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Ultrasonic detection of defects in highly porous polymeric membranes

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Microfiltration (MF) and ultrafiltration (UF) membranes are used extensively for sterile filtration and virus retention applications that necessitate stringent defect control during their manufacture. Current protocols used to detect structural defects during membrane fabrication are operator-dependent, resulting in a slow and subjective process with lowered yields. Moreover, several types of membrane defects are usually not identified until after the final membrane cartridge is assembled via expensive post-processing. We describe the use of an ultrasonic technique to non-invasively detect a variety of defects in a polymeric membrane including pinholes (fully and partially penetrating), sub-surface (macrovoids) and surface (scratches) defects. Ultrasonic techniques can be used to detect both through-thickness and partial penetration defects in polymeric membranes. Ultrasonic reflectometry (UR) has been employed to successfully detect defects ranging in size from ~ 600 µm for relatively large manually generated pinholes to much smaller macrovoid defects (~30 µm) created during membrane formation via the phase-inversion process. The experimental demonstration of the detectability of these defects is particularly important given the complexity of wave propagation in highly porous materials with interconnected pores.

Keywords: Ultrasonic Reflectometry (UR), membrane characterisation, polymeric membrane morphology, waves in porous materials, defect detection.

Introduction

Membranes are used extensively for a wide variety of commercial separation applications including those in the food processing, water purification and pharmaceutical industries. In general, a membrane acts as a barrier phase between two other phases allowing selective transport of certain components between the two phases[1]. Currently, polymeric membranes are most commonly employed for commercial applications due to several significant advantages including high selectivity and flux as well as flexibility of form that enables high surface area to packaging volume ratios to be obtained. The significance of this application is demonstrated by the size of the industry associated with membrane separations. The combined US market for membranes used in separations and non-separating applications is estimated to grow from $5 billion dollars in 2004 to $6.9 billion in 2009[2].

The most common method for fabricating polymeric membranes is via phase inversion whereby a homogeneous polymer solution is inverted into a two-phase system by varying composition or temperature. This results in a polymer-continuous matrix with a trapped solvent-rich liquid, which is then extracted to obtain a porous structure. In certain cases, membranes may also be cast on a non-woven support. Polymeric membranes may be classified as symmetric or asymmetric, where the former have a uniform structure through the cross-section whereas the latter typically have a dense skin on one surface. In addition, a membrane with uniform pores through the cross-section is termed isotropic and those with a pore-size gradient are termed anisotropic[3]. Membranes are further classified according to the size of the entities they are capable of excluding, ranging from micofiltration (~ 0.5 µm) to hyperfiltration (~ 0.5 nm). Typical total porosity of the polymeric membrane ranges from 50% to 90% with a membrane thickness on the order of 100 µm.

Integrity and uniformity of membrane pore structure are crucial for optimal membrane performance. Macroscopic and microscopic defects that often occur during membrane formation and manufacture can adversely affect membrane retention. Of particular concern is that polymeric membranes are increasingly used in sterile filtration and virus retention applications where structural defects that compromise integrity are unacceptable. Current industrial methods utilised for the detection of defects in membranes are manual and operator-dependent resulting in lowered yields. The most common detection methods involve visual examination using a light box to locate defect-containing regions and bubble-point measurements on the membrane samples at appropriate points in the fabrication process. These methods are quite subjective and often lead to unacceptable yield losses and increased membrane cost. Moreover, final testing of membrane modules to confirm their integrity occurs after expensive post-processing steps. Clearly, there exists a need for techniques that will enable membrane manufacturers to detect defects during the fabrication process, preferably in a timely and non-invasive fashion.

A real-time, non-invasive and non-destructive technique that shows considerable promise for defect detection is the use of ultrasonic reflectometry (UR). Over the last 10 years, UR has been successfully employed to study several membrane phenomena including membrane formation[4,5], membrane compaction[6-9] and membrane fouling[10-19]. More recently, UR has been utilised for characterising membrane pore structure[20]. In this paper we demonstrate the use of UR to facilitate the real-time, non-invasive identification of defects occurring during membrane fabrication or post-processing. Of particular importance, UR has the ability to distinguish between membrane defects that affect membrane performance and those defects (typically in the support layer) that are quite harmless.

