수정진동자를 이용한 점탄성 변화의 측정

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Monitoring Viscoelasticity Variation Using a Quartz Crystal Resonator

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INTRODUCTION

A quartz crystal resonator is composed of a thin quartz crystal sandwiched between two metal electrodes that establish an alternating electric field across the crystal, causing vibrational motion of the crystal. The motion is characterized with the resonant frequency and admittance of the resonator, and the characteristic is sensitive to the changes of mass and physical property of an overlayer on its electrode. Because the resonator is so sensitive, it can sense a variety of changes in microscale at the electrode interface. In polymerization, the rheological property of a reactant and product mixture continuously varies as the polymerization proceeds. The resonator has been implemented in the monitoring of a UV photopolymerization by measuring its resonant resistance[1]. Also, the nucleation and crystal formation in a cooling crystallization have been investigated with the quartz crystal resonator [2].

In this study the relations between the resonant characteristics of a quartz crystal resonator and the rhoeological properties of an overlayer applied on the electrode surface are developed from the mechanics of quartz movement. The elastic shear modulus and viscosity of the polyethylene overlayer are computed from the relations and experimentally obtained resonant properties. The computation results are compared with the bulk properties of polyethylene measured with a rheometer at low strain rate.

THEORETICAL ANALYSYS

Consider the thickness-shear motion of a thin circular-disk-shape quartz crystal with thickness h_Q having a pair of concentric electrodes with radius r_e on both sides as shown in Fig. 1.

For the case of thin film ($\Pi_1 \to \infty$), we get $\eta_{IR} - \eta_{Ic} = \eta'_L / \omega \rho_Q h_Q$ and the formula for the frequency shift Δf_{0L} as follows.

$$\Delta f_{0L} = -\gamma f_0 \frac{\eta'_L}{\rho_Q h_Q} \tag{1}$$

which corresponds to the Sauerbrey's formula [3] except for the parameter γ.

For the case of thick ($\Pi_1 \to \infty$) and elastic ($\Pi_2 \to 0$) solid, we have

$$q_{LR} = M \tan N \tag{2a}$$

$$q_{LI} = 0. \tag{2b}$$

Since $\psi_{II} - \upsilon$, υ_{max} is the largest and independent of the material property. Further, Eq. (2a) implies that there can be an infinite number of values of the parameter that produces a given value of , because at $N = (2n-1)\pi/2$ $(n = 1, 2, 3\ldots)$ becomes infinite. However, the case of thick elastic material may not be encountered so frequently.

EXPERIMENTAL

Materials

Polyethylene (Sigma-Aldrich Inc., U.S.A., Code No. 427799) having a number-average molecular weight of about 7,700 and a melting point of 90 ℃ was used as received. An AT-cut quartz crystal resonator having a base frequency of 8 MHz (Sunny Electronics Co., Korea) was utilized in this experiment. The electrodes of the resonator were silver finished.

Experimental setup

A schematic diagram of a quartz crystal resonator is demonstrated in Fig. 2(a). The polyethylene overlayer was placed on the one of electrode surfaces of the resonator, and the resonator was heated and cooled in an oil bath. Because the resonator surfaces can not be in contact with oil for the accurate measurements of its resonant frequency, conductance and susceptance, the resonator was placed in a specially designed module. The resonator was placed between two glass holders, and two o-rings keep the oil from wetting the electrode surface. Two brackets tighten the glass holders with four screws. The detailed dimension of the cell is given in the figure. After the module was assembled, fine particles of polyethylene were obtained by sieving the powder with a sieve of 250 μm. About one third of 0.1 mg of the polyethylene powder was placed on the top electrode of the resonator. The module was put in an oil bath demonstrated in Fig. 3. For the better control of resonator temperature, the module was immersed to the level of the upper o-ring in the bath. The bath temperature was adjusted by electric heating, and water cooling was also provided for the cooling cycle in the experiment.

Procedures

The experiment began at a temperature of about 25 ℃. After the experimental setup was stabilized for an hour, the bath temperature was raised at a rate of 1 ℃/min up to 100 ℃, and was lowered at a rate of 1.5 ℃/min. The first measurement was conducted at a temperature of 95 ℃. At the temperature the setup was steadied for two minutes, and the measurement was conducted for 8 minutes using an impedance analyzer (Agilent Technologies, U.S.A., Model 4192A). The conductance and susceptance were determined at a resonant frequency between 794 MHz and 804 MHz in a step of 50 Hz. The temperature was lowered by 4 ℃ down to 55 ℃, and the measurement was done in the same manner.

APPLICATION TO POLYETHYLENE SOLIDIFICATION

The formula and the analysis presented so far are applied to the experimental study on the measurement of material properties of polyethylene during its solidification process. As the material and geometrical constant for the quartz, we consider the following parameters many of which are commonly used for an AT-cut crystal.

$C_{66} = 2.947 \times 10^{11}\, dyn/cm^2$, $\varepsilon_{22} = 40 \times 10^{-14}$ F/cm, $\rho_Q = 2.651\, g/cm^3$,
$K^2 = 7.74 \times 10^{-3}$, $h_Q = 0.0205449$ cm.

Here, the depth of quartz h_Q was obtained in such a way that the resultant resonant frequency matches with the measured one $f_0 = 7{,}996\ [kHz]$ without any overlayer. Further, we consider the following properties for silver electrodes.

$h_e = 30$ nm, $\rho_e = 10.5 \times 3 \times 10^{-5}$ g/cm^2,

Then, we have $q_e = 0.00594$.

