고분자 점탄성 측정센서의 특성해석

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Characteristics of Polymer Viscoelasticity Measurement Sensor

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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. 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. [2,3] The resonant frequency and admittance of the resonator can be interpreted to the changes of mass and viscoelasticity of an overlayer at its electrode interface.

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. The visco-elastic overlayer attached on the top electrode is assumed to be of axisymmetric shape with radius r_L and thickness h_L. Then the equation of motion for the quartz can be written as

$$c_{66}\frac{\partial^2 u}{\partial y^2}+\eta_Q\frac{\partial^3 u}{\partial t\partial y^2}+e_{26}\frac{\partial^2 \phi}{\partial y^2}=\rho_Q\frac{\partial^2 u}{\partial t^2} \quad (1)$$

$$e_{26}\frac{\partial^2 u}{\partial y^2}-\varepsilon_{22}\frac{\partial^2 \phi}{\partial y^2}=0 \quad (2)$$

where t is the time and (r, y) denotes the radial and axial coordinates of the cylindrical coordinates system. Further, μ(r, y, t) is the mechanical displacement of the quartz along the x-direction, ϕ(r, y, t) the electric potential, c_{66} the elastic shear modulus of the quartz, e_{26} the piezoelectric constant of the quartz, ε_{22} the dielectric constant of the quartz, η_Q the viscosity of the quartz, and ρ_Q the volume density of the quartz material.

The impedance Z_m is assumed to be composed of resistance R_m, capacitance C_m and inductance L_m:

$$Z_m = R_m + i\omega L_m + 1/(i\omega C_m).$$

Comparing these two, we get

$$R_m = \frac{\pi\xi + q_{LI}}{8C_0K^2 f_0},\quad L_m = \frac{1}{32C_0K^2 f_0^2}\left[(1-8K^2/\pi^2) + 2q_{LR}/\pi\right],\quad C_m = \frac{8C_0K^2}{\pi^2 - 8K^2}. \tag{3}$$

The shift of resonant frequency $\Delta f_{0L} = f_{0L} - f_0$ becomes

$$\Delta f_{0L} = -\frac{q_{LR}}{\pi} f_0. \tag{4}$$

Following the R-L-C circuit theory, G_{max} is given by

$$G_{max}\Delta f_{12} = \frac{1}{2\pi L_m} = \frac{16K^2\varepsilon_{22}A_e f_0^2}{\pi h_Q} \tag{5}$$

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 °C 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 and Procedures

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 cell module illustrated in Fig. 2(b). 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. 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. The resonant frequency, resonant resistance and the temperature of oil bath were measured using home-made devices, and an A/D converter was employed for signal processing. The experiment began at a temperature of about 25 °C. After the experimental setup was stabilized for an hour, the bath temperature was raised at a rate of 1 °C/min up to 100 °C, and was lowered at a rate of 1.5 °C/min. The first measurement was conducted at a temperature of 95 °C. 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 °C down to 55 °C, 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.

$$c_{66} = 2.947\times10^{11}\ \text{dyn/cm}^2,\quad \varepsilon_{22} = 40\times10^{-14}\ \text{F/cm},\quad \rho_Q = 2.651\ \text{g/cm}^3$$
$$K^2 = 7.74\times10^{-3},\quad h_Q = 0.0205449\ \text{cm}.$$

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=7,966[kHz] without any overlayer. Further, we consider the following properties for silver electrodes.

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

Then, we have q_e=0.00594 , f_0=7,997.7 kHz

The experiment provided the conductance G and the susceptance B as a function of the frequency f for the case without overlayer at the room temperature and 11 cases with melted polyethylene at different temperatures, and a typical set of data at a temperature of 83 °C is shown in Fig. 3(a). First, for the unloaded case, we read G_{max} from the radius of a circle matching the Nyquist plot as shown in Fig. 3(b). 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=0.0502cm. This in turn provides the thickness of the PE particle; h_L=0.0184cm. Since the melted particles do not change their shape with temperature, d_L and h_L are fixed in the subsequent calculations. It is true that a parameter set (μ_L, η_L) results in one set of parameters q_{LR} and q_{LI} and therefore one set of values G_{max} and Δf. However as analyzed in the previous section, the inverse is not true. In fact, infinite number of parameter set (μ_L, η_L) can result in a given parameter set G_{max} and Δf. To find the parameter set (μ_L, η_L) corresponding to each of the 11 data set (G_{max} , Δf), we generate a map on the (μ_L, η_L) space as shown in Fig.4. Intersection of contour lines of G_{max} and that of Δf then gives us the parameters μ_L and η_L. Fig. 5. 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.

