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ANALYSIS OF ULTRASONIC TECHNIQUES FOR THE CHARACTERIZATION OF MICROFILTRATION POLYMERIC MEMBRANES

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ABSTRACT

The use of polymeric membranes is extremely important in several industries such as nuclear, biotechnology, chemical and pharmaceutical. In the nuclear area, for instance, systems based on membrane separation technologies are currently being used in the treatment of radioactive liquid effluent, and new technologies using membranes are being developed at a great rate. The knowledge of the physical characteristics of these membranes, such as, pore size and the pore size distribution, is very important to the membranes separation processes. Only after these characteristics are known is it possible to determine the type and to choose a particular membrane for a specific application. In this work, two ultrasonic non destructive techniques were used to determine the porosity of membranes: pulse echo and transmission. A 25 MHz immersion transducer was used. Ultrasonic signals were acquired, for both techniques, after the ultrasonic waves passed through a microfiltration polymeric membrane of pore size of 0.45 μm and thickness of 180 μm. After the emitted ultrasonic signal crossed the membrane, the received signal brought several information on the influence of the membrane porosity in the standard signal of the ultrasonic wave. The ultrasonic signals were acquired in the time domain and changed to the frequency domain by application of the Fourier Fast Transform (FFT), thus generating the material frequency spectrum. For the pulse echo technique, the ultrasonic spectrum frequency changed after the ultrasonic wave crossed the membrane. With the transmission technique there was only a displacement of the ultrasonic signal at the time domain.

1. INTRODUCTION

Membrane separation processes have obtained important recognition as a viable and safe separation technique. A membrane is used as a barrier to separate two phases, fully or partially restricting the passage of one or several species present in the phases. Normally, the characterization of a membrane is done by means of the determination of its transportation properties (permeability and selectivity), morphological characteristics, and physical-chemical properties [1].

Knowing the size of the membrane's pore is of great utility in order to define its applicability. There are several techniques to measure a pore's size, as well as the pore size distribution in a membrane. However, most of these techniques are either destructive, the analysis is carried out based on a sample, or high-cost equipment is used. The development of a technique which allows the evaluation of membranes in line, in a fast, low-cost, non-destructive manner, such as the ultrasonic one, is very interesting.

Several characterization methods for the membrane pores have been reviewed by Nakao [2]: The method of electronic microscopy observation directly characterizes the membrane pore's structure. The bubble point method, which is based on the measurement of the necessary pressure to make a gas flow through a membrane which pores are filled with a liquid. This method can measure active pores and the pore size distribution when the pressure is increased. The thermoporometry, in which the temperature of the liquid solidification and/or the continuous melting is lower in smaller pores, thus measuring the freezing and/or melting Thermodiagram, so that the pore's size and distribution can be determined. The last reviewed method is the one based on the molecular transportation through a membrane.

Non-destructive essays are largely used in modern industry for the characterization of materials (grain's and pore's sizes, inclusions, among others) and in the detection of discontinuities in their structure (small superficial flaws, presence of cracks, and other physical interruptions).

Ramaswamy et al. [3] used an Ultrasonic Frequency Domain Reflectometry technique (UFDR) in which they observed that with the increase in the pore's size, there is a significant increase in the attenuation of the frequency. The group also used a simple-model Artificial Neural Network in order to predict the size of PVDF and MCE membrane pores, which pores are in the range between 0.1 μm and 0.6 μm, based on the amplitude of the signal of the ultrasonic wave.

The ultrasound signal is generated by exciting a piezoelectric crystal of a transducer by means of a difference in the applied potential. In general, a transducer is a device which converts one kind of energy into another. Ultrasonic transducers convert electric energy into mechanic energy and vice-versa. Since the emitted ultrasound signal crosses the membrane, the received signal brings with it information about the membrane's influence in the pattern of the ultrasonic wave. Thus, by analyzing the characteristics of the received ultrasound wave, it is possible to obtain information about the material which is under investigation. The basic measures performed in the ultrasound signals are: signal amplitude and signal's elapsed time. In general, the speed of the sound in an environment depends on the frequency of the ultrasonic pulse [4].

The wave's propagation velocity is given by:

$$V = \lambda . f \tag{1}$$

where f is the frequency and X is the wavelength [5].

One of the factors that govern the behavior of ultrasonic waves in a determined medium is the environment's characteristic acoustic impediment, which can be described by:

$$z = V . \rho \tag{2}$$

being v the wave's propagation speed defined in equation 1 and X the medium's density. The acoustic impediment in water is 1.5x106 Kg/m².

