

Use of Ultrasonic Time-Domain Reflectometry for Real-Time Measurement of Thickness Changes During Evaporative Casting of Polymeric Films

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ABSTRACT: The dry-cast membrane-formation process is a principal technique by which asymmetric porous membranes as well as dense films can be obtained. Much insight into the fundamental nature of this process can be obtained via real-time measurements of mass and thickness changes. The former requires an equation of state for the density to obtain the average instantaneous film thickness. Optical techniques for the latter such as interferometry and reflectometry usually require transparent samples and good reflecting surfaces; in many cases, such characteristics cannot be obtained. In this article, we report the adaptation of ultrasonic time-domain reflectometry (TDR) for real-time, noninvasive measurement of thickness changes of polymeric films. Ultrasonic TDR does not depend on optical characteristics and is based upon the reflection of longitudinal plane waves at the interface between two media with different acoustic impedances. The technique utilizes the acoustic velocity, which, in general, is a function of temperature and composition. Representative ultrasonic-TDR thickness data are presented for the cellulose acetate (CA)–acetone, CA–acetone–water, and polysulfone (PSf)–tetrahydrofuran systems. Values are compared to those obtained independently using a direct micrometer measurement as well as mass-loss data. In general, the results are in excellent agreement with a maximum error of less than 5%. In addition to overall changes in thickness, preliminary data indicate that ultrasonic TDR can be used to locate the interface between the polymer solution and an opaque solidified region. The latter is a characteristic of polymer systems that undergo a phase separation during solidification. Ultrasonic TDR thus appears to be a promising technique that can be applied to a wide range of polymer systems. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2013–2019, 1998

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INTRODUCTION

Ultrasonic techniques have been utilized in polymer science for more than 40 years for the characterization of emulsions and colloidal suspensions. The scattering characteristics of acoustic waves were used by Erwin and Dohner¹ to study the dispersion of particles in a polymer, and Singh and Singh^{2,3} utilized composition-dependent nonlinearities in the acoustic velocity to characterize polymer–polymer compatibility. Other work has focused on the absorption and attenuation of ultrasonic waves in various polymeric materials.⁴ Although a limited number of studies have considered melting and solidification in organic materials, ultrasonics has been more commonly employed for characterizing the phase-transition behavior of metallic systems.⁵ Ultrasonic techniques, including acoustic microscopy, have been extensively used to measure the thickness of thin films and coatings. In recent years, technology has been developed for *in situ* measurement of the thickness during chemical vapor deposition (CVD) film growth.^{6,7} Despite these developments, ultrasonic techniques have been underutilized, particularly for the study of dynamic processes.⁸

The applicability of ultrasonics for real-time measurement of polymeric thin-film phenomena has been demonstrated by recent work regarding the development of ultrasonic time-domain reflectometry (TDR) for monitoring compaction (creep), fouling, and solidification in membrane-based separation systems.^{9–12} To build upon this latter work, the objective of the present study was to determine whether ultrasonic TDR can be used to measure real-time changes in the thickness of polymeric films undergoing solidification during evaporative casting. Ternary systems such as cellulose acetate (CA)–acetone–water are of particular importance in the fabrication of polymeric membranes used for a variety of commercially important separations.¹³ In addition to the overall changes in film thickness that are the primary focus of this work, we evaluated the capability of ultrasonic TDR for characterizing the demixing front that accompanies phase separation in certain polymer–solvent–nonsolvent systems.^{13,14}

Although noninvasive techniques such as gravimetric analysis (GA) can be used to study the evaporative casting process by measuring the overall weight loss as a function of time,¹⁵ it is not always possible to implement GA under practical circumstances. Consequently, many optical tech-

niques such as interferometry¹⁶ and neutron reflectometry¹⁷ have been used for the study of thin-film behavior. Other techniques such as X-ray diffraction¹⁸ and magnetic resonance imaging¹⁹ are most appropriate for thick films; dielectric measurements using comb electrodes,²⁰ attenuated total-reflectance (ATR) infrared spectroscopy,²¹ and ATR fluorescence spectroscopy²² can provide information about the material properties in the region of the polymer film–solid support interface. Although optical techniques can be relatively simple to utilize, a major disadvantage is that they require nonopaque samples and often good reflecting interfaces. Unfortunately, in many cases, the phase separation that occurs during the evaporative casting of a polymer film will generally give rise to extensive light scattering such that the affected region of the film becomes opaque. For these situations, ultrasonic TDR offers an important potential advantage since it does not depend upon the optical characteristics of the film.

