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RAPID COMMUNICATION

Measurement of thermal property of polystyrene using dual quartz crystal resonators

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Abstract−A new device using dual quartz crystal resonators is proposed to determine the thermal property and morphological change of polystyrene. The resonators are installed in a small aluminum cell directly heated and air cooled according to the programmed temperature variation. The resonant frequencies of the dual resonators-one for reference and the other for sample-are measured and analyzed for the morphological change while their temperature varies. The temperatures of the changes are compared with the DSC thermogram and previously reported studies, and it is found that the measurements are comparable to those of the DSC. The proposed device is simple and easy to construct, and a portable system is available with some modification.

Key words: Thermal Property Measurement, Quartz Crystal Resonator, Dual Resonator, Morphology Monitoring

INTRODUCTION

The thermal property of polymer is an important factor in selecting a particular material for specific application. The property predicts the variation of mechanical property of polymer in long-term use and high temperature durability, the key characteristic of polymer material selection. A differential scanning calorimeter (DSC) is useful for determining the thermal property of polymer, and it has been utilized in a wide variety of polymer studies, such as thermal property measurement, degradation and crystallization. In spite of the fact that the DSC is good for measuring polymer properties, its availability is limited due to the cost and size of the equipment. It is necessary to develop a small and readily available device to determine the polymer properties.

A quartz crystal resonator comprising two metal electrodes and a thin quartz plate is sensitive to mass changes due to loading on one of the electrodes and the viscoelastic property at the interface of the crystal and its electrode [1] For example, a 9 MHz resonator detects a mass variation of 1.4 ng/Hz from resonant frequency measurement [2] and a viscosity change of 4.3×10^{-6} Pa·s/Ω from resonant resistance [3]. This sensitive detection has been used to measure the adsorbed amounts of a specific components in gas [4,5] and liquid phases [6]. It also detects the beginning moment of crystal formation in crystallization processes [7-10] and the polymerization degree in UV polymerization [11,12]. When a thin film of polymer is coated on the electrode surface of the quartz crystal resonator, the viscoelasticity variation of the film due to its temperature change can be detected by monitoring the resonant frequency of the resonator [13,14]. The thermal property of the polymer changes with varying temperature and its viscoelasticity also varies with temperature. Because the resonant frequency sensitively detects the variation of the viscoelasticity, monitoring the frequency can trace the change of the thermal property.

In this study, the quartz crystal resonator is applied to monitor the variation of thermal property of polystyrene with the programmed variation of temperature. Using a dual resonator system-one for reference and the other for sample-the effect of temperature variation on the frequency is eliminated to determine the intrinsic variation of thermal property. The measurements are compared with those from the DSC for the performance evaluation.

EXPERIMENTAL

1. Materials

Isotactic polystyrene (Sigma-Aldrich Inc., U.S.A., Code No. 450383) having a weight-average molecular weight of about 400,000 and a melting point of 212 °C was used as received. Tetrahydrofuran (THF, J. T. Baker Inc., Canada, HPLC Reagent, Code No. 9440-03) was used as a solvent.

2. Analytical Instruments

Thermal analysis was conducted with a differential scanning calorimeter (TA Instruments Inc., U.S.A., Model Q-10).

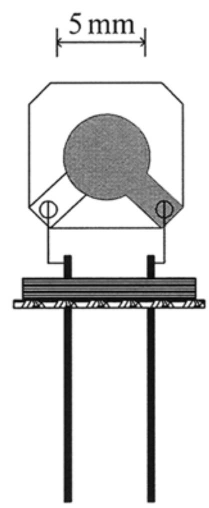

Fig. 1. Schematic diagrams of quartz crystal resonator.

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3. Resonator and Frequency Counter

An AT-cut quartz crystal resonator having a base frequency of 8 MHz (Sunny Electronics Co., Korea) was used in this experiment (Fig. 1). The electrodes of the resonator were silver finished. The resonant frequency and the temperature of the resonator were measured using home-made devices, and an A/D converter was employed for signal processing. The digital signals of the resonant frequency and temperature were provided to a PC for the data analysis.

4. Experimental Procedure

The polystyrene sample is dissolved in tetrahydrofuran at a concentration of 10 wt%, and about 0.1 μL of the solution is spread on the electrode of the resonator. The coated resonator is dried for 10 minutes in air. The cell module holding the quartz crystal resonators is shown in Fig. 2. Two resonators are placed in a small aluminum container of 20 mm in diameter and 15 mm high. Two thin glass plates separate the resonators, and a thermocouple is installed for temperature measurement. While the bottom resonator is used for reference, the top is the sample resonator.

