Acoustic Resonant Spectroscopy for Characterization of Thin Polymer Films

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Acoustic resonant spectroscopy for characterization of thin polymer films

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An acoustic resonant spectroscopy technique for measuring the acoustic impedance, ultrasonic velocity, and density of micron-scale polymer films is developed. The method, which is based on spectral analysis, observes the acoustic resonance between water, the film, and a tungsten plate with high acoustic impedance in the frequency range of 20–70 MHz. The interface between the film being examined and the plate is vacuum sealed, enabling us to characterize the low-density polyethylene film with acoustic impedances as low as about 1.9 MN m^{-3} s and the poly(vinyl chloride) film as thin as about 8 μm. The error in the film density measurements is found to be less than 1%, and the validity of the technique is verified. © *2006 American Institute of Physics.*
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I. INTRODUCTION

There has been a growing scientific and practical interest in thin polymer films for applications in physics,[1,2] engineering,[3,4] and biology,[5,6] and the importance of these films has recently come to the fore. It is well known that the polymer nano- and microstructures depend on a number of process variables such as temperature, pressure, rheological history, etc. Acoustic properties, e.g., the acoustic impedance, ultrasonic velocity, ultrasonic attenuation, and so on, have been used to characterize the physical and chemical properties of polymer materials, and those of bulk polymers have been extensively studied.[7,8] However, the techniques for determining the acoustic properties of thin polymer films are extremely limited compared with those for bulk polymers. The acoustic techniques for characterizing thin films are classified into two categories: one is performed in the time domain,[9] and the other in the frequency domain.[10–12] Hänel succeeded in making simultaneous measurements of the sound velocity and the thickness of poly(vinylidene fluoride) film with a thickness of 35 μm by time-resolved acoustic microscopy.[9] However, in the aforementioned time-domain technique, the superimposition of echoes on the signal to be analyzed becomes a serious problem for thinner films. Ultrasonic spectroscopy techniques based on spectral analysis have been used successfully to characterize layered media on substrates, e.g., a magnetite layer on mild steel,[10] some sputtered films on *Z*-cut sapphire,[11] and so on. However, these techniques are unavailable in many cases for the characterization of thin polymer films because the films are usually offered for testing without a supporting substrate. Kumar *et al.* successfully determined the acoustic impedance of a 20-μm-thick poly(ethylene terephthalate) film without having any substrate.[12] The accuracy of the method, however, for lower acoustic impedance films is much reduced. Therefore, a precise method to measure the acoustic properties of very thin, very low acoustic impedance polymer films is very much in demand.

It has been discovered experimentally that good acoustic coupling between polymer films and solid samples can be obtained by evacuating the space between them without the use of an adhesive layer.[13] In this article, we propose an acoustic resonant spectroscopy technique based on spectral analysis that can be used to accurately determine the acoustic properties of freestanding micron-scale polymer films. The film under examination is vacuum sealed on to a high acoustic impedance plate, and the acoustic resonance of the water/film/plate system is observed. The method is demonstrated in the high frequency range of 20–70 MHz which enables characterization of very thin or low impedance polymer films.

II. THEORY

Let us consider the transmission system comprised of the coupling liquid, the thin film, and the back plate, where their acoustic impedances are denoted by Z_C, $Z_T(=\rho_T c_T)$, and Z_B, respectively. ρ_T and c_T are the density and the longitudinal wave velocity of the film. For plane acoustic waves that are normally incident on a planar film, the echo transmittance of three media, T_1, is given in the literature,[14] and can be represented by[15]

$$T_1 = T_2[\cos^2(2\pi\nu/c_T)d + A\sin^2(2\pi\nu/c_T)d]^{-1}, \quad (1)$$

where $T_2[=4Z_C Z_B/(Z_C+Z_B)^2]$ is the echo transmittance in the case without the film, ν the frequency, d the film thickness, and

$$A = \{(Z_T^2 + Z_C Z_B)/[Z_T(Z_C + Z_B)]\}^2. \quad (2)$$

The ratio $\theta(=T_1/T_2)$ has its maximum value, θ_r, at the resonance frequency, ν_r; θ_r and ν_r are given by $\theta_r = A^{-1}$ and $\nu_r = c_T/4d$. From Eq. (2), we obtain $Z_T^2 - BZ_T + Z_C Z_B = 0$, where $B=(Z_C+Z_B)/\theta_r^{0.5}$; for $Z_T < (Z_C Z_B)^{0.5}$, we find

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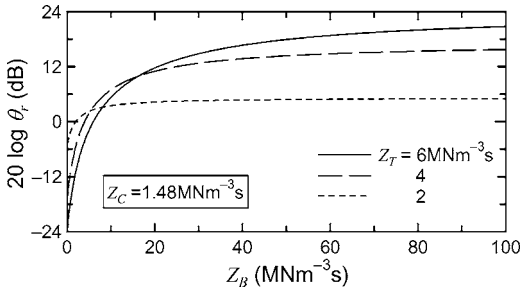