In order to best demonstrate the utility of the technique, polymeric membrane defects have been classified into two types:

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fully penetrating (pinholes) and subsurface defects including partially penetrating and macrovoid defects. The UR technique has been tested on defects with sizes ranging from relatively large manually generated pinholes (~ 600 μm) to much smaller macrovoid defects (~ 30 μm) generated during the phase-inversion process. Finally, the technique has been applied to defects (pinhole and surface scratch defects) occurring in the active layer of commercial supported ultrafiltration (UF) membranes. Because of the complexity of describing the propagation of waves in highly porous materials, and the lack of material properties in a partially cross-linked polymer, the demonstration of defect detection in this paper is solely experimental. Techniques to add modelling to the initiative are currently underway.

Materials and methods

The theory of ultrasonic characterisation and the principles underlying the UR technique are described in detail in an earlier publication[21]. A schematic of the UR set-up used for this work is shown in Figure 1. In UR, a single piezoelectric ultrasonic transducer is used to generate the ultrasonic signal and also detect the waves reflected from the membrane. In this case, a focused immersion ultrasonic transducer is employed with water as the contact medium for good signal strength. The ultrasonic wave generated by the transducer passes through the water and is reflected by the membrane sample at the top (reflection A) and bottom (reflection B) interfaces due to the difference in acoustic impedance of water and the membrane. Depending upon the peak frequency of the transducer, which determines the duration of the signal in the time domain, the two reflections may overlap each other or be clearly separated in time. A defect in the wave path results in a distortion of the signal and can be used to locate its presence. The amplitude of the signal reflected from the front surface of the membrane is characteristic of that surface and will evidence changes in the case of defects that affect the front surface. On the other hand, the signal reflected from the back surface has travelled through the membrane cross-section twice and is representative of the internal structure (pore size and overall porosity) of the membrane as well as the roughness of the back surface of the membrane. Consequently, subsurface defects require the analysis of the signal from the back surface.

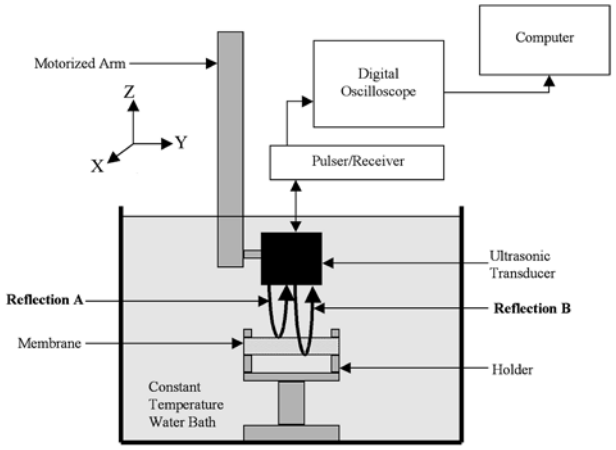

Figure 1. Schematic representation of the UTDR characterisation system

UR system

In this study, a focused ultrasonic transducer with a peak frequency of 90 MHz (Panametrics, Inc., Model No: V3512) and an approximate beam diameter of 75 μm was used. The transducer used has a -20 dB waveform duration of approximately 0.025 μs and a -6 dB bandwidth of approximately 75 MHz. For reference this gives the wavelength at the nominal centre frequency in water of 16 μm and of approximately 25 μm in polymers of the type used in this work. The transducer was attached to a Velmex 3-axis Unislide (Model No. MB4018Q1J) motorised arm via a Newport (Model No. LP-1) 5-way positioning holder that enabled membrane scans. Membrane samples were immersed in a controlled temperature water bath (28.4ºC) for the experiments. Membrane samples (2" diameter) were pre-wet with distilled water, and the water bath was allowed to equilibrate at room temperature for 24 h to eliminate gas bubbles that could interfere with the measurements. The transducer was rastered over the membrane, and ultrasonic responses were obtained from points on a predetermined grid with uniform spacing between the grid points. At each point, the mean value from 100 scans was obtained which required 2 s of processing time. The scanning, data acquisition and data analysis were automated via a Labview® program.

Pinholes

Pinhole defects were manually inserted into commercial microporous polyvinylidenefluoride (PVDF) membranes by puncturing the membranes with a sharp-pointed punch. The defects fully penetrated the cross-section of the membrane (~130-150 μm thickness) and were approximately cylindrical in shape. A surface scanning electron micrograph (SEM) of a PVDF membrane with pinholes (150-180 μm diameter) is shown in Figure 2.