When the ultrasonic wave crosses surfaces with different acoustic impediment, any of the following phenomena can occur: reflection, refraction, diffraction, and mirroring. The greater the difference of impediment between two mediums, the greater the wave transmission will be. When the impediment of the medium of the incident wave is equal to the impediment of the medium in which the wave is transmitted, there is no reflection of the wave, i. e., the whole wave is transmitted [6].

In immersion techniques, the sample is immersed in water during the test. The water acts as a coupler in order to transfer the transducer's mechanic energy into the sample and vice-versa.

The pulse echo ultrasound technique is the most used one, due to its simplicity and efficiency. This technique involves the detection of echoes produced by the reflection of the ultrasonic pulse in a discontinuity present in the material or by the interface of a proof body. Only one transducer is used to emit the ultrasonic pulse and receive the reflected echo. When the emitted pulse encounters a reflecting surface, a part or the whole of the energy is reflected, returning to the transducer. In the direct transmission technique, on the other hand, two transducers are used, one as a transmitter, and the other one as a receiver. The ultrasonic pulse emitted by the first transducer crosses the sample, which is placed in the middle, and is captured by the second transducer.

The aim of this work is to verify whether the ultrasonic waves emitted by an immersion transducer of 25 MHz interact with the microporous membrane of 0.45 μm pore size and 180 μm width, altering the initial pulse which was obtained in water. It also aims to verify which technique (echo pulse or transmission) presents better results.

2. MATERIALS AND METHODS

2.1. Samples

The membrane used in the experiment (purchased from Milipore tm) is a biologically inert mixture of acetate and nitrate of cellulose, which are polymers resulting from the chemical modification of other polymers. The changes in the molecular weight, in solubility, and in electrical and mechanical resistance allow a great diversification in its application [7]. These membranes are used for analytical and research purposes.

Some of the membrane's specifications were provided by the producer: 47mm-diameter white filter, pore size of 0.45μm, thickness of 180 μm (much smaller than the ones usually analyzed by ultrasonic techniques), 79% porosity, 1.51 refraction index, hydrophilic wetting capacity, soft surface, maximum operation temperature of 75° C.

Figure 1 shows the membrane's microscopic structure, obtained in the Scanning Electronic Microscope of the Macromolecules Institute of the Federal University of Rio de Janeiro.

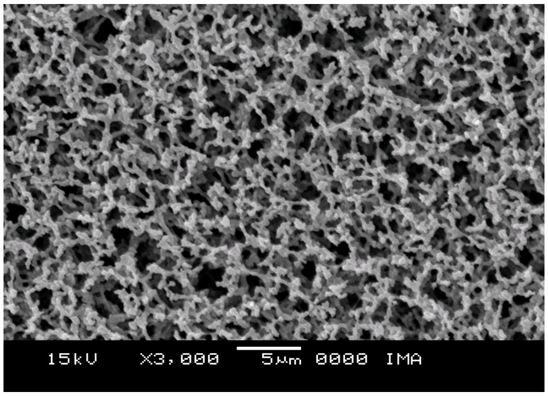

Figure 1. Picture of the membrane obtained by SEM.

2.2 Experimental apparatus

The following equipment was used: an EXPLORER II ultrasonic pulse generator and receptor device (by MATEC Instruments); an IBM-PC; two longitudinal waves immersion transducers; an emitter and a receiver, with 25 MHz frequency (Panametrics Model V324, nominal size 0.25in, minimum target focus of 0.50 in and maximum of 5.25 in); a thermostat; and an immersion tank (Figure 2).

These immersion transducers offer the advantage of uniform coupling between the transducer and the sample. They are made of 303 corrosion-resistant, stainless steel, with chrome-plated bronze connectors. The transducers can be used for the acquisition of data by pulse echo and by transmission. Such control is made in the EXPLORER II.

EXPLORER II is a computer with a conventional structure (mother-board, processor, memory etc.). It works with a 233 MHz Intel Pentium II processor and 64 Mb of RAM memory. The operational system is Windows 95, and the software used for the acquisition of data is MUIS 32, also from MATEC Instruments. It has two mother boards: one is a TB1000 by MATEC Instruments, which is responsible for the generation of the ultrasonic signal; and the other one is a STR8100D by SONIX, which performs the acquisition of the signal. Both of them have an ISA bus.