The whole experimental setup is demonstrated in Fig. 3. The heat for the heating cycle is provided by an electric wire heater installed beneath the cell module, and the heat supply is controlled from the PC according to the programmed temperature profile. In the cooling cycle, the heat supply is reduced for the temperature up to 50 °C, and then the heating electricity is cut off. For below the temperature the fan placed at the bottom blows cool air through outside the cell module. The fan speed is also controlled with the signal from the PC.

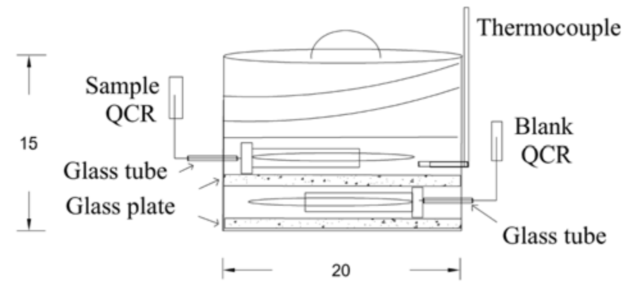

Fig. 2. A schematic diagram of the measuring module.

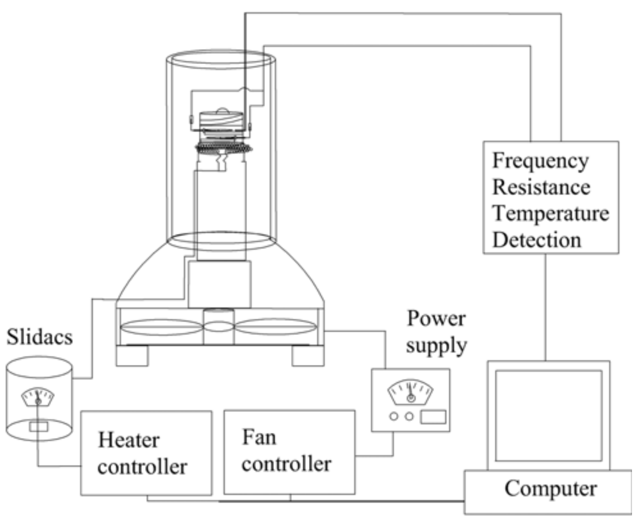

Fig. 3. A schematic diagram of the experimental setup.

5. Frequency and Physical Property Variation

The frequency variation due to the viscosity change of the polymer sample placed on the electrode surface of a quartz crystal resonator is computed from the following equation [15,16]:

$$\Delta f \approx \frac{1}{2\pi\rho_0 h_0}\sqrt{\frac{\rho\eta\varpi}{2}} \tag{1}$$

where f is the resonant frequency, ρ is density, h is thickness, η is viscosity, ω is angular velocity, and the subscript denotes the quartz plate. The subscript 0 denotes the properties of quartz plate, and the properties of the polymer sample are represented without the subscript. As the resonator temperature varies, the viscosity and density of the thin polymer film coated on the resonator surface change and so does the resonant frequency.

RESULTS AND DISCUSSION

In this experiment a reference resonator is used to eliminate the effect of temperature variation on the resonant frequency of the polymer coated resonator. In Fig. 4(a) the frequency difference between the reference and sample resonator is shown with the temperature increase at a rate of 10 °C/min. The DSC thermogram of the same