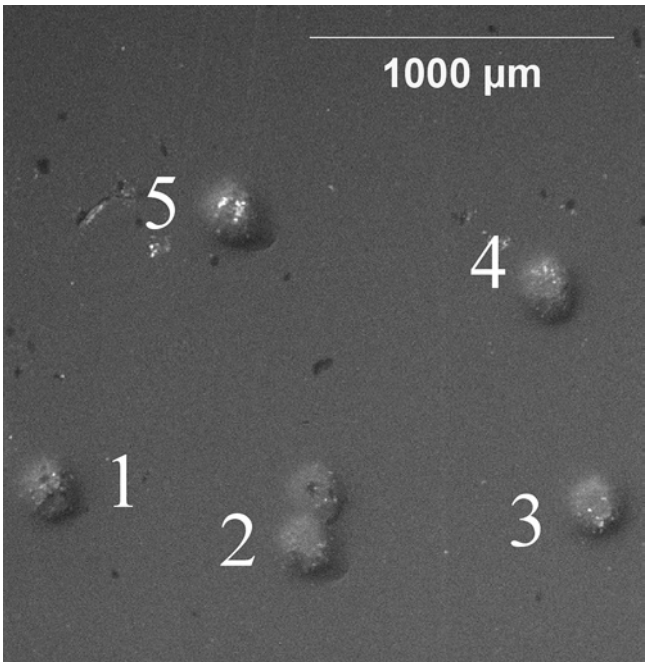

Figure 2. SEM micrograph of a 0.1 μm PVDF membrane with five manually inserted pinholes

The defect detection capabilities of the UR system depend on several parameters including the beam diameter of the ultrasonic signal, defect size and sampling frequency across the membrane surface. In the case of pinhole defects that have diameters on the order of the beam diameter, the detection is relatively straightforward. When the acoustic beam strikes such a defect, it passes through the membrane completely or evidences significant scattering resulting in a weak reflected signal. In order to detect the presence of such a defect, the inverse of the peak amplitude of the reflected signal in the time domain or the frequency domain is plotted *versus* the grid location. The inverse amplitude serves to smooth out small local variations in the acoustic response while magnifying the large signal loss caused by scattering.

Subsurface defects

A laser-milling technique was used to generate partially penetrating defects in the PVDF membranes. Due to the high degree of variability in the technique, it was not possible to closely control the diameter or the penetration depth of the defects. Figure 3 shows a representative surface SEM micrograph of a PVDF membrane containing partially penetrating defects generated via the laser-milling method. In general, the defect diameter was between 100-300 µm and the penetration depth increased with increasing diameter.

The presence of defects below the membrane front-surface can be detected by the analysis of the signal reflected from the back surface. The signal reflected from the front surface remains unaltered in the presence of subsurface defects. In the vicinity of the defect, the wave approaching the back surface is scattered and results in a lowered amplitude of the reflected wave.

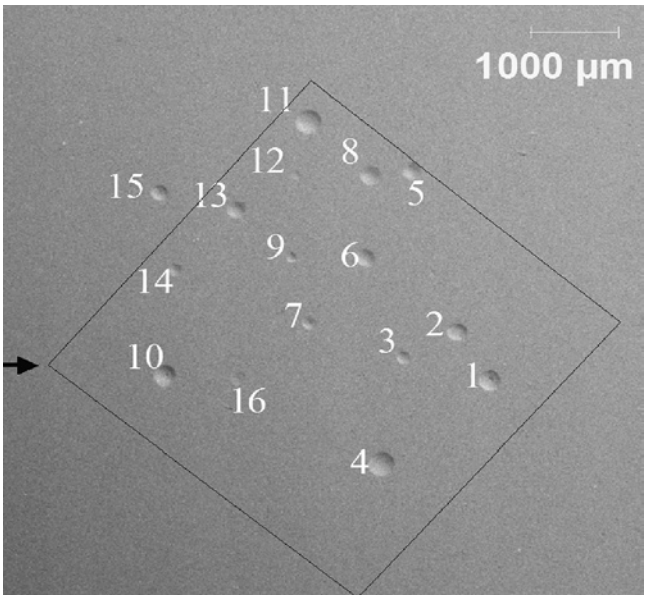

Figure 3. Top-surface SEM micrograph of a microporous PVDF membrane exhibiting a field of partially penetrating pinhole defects generated via laser milling. The black box represents the UTDR scan area and the arrow indicates the origin for the scan

Macrovoids

Macrovoids are oversized often teardrop-shaped pores that form in membranes prepared via phase inversion. Macrovoids are generally undesirable since they result in a loss of selectivity and compromise mechanical strength. Cellulose acetate (CA) membranes were fabricated in the laboratory using the procedure described by Konagurthu *et al*[22]. Since it is difficult to control the exact size and location of macrovoids in a membrane, CA membranes with and without macrovoids were generated and analysed separately. The membranes were transferred to a water bath immediately after phase-separation to prevent drying and contraction. This prevented shrinkage artefacts and presented a relatively uniform surface for acoustic characterisation. The membranes had a thickness of approximately 70 µm when dry. Macrovoids penetrated to over 80% of the membrane thickness and had diameters ranging from 10-30 µm.