THEORY

Ultrasonic measurements are based upon the propagation of mechanical waves; their velocity is dictated by the medium through which they travel. Ultrasonic velocity characterizes the speed at which the compression and subsequent rarefaction of medium molecules occurs. The velocity of the compression wave through the solid medium, c , is a function of the physical properties²³ according to

$$c = \sqrt{\frac{E}{\rho} \frac{(1 - \nu)}{(1 + \nu)(1 - 2\nu)}} \quad (1)$$

where E is the Young's modulus; ν , Poisson's ratio; and ρ , the medium mass density. When an ultrasonic wave encounters an interface between two media, energy is partitioned among reflection, transmission, and mode-conversion phenomena. For waves normally incident on a plane "welded" boundary between two solids, the energy partition is controlled by the ultrasonic impedance contrast (Z_1/Z_2), where $Z = \rho c$.²⁴ The amplitude of the reflected wave relative to the incident wave, A , is given by

$$A = \left[\frac{Z_1 - Z_2}{Z_1 + Z_2} \right] \quad (2)$$

where the subscripts refer to the materials on either side of the interface.

The response of a system of interfaces to incident ultrasonic waves can be measured in either reflection (pulse-echo, single transducer) or transmission (two transducers directly opposed). In transmission, a measure of the loss or attenuation as a function of frequency is given; in reflection, at high frequency, the transducer receives "echoes" from each discrete interface. When the velocity in the medium is known, the time delay between the initiation of the emitted and received transducer signals, that is, the arrival time, gives a measure of propagation path or thickness according to

$$dl = \frac{1}{2} c dt \quad (3)$$

Here, dl is the distance between the interface and the transducer and dt is the arrival time. When c is known as a function of composition and temperature, an exact value of Δl can be determined. Fundamental aspects of ultrasonic measurement, measurement systems, modeling, transducers, resolution, and accuracy have been reported in the literature.^{24–26} The specific case regarding the capabilities and limitations of ultrasonic TDR for applications in membrane science was described by Bond et al.²⁷

EXPERIMENTAL

The polymeric systems for these initial experiments were selected to meet the following criteria: (1) relevance for membrane applications; (2) generation of dense polymeric films from binary solutions with evaporation kinetics that would enable measurement over the full range of solidification behavior; and (3) extension to a ternary composition in which the phase separation that occurs during evaporation results in a microporous asymmetric film structure. Based upon these considerations, binary solutions were made from 15 wt % cellulose acetate (CA; Eastman, Kingsport, TN, 398-10 with a molecular weight of 40,000)–acetone (Baker, Inc., Phillipsburg, NJ, reagent grade) and 10 wt % polysulfone (PSf; P1700, Amoco)–tetrahydrofuran (Baker, Inc., reagent grade). Using distilled water as the nonsolvent, ternary 10–65–25 wt % CA–acetone–water solutions were also prepared. After an appropriate amount of stirring to ensure complete mixing, all

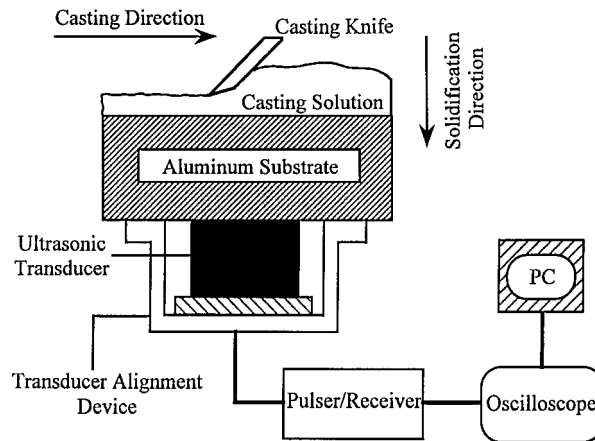


Figure 1 Schematic of the integrated casting apparatus and ultrasonic TDR measurement system.

solutions were used fresh. The casting experiments were all conducted at ambient conditions (23°C).

