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# Monitoring of Thermal Oxidation of Thin Polymer Films by Means of Acoustic Resonant Spectroscopy

音響共鳴スペクトロスコピーによる高分子薄膜の熱酸化モニタリング

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## 1. Introduction

Thin polymer films have been widely used in many fields of application. Because the polymer films are degraded by the thermal oxidation under high temperature [1], it must be valuable to monitor the degradation for ensuring their reliablity. So far to characterize thin polymer films, the acoustic resonant spectroscopy where the acoustic resonant phenomenon among the water, the film and the back plate is observed has been reported [2]. This acoustic resonant spectroscopy measure the acoustic properties, i.e., the acoustic impedance, the sound velocity and the density of the film. Also the technique can be used to detect the micro defects in the film [3]. Moreover, if we use the transparent glass plate as the back plate, it is possible to acquire the optical microscope images of the film together with its acoustic properties [4].

In this study, we tried to monitor the thermal oxidation of the linear low-density polyethylene (LLDPE) films by means of the acoustic resonant spectroscopy. The thickness of the LLDPE film was 11.6 μm and it was heat treated in a furnace for maximum 10 hours and offered for the testing.

## 2. Principal of Acoustic Resonant Spectroscopy

The echo transmittance of the ultrasonic transmission system consisting of the water, the thin film and the back plate is denoted by $T_1$, and that of the system consisting of the water and the back plate is denoted by $T_2$. The ratio of the echo transmittances $\theta$ (= $T_1$ / $T_2$) takes its maximum value $\theta_R$ at the resonant frequency $f_R$ [2]. The values of $\theta_R$ and $f_R$ are given by

$$\theta_R = [Z_T (Z_W + Z_B) / (Z_T^2 + Z_W Z_B)]^2, \quad (1)$$

and

$$f_R = c_T / 4d, \quad (2)$$

where $Z_T$ (= $\rho_T c_T$), $Z_W$ and $Z_B$ are the acoustic impedances of the film, the water and the back plate, respectively. $\rho_T$, $c_T$, $d$ are the density, sound velocity and the thickness of the film. From Eq. (1), we find

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

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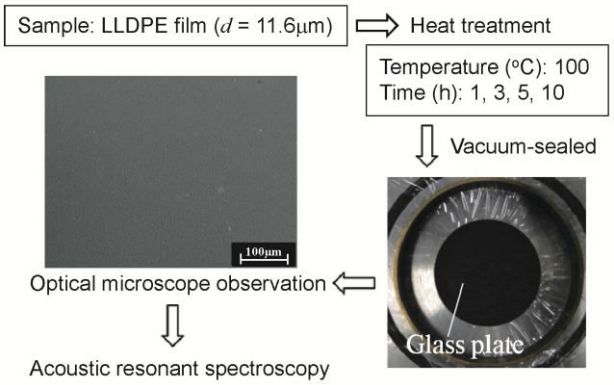


Fig. 1 Flow chart of experiments.

where B = ($Z_C$ + $Z_B$) / $\theta_R^{0.5}$. If $Z_W$ and $Z_B$ are known, $Z_T$ is determined by measuring $\theta_R$. Moreover, if one among the three parameters, $d$, $\rho_T$ and $c_T$ is known, remained two parameters can be decided from the measured $f_R$ and the determined $Z_B$.

## 3. Experimental Procedure

The sample was the LLDPE film having $d$ of 11.6 μm. The LLDPE films were heat treated in air atmosphere furnace at 100°C for 1, 3, 5 and 10 hours. In this study, we used the glass plate as the back plate ($Z_B$ = 13.54 MNm$^{-3}$) for acoustical-optical hybrid microscopy [4]. The heat treated film was vacuum sealed onto the glass plate (Fig. 1), and first, offered for the optical microscope observation.

After the optical microscope observation, the film onto the glass plate was examined by the acoustic resonant spectroscopy. The ultrasound is emitted by the ultrasonic transducer with the nominal frequency of 100 MHz and the diameter of the piezoelectric element of 3.2 mm, and the echo reflected at the back of the plate was recorded by the same transducer.

The amplitude spectra of the back-wall echo of the plate is denoted by $\varphi_1$, and that without the film is $\varphi_2$. The amplitude ratio is given by

$$\gamma = \varphi_1 / \varphi_2. \quad (4)$$

Under the assumptions that the signal loss due to the ultrasonic attenuation in the film and that at the film/glass plate interface can be negligible, $\gamma$

corresponds to $\theta$. These assumptions were confirmed to be valid for typical polymer films without any defects [2]. Therefore in this study, we measured $\gamma_R$ and $f_R$, and obtained $\rho_T$, $c_T$ and $Z_T$.