FIG. 1. Behavior of θ_r as a function of Z_B.

$$Z_T = [B - (B^2 - 4Z_C Z_B)^{0.5}]/2. \quad (3)$$

If Z_C and Z_B are known, and we measure θ_r, Z_T is determined from Eq. (3) without knowing the values of c_T, ρ_T, and d. The values of θ_r for Z_T of 6, 4, and 2 MN m^{-3} s are shown in Fig. 1 as a function of Z_B. Here we assume water is the coupling liquid (Z_C=1.48 MN m^{-3} s). The values of Z_T of typical polymer materials range from 2 to 6 MN m^{-3} s. The values of θ_r are greater than unity for $Z_C < Z_T < Z_B$, and for any value of Z_T, the larger the value of Z_B, which signifies a greater mismatch between Z_C and Z_B, the larger the value of θ_r. Figure 1 and Eq. (3) show that a back plate with higher Z_B is indispensable for the absolute and accurate determination of Z_T from the observed θ_r. Furthermore, if we know one of the parameters, c_T, ρ_T, or d, and use the measured ν_r, the remaining two parameters can be completely determined. The acoustic resonant phenomenon is a frequency dependent phenomenon in which θ_r occurs at ν_r in the coupling liquid-thin film-back plate transmission system, and this phenomenon is utilized in the present technique to determine the acoustic properties of thin polymer films. In this article, we call this technique the acoustic resonant spectroscopy technique.

III. EXPERIMENTAL ARRANGEMENT

A schematic of the experimental setup and a block diagram of the acoustic measurement system are shown in Fig. 2(a). All the experiments were conducted at room temperature (293 K). The examined were a low-density polyethylene (LDPE) film with d=12.1 μm, and a poly(vinyl chloride) (PVC) film with d=7.8 μm. In order to clearly observe the

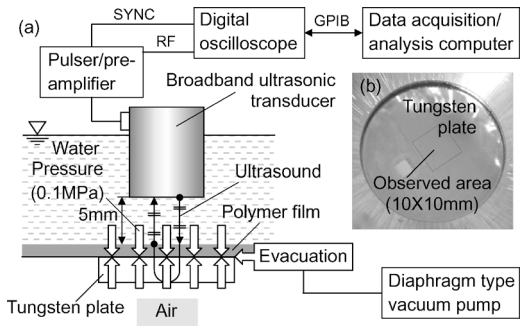

FIG. 2. Experimental details. (a) Schematic of experimental setup and a block diagram of the acoustic measurement system. (b) Photograph of a vacuum-sealed polymer film/tungsten plate interface, where the air between the film and the tungsten plate is evacuated by a diaphragm-type vacuum pump.

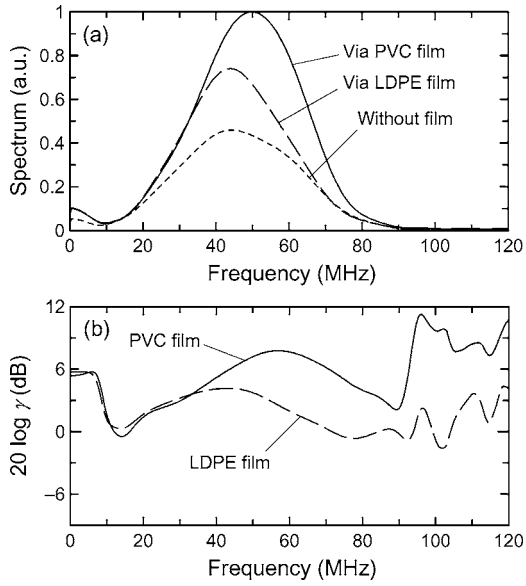

FIG. 3. Results of the frequency analysis. (a) Amplitude spectra of the back-wall echoes of the tungsten plate with (ϕ_1) and without (ϕ_2) the polymer film. (b) Amplitude ratio $\gamma(=\phi_1/\phi_2)$.

acoustic resonance between the coupling liquid, the film being examined, and the back plate, water was used as the coupling liquid and a pure tungsten plate (99.95%) with a high Z_B of 99.84 MN m^{-3} s was used for the back plate. To improve the acoustic coupling at the film/tungsten plate interface, we applied a pressure of about 0.1 MPa to the interface by evacuating the air between the film and the plate.[13] Figure 2(b) shows the vacuum-sealed film/tungsten plate interface. The surface of the tungsten plate was mirror polished, and a 10 mm square groove was patterned to enable identification of the measurement location. A flat type, broadband ultrasonic transducer, with a nominal frequency of 50 MHz and a piezoelectric element of 3.2 mm diameter, was employed in this study, and the near field length of the transducer was 85.1 mm in water.[16] The ultrasonic transducer had a 7.5 mm length silica delay line (sound velocity =5684 m/s) in front of the piezoelectric element, and the polymer films examined were placed 5 mm from the front surface of the delay line. The position of the film, where the acoustic resonance was observed, was in the near field, and the plane wave theory is applicable to the present experiments.[17] The amplitude spectra of the back-wall echoes of the tungsten plate with (ϕ_1) and without the film (ϕ_2) were recorded at several points in the observed area shown in Fig. 2(b), and these were stored in a computer for future data analysis. In all cases, either with or without the film, a waterproof jig attached to the back of the plate was used to keep the back of the plate in air.