The specially designed integrated casting platform and pulse-echo measurement system is shown in Figure 1.¹² The arrangement enabled films with initial thicknesses ranging from 1000 to 1200 μm to be easily knife-cast directly on the aluminum substrate using a thickness-calibrated glass casting knife assembly (not shown). When the cast film has contacted the aluminum substrate, a signal is sent from the pulser–receiver (Panametrics Model 5072) to the ultrasonic transducer (Panametrics Type V111, 0.5-in. diameter, 10 MHz contact transducer), which, in turn, generates an ultrasonic pulse toward the substrate and the evaporating film. At the respective aluminum–polymer and polymer–gas interfaces, the longitudinal waves are reflected toward the transducer which detects the reflected wave pressure or displacement. The changes in pressure produce a voltage which is then amplified and transmitted through the pulser–receiver to a digital oscilloscope (Lecroy 9350AM). The oscilloscope displays the electrical signals or “system response functions” (time-amplitude traces). During a casting experiment, the response functions are rapidly sampled and the digitized records are stored on the computer harddrive for later analysis.

An important aspect of the apparatus design involves the coupling between the transducer and the bottom surface of the substrate. The arrangement employed a mechanical fixture to align the transducer and exert sufficient pressure to ensure adequate contact between the transducer and the casting block through a layer of petroleum jelly

used as a couplant. In addition, careful adjustment of the damping and attenuation of the ultrasonic signals is required; the optimized result enables the unambiguous determination of the arrival times of the various reflected signals.

Complete ultrasonic data were obtained for six films of which three corresponded to the two binary and one ternary composition, respectively, and an additional three provided replicates for each of these compositions. To verify that the initial casting compositions provided the desired morphology, the structural characteristics of the solidified films were examined using a Cambridge Stereoscan 250-Mk3 scanning electron microscope (SEM) and standard preparation protocols.¹⁵

RESULTS AND DISCUSSION

Representative ultrasonic data for the 10–65–25 wt % CA–acetone–water casting solution are shown in Figure 2. Here, the ultrasonic signal amplitude is plotted versus arrival time for four progressively increasing times during the evaporation process. The uppermost plot [Fig. 2(a)] was obtained immediately after casting, that is, at zero evaporation time, and evidences two distinct waveforms identified as **A** and **C**. Waveform **A** is due to the reflection of the ultrasonic wave from the casting solution–aluminum substrate and waveform **C** results from the reflection from the polymer solution–gas interface. At an evaporation time of 70 s [Fig. 2(b)], waveform **C** appears at a decreased arrival time due to film shrinkage and has a decreased amplitude and somewhat more complex pattern (**B** + **C**) as a result of solution solidification. The latter indicates a superposition of waveforms, that is, an incomplete separation in the time domain. At an evaporation time of 165 s [Fig. 2(c)], this more complex pattern has resolved itself into two distinct waveforms **B** and **C**. While **C** still represents the reflection from the polymer solution–gas interface, waveform **B** corresponds to the interfacial region between the casting solution and the phase-separated portion of the film; this interface is best described as a “mushy zone” in analogy with thermally induced solidification studies.¹² Although more comprehensive studies of this region are necessary in order to fully understand the nature of the corresponding ultrasonic spectrum, we expect that changes in **B** reflect continuous changes in the structure and properties of the mushy zone.