The detection of macrovoids poses a significant challenge due to their small size. Since macrovoids are sub-surface defects, their detection requires the analysis of the back-surface reflection. However, since there are no membrane formation techniques to generate macrovoid and macrovoid-free regions in a controlled manner in the same membrane sample, it is not possible to demonstrate the presence of individual macrovoids. Instead, the back-surface reflection from 25 different points on each sample of both membrane types was collected and compared in the frequency domain. Analysis of variance (ANOVA) was used to compare the signals from the macrovoid-containing and macrovoid-free CA membrane samples[22].

Defects in commercial membranes

Composite UF membrane samples containing commonly observed defects were obtained from a commercial membrane manufacturer. The asymmetric composite membrane consisted of an active layer (~100 µm thick) and a highly porous, non-woven fibre backing (200 µm thick). The active layer in turn was fabricated with a thin dense skin (<1 µm) and a microporous support layer whereby the two sublayers were formed from two different polymers. SEM micrographs of the cross-section of the UF membrane and surface views of the membrane defects are presented in Figure 4.

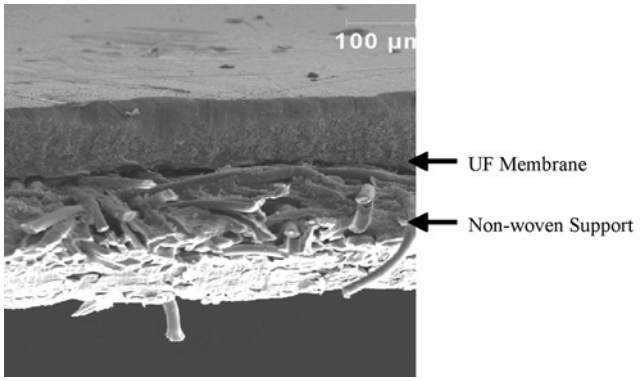

Figure 4. SEM micrograph showing a representative cross-section of a commercial composite ultrafiltration membrane composed of an active layer with dense and microporous sublayers atop a highly porous non-woven support

The 90 MHz transducer was used for these experiments with a grid spacing of 0.25 mm and a scan time of 2 s per point for an average of 100 sweeps per point. The highly non-uniform nature of the backing results in significant point-to-point variability in the reflected ultrasonic signal. In contrast, the membrane surface is relatively smooth and produces a uniform reflected signal. Since the overall thickness of the active layer is approximately 100 µm, it is possible to clearly separate and monitor the front-surface acoustic reflection. Since the defects of concern in the case of the UF membranes are those in the active layer as opposed to the backing, the front-surface reflection can be effectively used for their identification.

Results and discussion

Pinholes

Figures 5(a-c) are plots of the inverse of the peak amplitude in the time domain reflected from the membrane shown in Figure 2 *versus* the grid position as a function of grid spacings of 0.125 mm, 0.25 mm and 0.5 mm, respectively. Clearly, there is a decrease in the resolution of the technique as the grid size is increased from 0.125 mm to 0.25 mm. However, even at this lower resolution, every defect has been located. Upon further increase of the grid spacing to 0.5 mm, there is significant loss in detection efficiency with the detection of only one defect, which is the largest one in the set. Hence, the optimum grid spacing to detect defects of such size using a 90 MHz transducer is about 0.25 mm. This implies that in order to successfully detect every defect, the grid spacing would have to be less than or equal to the sum of the beam diameter