We next obtain the parameters μ_L and η_L for loaded cases. The measurement was done with 6 particles of PE melted on the electrode surface. The total mass of the particles is 0.033 mg. It is assumed that all the 6 particles contribute to a single particle, its size being determined by summing up all the particles' size; $d_L = 0.0502$ cm. This in turn provides the thickness of the PE particle; $h_L = 0.0184$cm. Since the melted particles do not change their shape with temperature, d_L and h_L are fixed in the subsequent calculations. Fig. 4 presents $G_{\max}$ and Δf measured from the experiment at 11 different temperatures. To find the parameter set (μ_L, η_L) corresponding to each of the 11 data set $(G_{\max}, \Delta f)$, we generate a map on the (μ_L, η_L) space as shown in Fig. 5. Intersection of contour lines of $G_{\max}$ and that of Δf then gives us the parameters μ_L and η_L. Fig. 6 exhibits the parameters obtained in this way at the fundamental mode of the overlayer vibration. We see that as the temperature decreases from the melting point, the shear modulus decreases but the viscosity increases.

CONCLUSION

The relations of the viscoelastic properties of a polymer overlayer placed at the electrode interface of a quartz crystal resonator and its resonant charateristic are developed to measure the property variation during the polymer solidification. The procedure is applied to a polyethylene processing, and the measurement is compared with that of a melt polyethylene determined instrumentally. The comparison indicates that the measurements are comparable to those of the melt to imply the possibly wide implementation of the proposed measurement technique in the field of polymer processing.

ACKNOWLEDGMENTS

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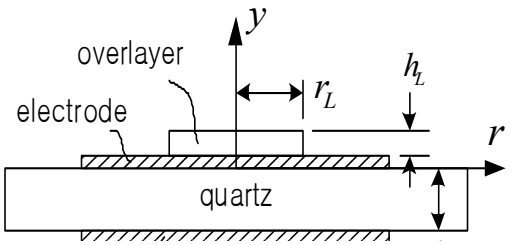

Fig. 1. Sketch of a quartz crystal resonator with electrodes on both sides and a viscoelastic overlayer attached on the external surface of an electrode.

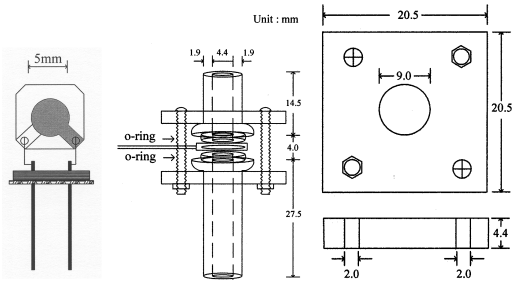

Fig. 2. Schematic diagrams of quartz crystal resonator (a), resonator cell module (b) and holding bracket (c).

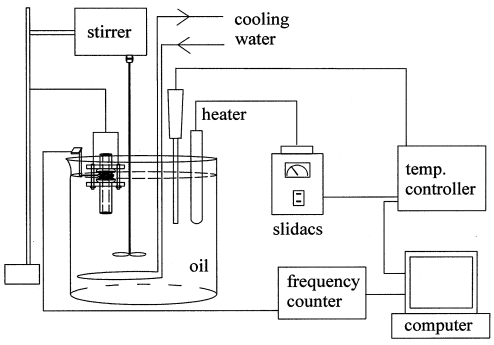

Fig. 3. A schematic diagram of experimental setup.

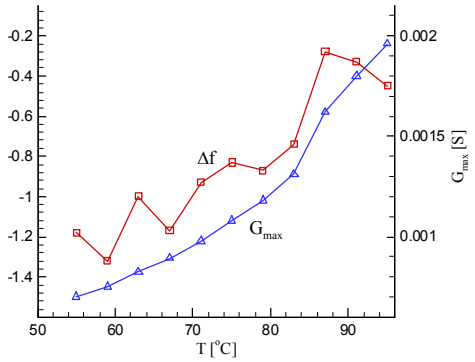

Fig. 4. Experimental results of Δf and $G_{\max}$ obtained at 11 different temperatures.

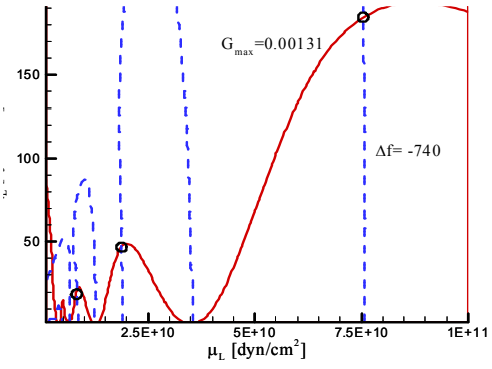

Fig. 5. Typical map for determining μ_L and η_L of a viscoelastic overlayer. Solid lines are contour lines for $\Delta f = -740[Hz]$ and dashed lines for $G_{\max} = 0.00131[S]$ at 83 ℃ .

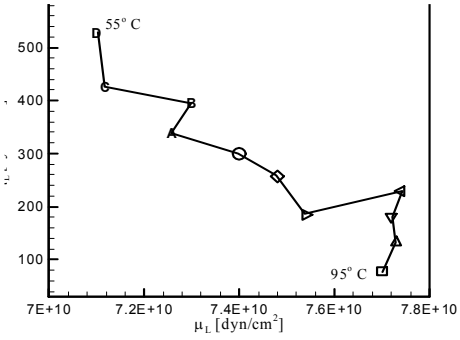

Fig. 6. Predicted values of μ_L and η_L of a viscoelastic overlayer at each temperature with fundamental mode of oscillation. The temperature starts from 95℃ decreasing down to 55℃ with 4℃ increment.