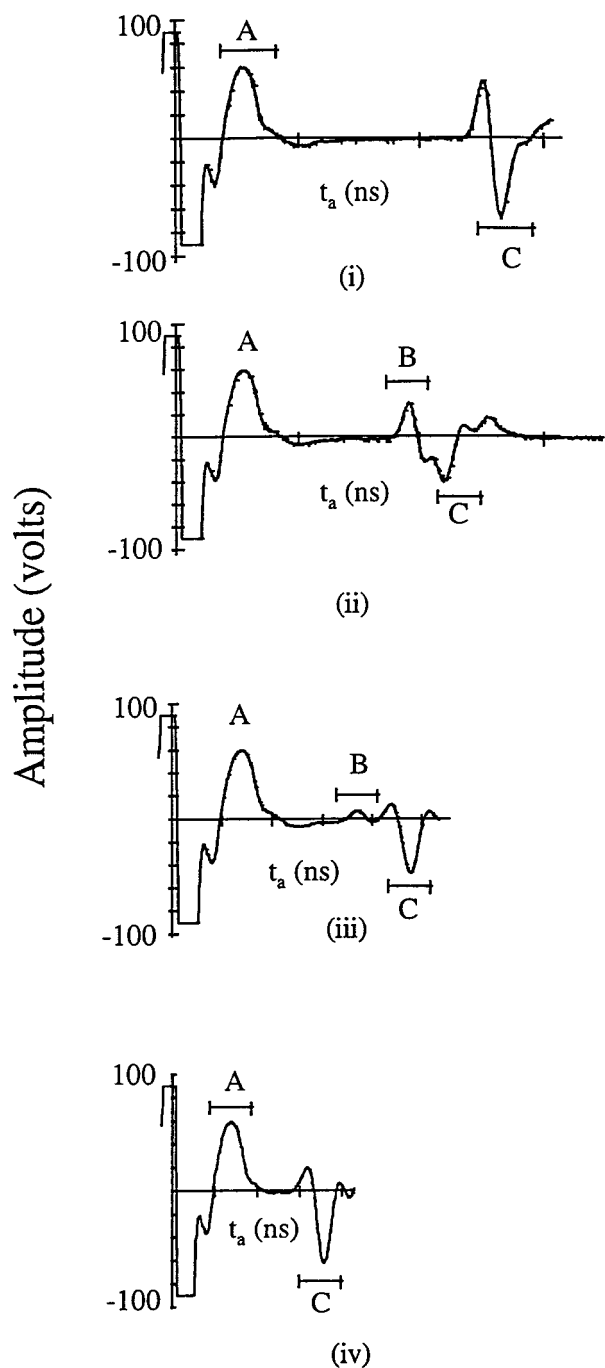


Figure 2 Representative ultrasonic TDR data plotted as amplitude versus arrival time for the 10–65–25 wt % CA–acetone–water system as a function of evaporation time. Spectra (a), (b), (c), and (d) correspond to evaporation times of 0, 70, 165, and 450 s, respectively, and the waveforms identified as **A**, **B**, and **C** correspond to reflections from the casting-substrate/solution, solution/solidified layer, and solidified layer/gas interfaces, respectively.

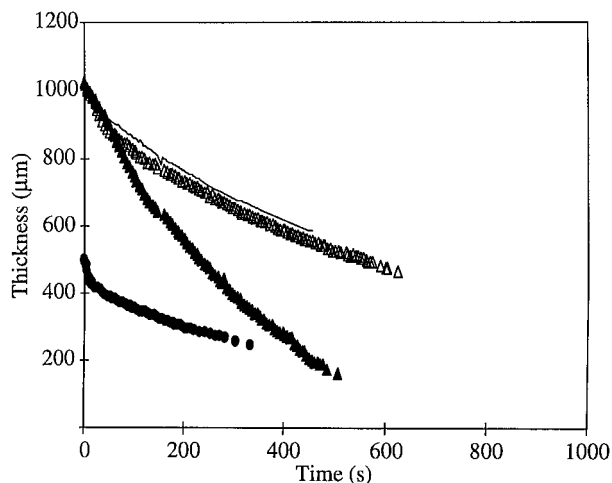


Figure 3 Representative real-time thickness data obtained via ultrasonic TDR for the (Δ) CA–acetone–water, (\blacktriangle) CA–acetone, and (\bullet) PSf–tetrahydrofuran systems. The solid line indicates the results of thickness measurements for the CA ternary system using a gravimetric technique.

With increasing evaporation time, additional densification via phase separation occurs and the overall film thickness continues to decrease. These aspects are represented in Figure 2(b,d) as reflections **B** and **C** systematically move toward reflection **A** which remains invariant in time and space; the range of intermediate evaporation times over which reflection **B** appears as a distinct waveform depends upon the resolution of the ultrasonic measurement system. The microporous structure of the densified films was observed via SEM analysis and confirmed that phase separation had occurred. The overall characteristics of the ultrasonic spectrum obtained during the evaporation from the CA and PSf binary solutions were similar except for the absence of reflection **B** since no demixing occurs in these systems. Indeed, SEM analysis confirmed that the binary compositions produced only dense films.