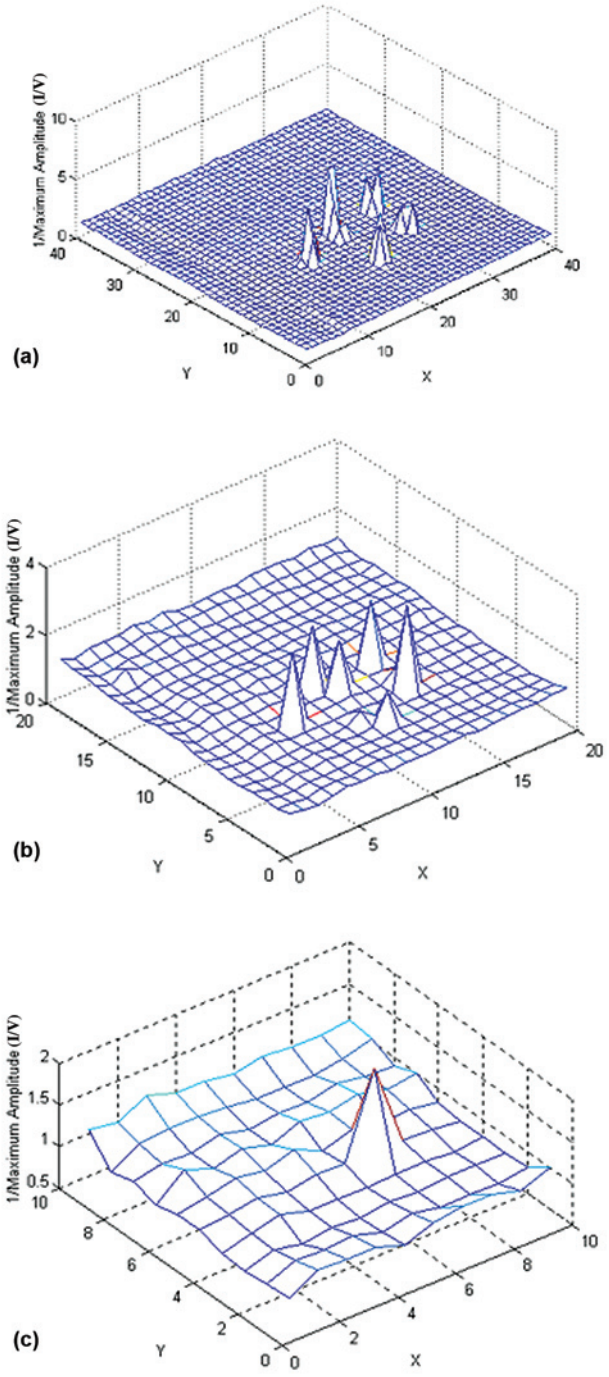

Figure 5. Plots of the inverse of the maximum amplitude in the time domain (90 MHz ultrasonic transducer) *versus* grid location for the membrane sample containing pinholes shown in Figure 2. The grid spacing is systematically varied: (a) 0.125 mm; (b) 0.25 mm and (c) 0.5 mm

(75 μm at 90 MHz peak frequency) and the estimated minimum defect size (150 μm). In the present case, use of this grid spacing would require approximately 15 min for a 25 mm^2 area of the membrane surface. Utilising the ever-growing speed of signalling and data acquisition, an array of transducers could be employed to scan a moving membrane with significant improvement in efficiency. This approach would enable application of this technique on-line during membrane production. However, successful commercial application of this technique is subject to advancements in ultrasonics hardware that would make high frequency transducer arrays economically viable.

Subsurface defects

As previously described, the detection of defects present below the front surface of the membrane requires the analysis of the signal reflected from the back surface of the membrane. This is best done by monitoring the amplitude of the back-surface signal. An ultrasonic scan of a membrane containing subsurface defects (Figure 3) is presented in Figure 6. The time-domain signal obtained from the membrane was split between the front and back surfaces, and the maximum in the second half of the signal was determined by averaging. The position of the signal was maintained constant throughout the experiment to ensure minimum variability in acquiring the back-surface reflection. A Labview® program was developed to acquire the time-domain signal from the oscilloscope and store the maximum amplitude from the back surface. The inverse of the peak amplitude of the signal reflected from the back surface of the membrane in the time domain using a 90 MHz transducer is plotted as a function of grid position using a grid spacing of 0.25 mm (Figure 6). This combination resulted in identifying 13 of the 15 defects in the 25 mm^2 scan area. The detection efficiency could be increased to 100% by using a finer grid spacing and additional signal averaging at every grid point at the cost of increasing the scan time.