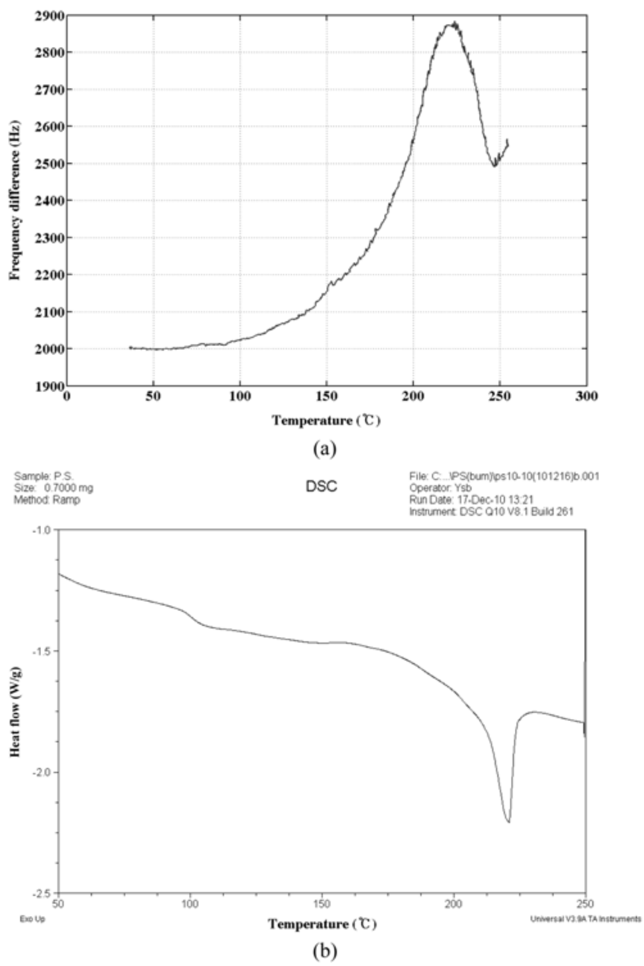

Fig. 4. Measured frequency variation (a) and the DSC thermogram (b) in heating cycle at a rate of 10 °C/min.

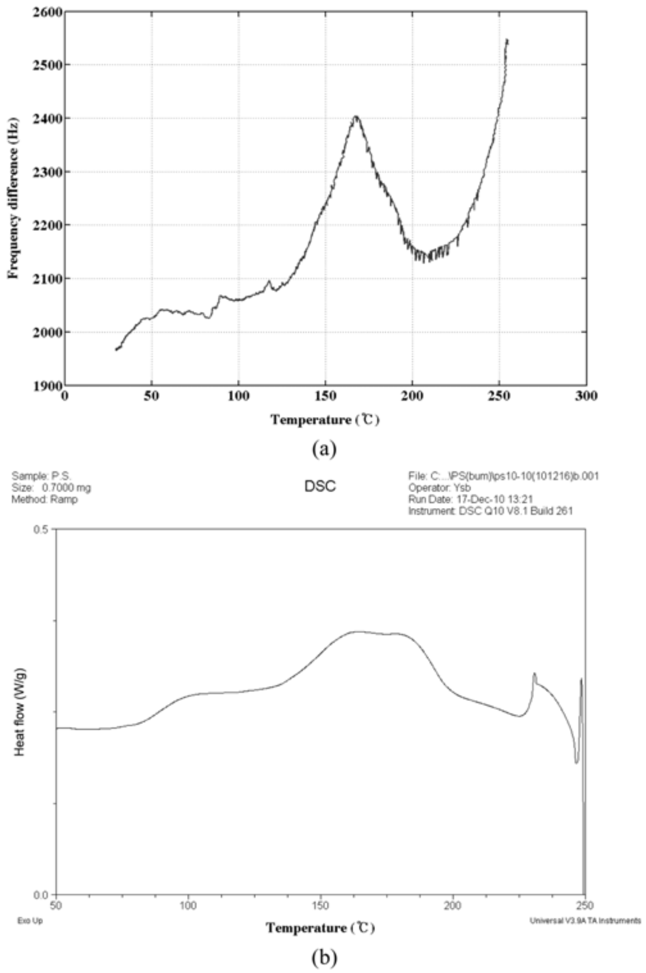

Fig. 5. Measured frequency variation (a) and the DSC thermogram (b) in cooling cycle at a rate of 10 °C/min.

sample and temperature is plotted in Fig. 4(b). Though the direction of slopes is opposite, two curves indicate the deflections at nearly same temperatures. The first slight deflection around 95 °C indicates a glass transition [17], and the second around 150 °C is of cold crystallization. The broad peak centered around 220 °C demonstrates melting of the sample. These observations are found from the DSC thermogram and Yamato and Kimura [17]. While the sample is cooling after complete melting around 250 °C, the frequency difference is demonstrated in Fig. 5(a). The apparent melt crystallization is observed with a peak around 160 °C, while a broad peak around the same temperature is shown in Fig. 5(b). The melt crystallization is observed in the previous studies [17,18]. There are two small peaks around 120 °C and 90 °C. Though the latter is related to the glass transition, the former is not explained with the DSC thermogram and further examination is necessary.

A similar device using single quartz crystal resonator has been proposed in Kim et al. [12], but the detection of the morphological change of polymer material was more difficult than this dual resonator system. Though the proposed device using dual quartz crystal resonators is simple and easy to construct, its performance is comparable to the DSC.

CONCLUSIONS

A simple device measuring the thermal property of polymer using dual quartz crystal resonators is proposed and tested with polystyrene. The dual resonators are installed in a small aluminum cell directly heated and air cooled according to the programmed temperature variation. The resonant frequencies of the reference and polystyrene sample are measured and analyzed for the morphology change when the cell temperature varies. The measured temperatures of the morphological changes are compared with the DSC thermogram and previously reported studies. It is found that the measurements are comparable to those of the DSC though the proposed device is simple and easy to construct.

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