IV. RESULTS AND DISCUSSIONS

The amplitude spectra ϕ_1 obtained via LDPE and PVC films, and ϕ_2, which are the average spectra measured in the observed area, are shown in Fig. 3(a). Figure 3(a) clearly shows that $\phi_1 > \phi_2$ in the ν range of 20–70 MHz for measurements both via LDPE and PVC films. The amplitude ratio, γ, of the ultrasonic transmission via a film in compari-

TABLE I. Acoustic properties of measured polymer films. Bulk constants are in parentheses.

Thin polymer film	Z_T (MN m^{-3} s)	c_T ($\times 10^3$ m/s)	ρ_T ($\times 10^3$ kg/m^3)	Ref.
LDPE	1.89±0.01	2.06±0.03	0.92±0.02	
	(1.92)	(2.09)	(0.92)	7
PVC	2.35±0.01	1.75±0.01	1.35±0.02	
	(3.02)	(2.24)	(1.35)	8

son with that without a film is expressed as $\gamma(=\phi_1/\phi_2) = \theta\xi\psi$, where ξ and ψ are related to the ultrasonic attenuation in the film and the signal loss at the film/plate interface, respectively. The relationships between γ and ν for LDPE and PVC films are shown in Fig. 3(b). The maximum value of γ for the LDPE film was 1.61±0.01 at 42.6±0.6 MHz, and that for the PVC film was 2.42±0.01 at 56.0±0.4 MHz. The ultrasonic attenuation in the film can be ignored because the examined films were very thin, i.e., $\xi=1$. Also, if we assume no signal loss at the film/tungsten plate interface ($\psi=1$), the maximum value of γ corresponds to θ_r, and ν, where γ takes its maximum value, is coincident with ν_r. The validity of this assumption for each film is supported by the fact that no conspicuous shades were observed in the acoustic image at the back of the plate obtained using a 100 MHz focused ultrasonic transducer, and acoustically coupled film/tungsten plate interfaces were successfully accomplished over the observed area with the application of about 0.1 MPa pressure.[15] Finally, acoustic resonance between the three media was clearly observed with both LDPE and PVC films.

By substituting the maximum values of γ instead of θ_r into Eq. (3), the values of Z_T of the LDPE and PVC films were determined to be 1.89±0.01 and 2.35±0.01 MN m^{-3} s, respectively. The determined acoustic properties of LDPE and PVC films are summarized in Table I together with the bulk constants.[7,8] The variation of Z_T in the observed area for both films was about 0.5%. On the other hand, the variations of Z_T for both films obtained without evacuation of the air between the film and the tungsten plate were much larger than those obtained with evacuation, and the values of Z_T determined for both films without evacuation were smaller than those with evacuation. The values of c_T were determined by $4d\nu_r$, and those of ρ_T were determined by Z_T/c_T. The values of ρ_T of LDPE and PVC films were also measured using an electric balance, where pipes made of the films were prepared for precise ρ_T measurements. The measured values were $(0.91\pm0.01)\times10^3$ and $(1.34\pm0.02)\times10^3$ kg/m^3 for the LDPE and PVC films, respectively. The values of ρ_T of LDPE and PVC films determined by the present acoustic resonant spectroscopy are in good agreement with these within an error of 1%, and the validity of the present technique was verified. All the values of Z_T, c_T, and ρ_T of the LDPE film measured by the present technique are in good agreement with the reported bulk properties.[7] On the other hand, both the values of Z_T and c_T of the PVC film measured are 22% less than those of bulk material.[8] The difference in the acoustic properties between PVC film and its bulk may be due to variations in the composition or structure which depend strongly on the fabrication process.

One side of the films being examined in this study was in water, but this was allowable, because LDPE and PVC films are known to have low water absorption.[18,19] For a film with high water absorption, e.g., porous films, the ultrasound should be transmitted from the tungsten plate side, and observation of the acoustic resonance between the tungsten plate, the film, and air is practical. A nonfocused ultrasonic transducer was employed in this study. Note that the use of a focused ultrasonic transducer allows us to map or image the acoustic properties of thin polymer films. The present acoustic resonant spectroscopy technique is potentially useful for characterizing the acoustic properties of polymer films prepared without a substrate, especially for low acoustic impedance polymer films and for very thin, micron-scale polymer films.

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