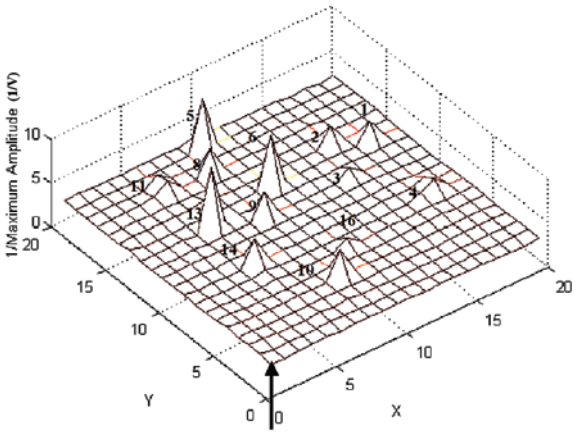

Figure 6. Plots of the inverse of the maximum amplitude in the time domain (90 MHz ultrasonic transducer) *versus* grid location for the membrane sample containing partially penetrating defects shown in Figure 3. The grid spacing is 0.25 mm

Macrovoids

The detection of macrovoid defects is more challenging than the cases studied above since the CA membranes used in the study were bath-cast in the laboratory resulting in greater variability and non-uniformity than typically observed in the commercial membrane samples. Nonetheless, a statistically significant difference in the ultrasonic responses can be obtained for macrovoid-free and macrovoid-containing CA membranes by using frequency-domain analysis that utilises the frequency-domain signal reflected from the back surface (Figure 7). Since the back-surface reflection has travelled through the entire membrane cross-section, it is more representative of the internal structure of the membranes and their differences. Clearly, for the membranes containing macrovoids, there is an increased attenuation of the signal at higher frequencies due to increased scattering as a result of the larger 'macropores'. At higher frequencies the signal attenuation will be too great for meaningful analysis and at lower frequencies, the wavelength is too large to detect any significant amplitude loss due to the macrovoid defects. Statistical analysis (ANOVA and a subsequent Tukey's test) was used to establish that there are significant differences in the mean values of the signal between the two sets of membranes in the frequency range from 40 to 60 MHz[23].

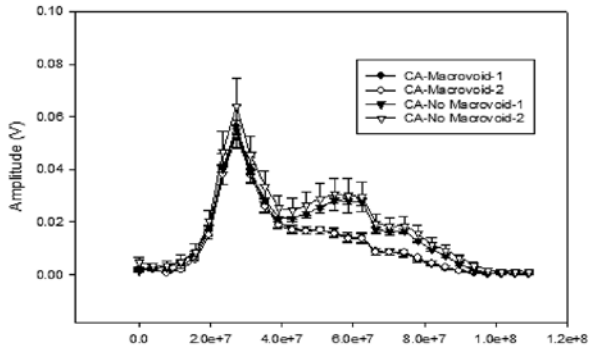

Figure 7. Frequency domain representation of the signal reflected from the back surface of cellulose acetate membranes with and without macrovoid defects

Defects in commercial membranes

The case studies of defect detection using manually generated defects discussed in the previous sections clearly suggest that the UR technique has significant capability for the detection of a broad range of pinhole and sub-surface defects in polymeric membranes. However, the final and most important goal of this part of the work is the detection of defects that are commonly observed during commercial membrane fabrication. For this purpose, defective membrane samples (cf. Section 2.5) were obtained from a commercial membrane manufacturer. Since the defects of concern are in the active layer of the membrane and not the support, it is necessary to selectively monitor the reflection from this active layer.

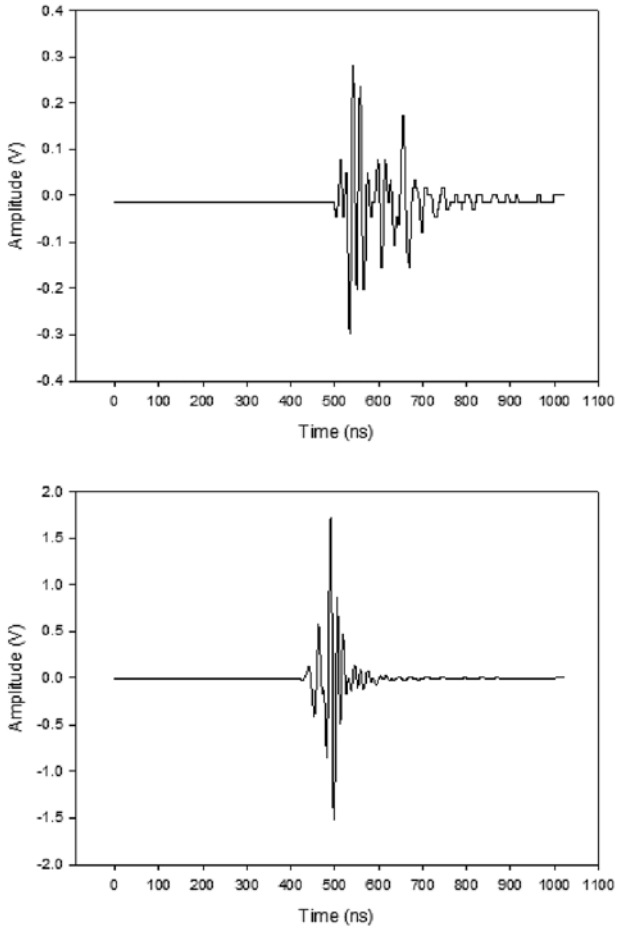

Figure 8. Time-domain ultrasonic reflection from two randomly selected points on a composite UF membrane (Figure 4) indicating the high point-to-point variability in the support material