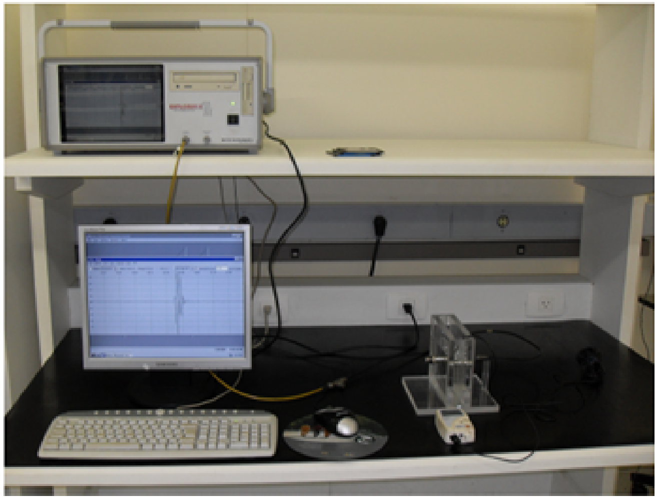

Figure 2. Experimental Apparatus

2.3. Immersion tank

The immersion tank (Figures 3a and 3b) was conceived and built by the technicians of the Ultrasound Laboratory at the IEN. It has two entrances for the transducers (an emitter and a receiver) which are evenly aligned, with a 5 mm distance between them. It is necessary to highlight the importance of the alignment of the transducers, so that it is possible to obtain the range of membrane frequencies. Any change in the angle can alter the range of the received wave.

The tank allows the analysis of four samples of membranes, by means of the insertion of a sample compartment (Figure 3c), which is composed of two acrylic plates. The membranes are placed between the plates and these are fixed with screws. It is possible to analyze two points of a same membrane, by means of the lateral height setting.

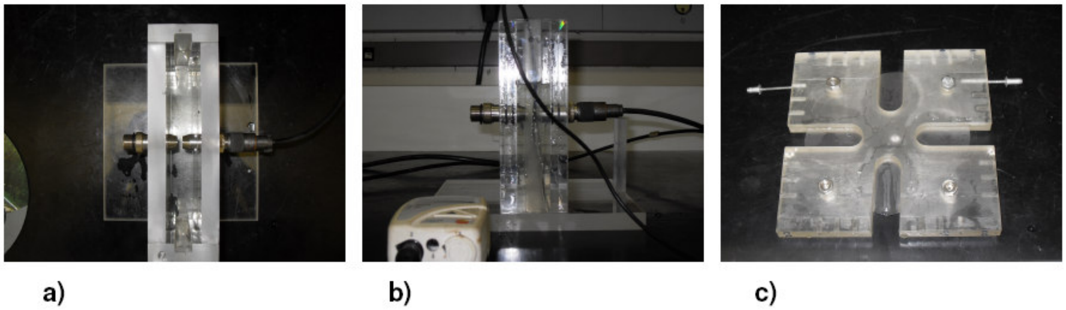

Figure 3. Immersion Tank: a) upper view, b) lateral view, and c) sample compartment

2.4. Experimental procedure

EXPLORE II was used only for the generation and acquisition of the ultrasonic pulse. Another computer was used for the analysis of the data, which has a 3.06 GHz Intel Pentium IV Dual processor, with 1 GHz of RAM memory.

Software MUIS32 has a FFT option of the ultrasonic pulse in real time, allowing the visualization of the pulse in the time domain and in the frequency domain simultaneously.

Ten signal measures were carried out in (distilled) water in the time domain (each signal was discretized in 512 points) and in the frequency domain (each signal was discretized in 256 points).

Then, the membranes were placed in the sample compartment and inserted between the transducers into the immersion tank. After the ultrasonic wave interacted with the membrane, ten more signals were collected in the time domain, and ten additional ones in the frequency domain.

The signals were collected with the pulse echo and transmission techniques, with measures taken in a single point of the membrane. The temperature of the water during the experiment was 21° C (± 0.2° C).

The software generates a file for each one of the signals in the acquired time and frequency spectra. The files are in .DAT format, and the information is saved in the “only text” format in columns that are separated by spaces. These measures were transferred to an electronic spreadsheet where the averages were calculated and the graphs bellow were created.

3. RESULTS AND DISCUSSIONS

The results of the pulse echo technique are shown in Figure 4. This figure presents results of the ultrasonic sound when it passes through the water both in the time and in the frequency domains (Figures 4a and 4c), and after crossing the membrane (figures 4b and 4d).