The measurements of elastic shear modulus and viscosity in Fig. 5 are compared with those of bulk polyethylene in melt state. Because the melt properties are of the movement of much lower frequency, a direct numerical comparison between them is not available. However, the tendencies of the increase of elastic shear modulus and the decrease of viscosity with the frequency elevation of sample movement show that the measurements of this study are comparable to the melt properties. In addition, the effects of temperature variation on the elastic shear modulus and viscosity are the same in the studies. While the instrumental measurement of rheological property is limited to polymer melt, the proposed measurement of this study has a wide range of the measurement providing various possible applications.

CONCLUSION

The relations between 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 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 application of the proposed technique in the field of polymer processing.

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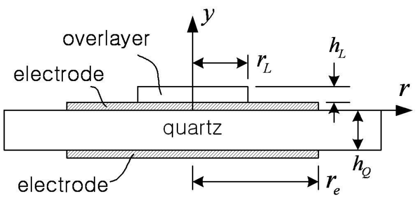
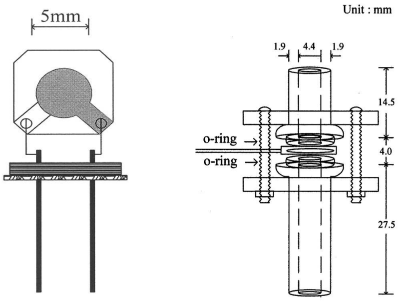
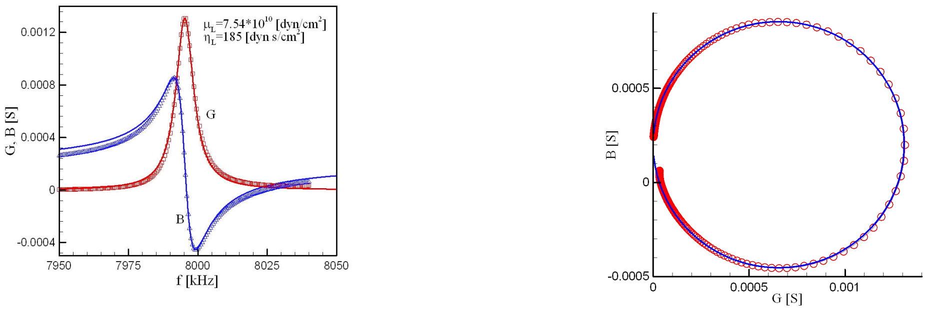


Fig. 1 Sketch of a quartz crystal resonator with electrodes on both sides and a viscoelastic overlayer attached on the external surface of an electrode.



(a) (b)

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



(a) (b)

Fig.3 Comparison between calculated (lines) and measured (symbols) conductance(G) and susceptance (B) at $T = 83[^{o}C]$. (a) in the f-G and f-B planes; (b) in the G-B plane (Nyquist plot).

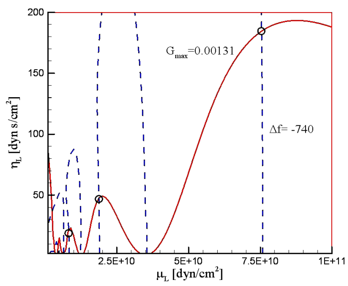


Fig.4 Typical map for determining μ_L and η_L of a viscoelastic overlayer. Solid lines are contour lines for $\Delta f = -740\,[\mathrm{Hz}]$ and dashed lines for $G_{\max} = 0.00131\,[\mathrm{S}]$ at 83 °C .

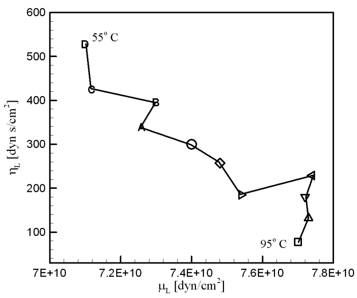


Fig.5 Predicted values of μ_L and η_L of a viscoelastic overlayer at each temperature with fundamental mode of oscillation. The temperature starts from 95℃ decreasing down to 55℃ with 4℃ increment.