By positioning the membrane such that the active layer faces the transducer and then monitoring the amplitude of the front-surface reflection, it is possible to eliminate contamination of the reflected signal due to the excessive variability in the support layer, which causes a highly non-uniform back-surface reflection.

Figure 8 compares the reflected signal from two randomly selected points on the non-woven fibre backing of the UF membrane (the active layer is removed). Hence, the data collection window in the oscilloscope was adjusted to contain the front-surface peak alone in the first half of the signal. A Labview® program was used to split the data and determine the maximum in the first half of the spectrum. This methodology was used to acquire the data, which was then plotted as the inverse of the maximum amplitude *versus* grid position as shown in Figure 9 for a membrane containing a pinhole (Figure 9(a)) and a 'scratch' (Figure 9(b)). The peak in the inverse of the amplitude reflected from the front surface of the membrane (Figure 9(a)) is a result of signal scattering at the pinhole defect that results in a weak reflection amplitude. Similarly, the series of peaks shown in Figure 9(b) are a result of the scratch defect on the surface. The presence of the scratch defect significantly diminishes the strength of the reflected signal received by the transducer due to a change in the direction of the reflected wave and scattering due to changes in surface roughness. SEM analysis indicated that the pinhole and scratch defects had size scales of 100 and 200 μm, respectively. These results indicate that the UR technique can be successfully used as a tool to characterise a variety of polymeric membrane defects commonly seen in industry in a range of membrane structures.

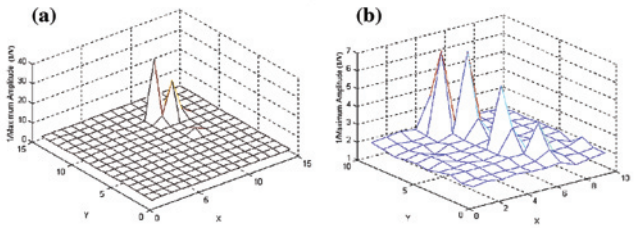

Figure 9. Ultrasonic scan of a composite commercial UF membrane with two different types of defects: (a) pinhole and (b) scratch

Conclusions

The UR technique has been successfully employed for the detection of a variety of defects in polymeric membranes. Clearly, by optimising the frequency, beam diameter, and grid spacing, the UR technique can be employed for the detection of a variety of defect types with size scales ranging from ~600 μm to a few microns.

The success of the technique with respect to defects commonly observed in commercial membranes is very encouraging and represents a significant improvement over current capabilities for defect detection in the polymeric membrane industry. The UR technique presents a more objective approach to the identification of defects in commercial membranes and has the potential to significantly improve yield and lower manufacturing costs. Obviously, the biggest advantage is the ability to employ the technique on-line during membrane fabrication for non-invasive defect detection. Although additional engineering is required for the development of an on-line system, immersion transducers and fabrication treatment tanks appear well matched for such system integration.