Figure 5 shows the results of the transmission technique. This figure presents results of the ultrasonic signal in the domains of both time and frequency when it passes through water (Figures 5a and 5c), and after it crosses the membrane (Figures 5b and 5d).

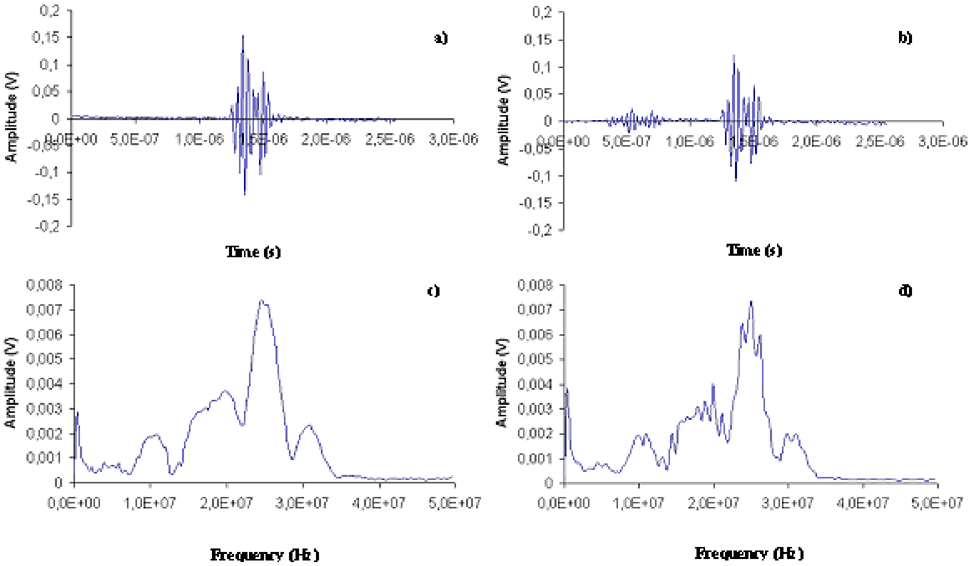

Figure 4. Pulse echo technique: a) signal in the time domain in water; b) signal in the time domain after the placement of the membrane; c) spectrum of frequency in water; d) spectrum of frequency after the placement of the membrane.

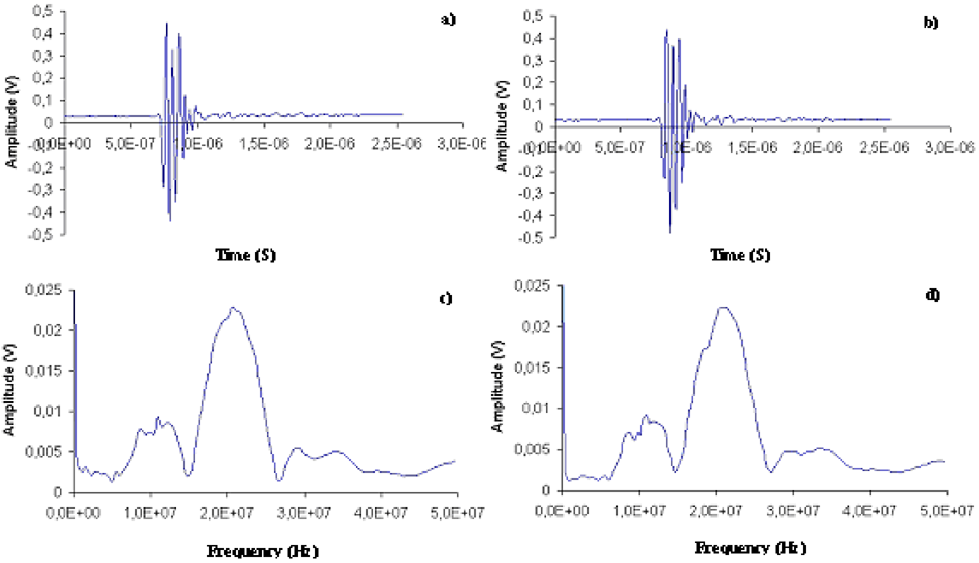

Figure 5. Transmission technique: a) signal in the time domain in water; b) signal in time domain after the placement of the membrane; c) spectrum of frequency in water; d) spectrum of frequency after the placement of the membrane.

