Concerning attenuation, for cellulose (codes M-3x and W-1x) membranes attenuation per wavelength is independent of pore size, bubble point, and water flow. For other membranes results are not yet determining. In addition, it is well knonw that attenuation is very sensitive to membrane fouling, wetting or damage, therefore it can be used determine the status of a membrane regardless of the grade.

CONCLUSIONS.

A method to characterize porous membranes has been presented. It is based on exciting thickness resonances in the membrane and sensing them. To this end airborne ultrasonic signals generated and received by air-coupled piezoelectric transducers were used. Results are obtained in an easy and straightforward way. The technique was applied to 20 different membranes. In all cases, the technique is applied successfully and provide a measurement of density and velocity and attenuation of ultrasonic waves in the membrane. These experimental results are compared with other properties of the membranes that are provided by manufacturers; they are pore size, water flow, and bubble point. For most cases, attenuation per wavelenght is independent of pore size, water flow, and bubble point. On the contrary, velocity shows a clear correlation with all these factors.; therefore, the use of these two parameters (velocity and attenuation) is a powerful technique to study membrane filters. In particular, this technique could be useful to membrane characterization, quality control of membranes, filter integrity tests, on-line assessment of the integrity, fouling, and performance of membranes. Further work is neccesary to determine the possibility to use this technique for different experimental and real operation conditions. In addition, some work is still neccesary to stablish the theoretical background for the observed relation between ultrasonic and filtration properties of a filter membrane.

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