Based upon knowledge of the original thickness of the casting solution (set by adjustments to the precision casting-knife assembly) and the ultrasonic velocity (Table I), the ultrasonic data can be transformed into real-time thickness values using eq. (3). Representative thickness data as a function of evaporation time are shown in Figure 3 for the binary and ternary CA solutions and the binary PSf solution. As expected from extensive modeling and experimental studies previously conducted on the CA–acetone and CA–acetone–water systems,¹⁵ evaporation occurs at different

rates so that the systems will attain their final thickness values at different times. Although the data in Figure 3 clearly show the expected differences in the rate of the thickness changes, limitations of the ultrasonic measurement system did not allow the “final” as-cast thickness values to be obtained. However, densification was sufficient over the time scale of the experiment to enable “final” film-thickness values, that is, those corresponding to the maximum times indicated in Figure 3, to be directly measured using a micrometer. These direct thickness measurements were 8 and 2% lower than the corresponding ultrasonically obtained thickness values for the binary and ternary CA systems, respectively. Such results would be expected given the additional film shrinkage due to continued evaporation that occurred over the small additional time period (~ 30 s) required for the micrometer measurements after completion of the ultrasonic measurements. In addition, a separate series of mass-loss experiments were conducted on the ternary CA solution in order to provide an independent set of continuous real-time measurements against which the ultrasonic TDR results could be compared (Fig. 3). While the conversion of mass loss to thickness change values involves some simplifying assumptions about the instantaneous composition and volume of mixing effects, excellent agreement between the two techniques is obtained.

Since the data presented here clearly indicate that ultrasonic TDR can provide real-time measurement of thickness changes that occur during the evaporative casting of polymeric films, the issue of technique resolution merits further discussion. The first requirement for ultrasonic TDR thickness measurements is that reflections from the desired interfaces be obtained. This is a function of the pulse-echo system employed and the inherent nature of the interfaces. For example, we were unable to completely characterize changes in the thickness of the phase-separated region (PSR). Reflections from this region were observed only at intermediate times for which the PSR thickness was sufficiently large for separation from the polymer–gas interface reflection but small enough for separation from the polymer–substrate reflection. For a given ultrasonic impedance ratio, resolution can be enhanced by appropriate choices of transducer frequency and optimization of the structure and dimensions of the substrate material.

Once reflections can be unambiguously re-

Table I Dependence of Acoustic Velocity on Composition

Initial Composition (wt %)	Velocity in Solution (m/s)	Velocity in Solidified Film (m/s)
10% CA, 90% acetone	1224	1246
15% CA, 85% acetone	1242	1268
20% CA, 80% acetone	1251	1280
25% CA, 75% acetone	1259	1292
10% CA, 65% acetone, 25% water	1319	1377
10% CA, 70% acetone, 20% water	1265	1325

solved, the accuracy of the thickness measurements depends upon arrival-time resolution and the accuracy of the ultrasonic velocity values utilized. In the present case, the former was ± 0.5 ns and the latter depended upon temperature and composition. Previous studies have demonstrated that maximum temperature decreases of $\Delta 23^\circ\text{C}$ are possible for films dry-cast from cellulose acetate solutions²⁸; however, the effect of this change on the ultrasonic velocity is expected to be modest. Literature values for the temperature dependence of ultrasonic velocity²⁹ indicate that a temperature decrease of 23°C results in velocity changes in acetone and water of $+8.9$ and -3.7% , respectively. Since the effect of compositional changes was less certain, we measured the ultrasonic velocity for the binary and ternary compositions for the initial solutions and the resulting densified films and membranes (Table I). These measurements indicate that the maximum differences as a function of composition were $< 5\%$; differences between the initial solution velocity and the value in the corresponding film were also $< 5\%$. Average values based upon the latter were utilized for the thickness results in Figure 3 by using ultrasonic velocities of 1255 and 1348 m/s for the binary and ternary CA systems, respectively. Overall, these considerations indicate that the pulse-echo measurement system employed in these studies had a thickness resolution of $\pm 5 \mu\text{m}$. Similar data for other systems of interest are necessary before the quantitative capabilities of ultrasonic TDR can be fully utilized. Nonetheless, ultrasonic TDR appears to have great promise as a real-time, nondestructive, noninvasive technique that can be applied to a wide range of polymer film-casting situations, particularly those for which other techniques cannot be employed.

CONCLUSIONS

These experiments clearly demonstrate that ultrasonic TDR implemented using modern digital instrumentation can provide a powerful tool for the study of solidification phenomena in polymer systems. Ultrasonic TDR provides a particularly valuable alternative when other methods, such as those that require a transparent optical path, cannot be employed. The insight gained from such real-time measurements can be used to test existing solidification models and, if necessary, provide a basis for their improvement.

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