In order to better evaluate these results, the signals were superposed in the time and frequency domains for each one of the analyzed techniques. Figure 6a shows the superposition of the signals in the time domain for the pulse echo technique before and after the placement of the membrane. Figure 6b shows the same superposition for the transmission technique.

It is possible to observe that in the pulse echo technique, after the ultrasonic wave crosses the membrane, a signal that is correspondent to it appears in the time range between 0.37 us and 0.79 us, and a signal in the time range between 1.24 us and 1.74 us, which is the same result obtained in water. However, it has a tiny attenuation in the amplitude, while in the transmission technique, there is only a displacement of the signal in time, which in the water is in the time range between 0.70 us and 1.10 us, and after it crosses the membrane the signal suffers a delay, appearing in the time range between 0.76 us and 1.16 us.

Figure 6c shows the superposition of the frequency spectra for the pulse echo technique, both in water and after the ultrasonic wave crosses the membrane. Figure 6d shows the same superposition for the transmission technique. In the pulse echo technique, the amplitudes of several frequencies are altered, which does not happen in the transmission technique, where the signal of the spectrum of frequencies in water is almost the same as the spectrum after the ultrasonic wave crosses the membrane.

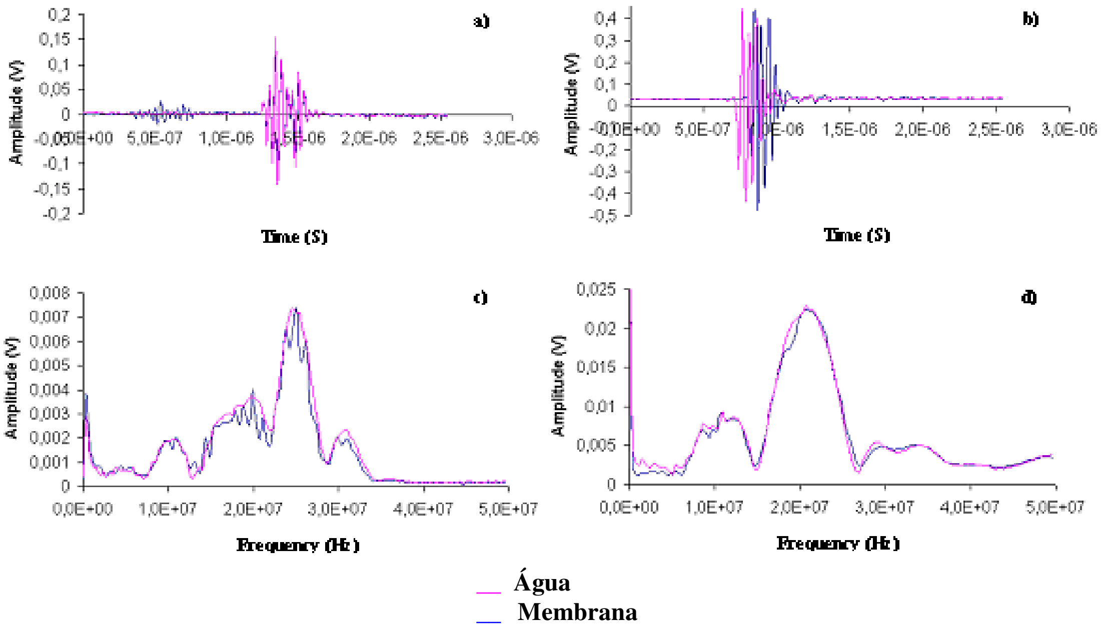

Figure 6. Comparison between the techniques: a) and c) pulse echo technique; b) and d) transmission technique.

Based on these preliminary results, it was possible to measure variations in the time and in the frequency of a microfiltration membrane with pores of 0.45 um of size and 180 um of width, using non-destructive techniques and an experimental apparatus of accessible cost. In order to verify the changes in the spectrum of frequencies, the most efficient technique was the pulse echo one, in which significant observations are noted.

Further research will be carried out with isoporous microfiltration membranes with different pore sizes, in order to study the interaction of the ultrasonic pulse in the frequency domain in relation to different pore sizes, and the pore size distribution, with the aim to enable the use of this ultrasonic technique in the determination of the pore sizes of polymeric membranes.

4. CONCLUSIONS

Based on the results, it is possible to conclude that a 25 MHz immersion transducer can detect interactions of a microporous membrane in the pattern of the ultrasonic wave. It is also possible to conclude that the pulse echo technique presented better results.

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