## 4. Results and Discussion

Optical microscope images of the LLDPE film vacuum sealed onto the glass plate are shown in Fig. 2. Compared with two images of the films with and without the heating, no changes in the appearance of two films due to the heating were confirmed.

Figure 3 shows the amplitude spectra of the back-wall echoes in the cases with and without the films. Compared with the amplitude spectra of the films with and without the heating, the center frequency of each spectrum, which is indicated by an arrow in Fig. 3, is found to be moved toward the lower frequency side by the heating. This fact indicated that the acoustic properties of the film were surely changed by the heating.

The acoustic properties, i.e., $\rho_T$, $c_T$ and $Z_T$, are shown Fig. 4 as the functions of the heating time. Here the ranges of all vertical axes are set to 25% of their value without heating. With increase in the heating time, $\rho_T$ gradually increased and $c_T$ gradually decreased. On the other hand, $Z_T$ was unchanged by the heating. The changes in $\rho_T$ and $c_T$ seemed to be saturated up to around 5 hours of heating. These changes in the acoustic properties were due to the thermal oxidation of the film and the changes might be correlated with the progress in the oxidation depended on the heating time.

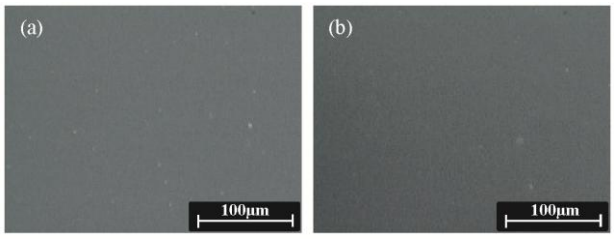


Fig. 2 Optical microscope images of the LLDPE films. (a) Non-heated. (b) Heated at 100°C for 10 hours.

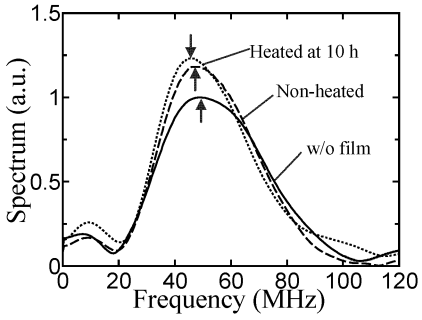


Fig. 3 Amplitude spectra of the back-wall echoes in the cases with and without the film.

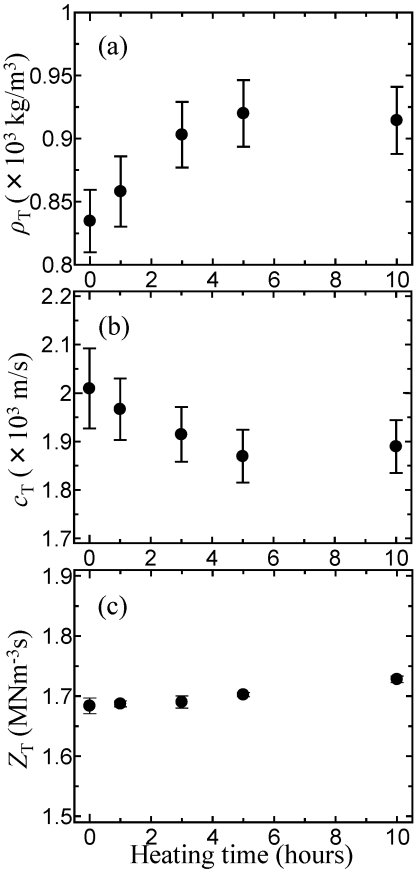


Fig. 4 The acoustic properties of the LLDPE films as the functions of the heating time. (a) $\rho_T$. (b) $c_T$. (c) $Z_T$.

## 5. Conclusions

In this paper, we tried to monitor the thermal oxidation of the linear low-density polyethylene (LLDPE) films with the thickness of 11.6 μm by the acoustical-optical hybrid microscopy. Although the thermal oxidation could not be visible in the optical microscope images, it was able to be detected as the changes in the acoustic properties of the film. Moreover the changes in the acoustic properties of the films depended on the heating time.


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