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References

1. H K Lonsdale, 'What is a membrane?' Journal of Membrane Science, Vol 43, pp 1-3, May 1989.
2. BCC Research Reports, 'Membrane technology: A new era', May 2005.
3. L J Zeman and A L Zydney, 'Microfiltration and ultrafiltration: principles and applications', Marcel Dekker, Inc, New York, pp 108-114, 1996.
4. A T Metters, 'Use of acoustic time-domain-reflectometry for real time measurement of polymeric thin film solidification', Master's thesis, University of Colorado, 1996.
5. W Kools, S Konagurthu, A R Greenberg, L J Bond, W B Krantz, T H van den Boomgaard and H Strathmann, 'Use of ultrasonic time-domain reflectometry for real-time measurement of thickness changes during evaporative casting of polymeric films', Journal of Applied Polymer Science, Vol 69, Iss. 10, pp 2013-2019, December 1998.
6. L J Bond, A R Greenberg, A P Mairal, G Loest, J H Brewster and W B Krantz, Review of Progress in Quantitative Nondestructive Evaluation, D O Thompson and D E Chimenti, (eds), Vol 14, Plenum Press, New York, pp 1167-1173, 1995.
7. R A Peterson, A R Greenberg, L J Bond and W B Krantz, 'Use of ultrasonic TDR for real-time noninvasive measurement of compressive strain during membrane compaction', Desalination, Vol 116, pp 115-122, September 1998.
8. V E Reinsch, A R Greenberg, S S Kelley, R Peterson and L J Bond, 'A new technique for the simultaneous, real-time measurement of membrane compaction and performance during exposure to high-pressure gas', Journal of Membrane Science, Vol 171, pp 217-228, June 2000.
9. P Aerts, A R Greenberg, R Leysen, W B Krantz, V E Reinsch and P A Jacobs, 'The influence of filler concentration on the compaction and filtration properties of Zirfon®-composite ultrafiltration membrane', Separation and Purification Technology, Vol 22-23, pp 663-669, March 2001.
10. A P Mairal, A R Greenberg, W B Krantz and L J Bond, 'Real-time measurement of inorganic fouling of RO desalination membranes using ultrasonic time-domain reflectometry', Journal of Membrane Science, Vol 159, pp 185-196, July 1999.
11. A P Mairal, A R Greenberg and W B Krantz, 'Investigation of membrane fouling and cleaning using ultrasonic time-domain reflectometry', Desalination, Vol 130, pp 45-60, September 2000.
12. A R Greenberg and W B Krantz, Fluid/Particle Separation Journal, Vol 15, Iss 1, pp 43-49, 2003.
13. Zh-X Zhang, A R Greenberg, W B Krantz and G-Y Chai, 'Study of membrane fouling and cleaning in spiral wound modules using ultrasonic time-domain reflectometry', New Insights into Membrane Science and Technology: Polymeric, Inorganic and Biofunctional Membranes, A A Butterfield and D Bhattacharyya (eds.), Elsevier, Amsterdam, pp 65-88, 2003.
14. R D Sanderson, J X Li, L J Koen and L Lorenzen, 'Ultrasonic time-domain reflectometry as a non-destructive instrumental visualization technique to monitor inorganic fouling and cleaning on reverse osmosis membranes', Journal of Membrane Science, Vol 207, pp 105-117, September 2002.
15. J X Li, R D Sanderson and E P Jacobs, 'Non-invasive visualization of the fouling of microfiltration membranes by ultrasonic time-domain reflectometry', Journal of Membrane Science, Vol 201, pp 17-29, May 2002.
16. J X Li and R D Sanderson, 'In situ measurement of particle deposition and its removal in microfiltration by ultrasonic time-domain reflectometry', Desalination, Vol 146, pp 169-175, September 2002.
17. J X Li, V Y Hallbauer-Zadorozhnaya, D K Hallbauer and R D Sanderson, 'Cake-layer deposition, growth, and compressibility during microfiltration measured and modeled using a noninvasive ultrasonic technique', Industrial and Engineering Chemistry Research, Vol 41, pp 4106-4115, August 2002.
18. J X Li, R D Sanderson, D K Hallbauer and V Y Hallbauer-Zadorozhnaya, 'Measurement and modelling of organic fouling deposition in ultrafiltration by ultrasonic transfer signals and reflections', Desalination, Vol 146, pp 177-185, September 2002.
19. J X Li, D K Hallbauer and R D Sanderson, 'Direct monitoring of membrane fouling and cleaning during ultrafiltration using a non-invasive ultrasonic technique', Journal of Membrane Science, Vol 215, pp 33-52, April 2003.
20. G-Y Chai, A R Greenberg and W B Krantz, 'Ultrasound, gravimetric, and SEM studies of inorganic fouling in spiral-wound membrane modules', Desalination, Vol 208, pp 277-293, 2007.
21. S Ramaswamy, A R Greenberg and M R Peterson, 'Non-invasive measurement of membrane morphology via UFDR: pore-size characterization', Journal of Membrane Science, Vol 239, pp 143-154, August 2004.
22. S Konagurthu, R Peterson, L J Bond, A R Greenberg, W B Krantz, D Kishoni, D Kuhns, L Burgess and A M Brodsky, 'Development of an acoustic technique for assessing structure-property characteristics of polymeric thin films using high pressure', 1996 IEEE Ultrasonics Symposium, pp 413-417, November 1996.
23. S Ramaswamy, 'Development of an ultrasonic technique for the non-invasive characterization of membrane morphology', PhD Dissertation, University of Colorado, May 2002.