수정진동자를 이용한 고분자 상전이의 측정

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Measurement of Polymer Phase Transition with a Quartz Crystal Resonator

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1. Introduction

Though polymerization degree is an important factor determining the quality of a polymer, its property is also dependent to the morphological structure of solid material. The thermodynamic properties of the polymer are good indicators for the property prediction, and thermo-analytical instruments are often utilized in the property measurements. A differential scanning calorimeter is widely used in the examination of the thermodynamic property of polymer materials.

A quartz crystal resonator comprised a thin quartz crystal sandwiched between two metal electrodes that establishes an alternating electric field across the crystal, causing vibrational motion of the crystal at its resonant frequency. This frequency is sensitive to mass changes and fluid property at the interface of the crystal and its electrode. For example, a 9 MHz oscillator detects a mass variation of 1.4 ng/Hz from resonant frequency measurement and a viscosity change of 4.3 x 10^{-6} Pa·s/Ω from resonant resistance. Because the resonator is so sensitive, it can be utilized to determine a phase change in microscale near the resonator interface without varying the composition of measured solution. The crystal formation and growth in a cooling crystallization has been monitored with the quartz crystal resonator to find the beginning moment of crystallization [1], to determine a metastable zone width, to measure the hysteresis between the processes of crystallization and dissolution and to monitor crystalline nucleation [2]. Also, the resonator was implemented in the monitoring of esterification and crystallization of a dilute lauric acid solution. Another type of phase change was also monitored to determine the dew point of organic vapor mixture.

In this study, the quartz crystal resonator was implemented in the determination of phase transition temperature, in which a DSC is employed. The temperatures of phase transition are determined from the variation of resonant frequency of the quartz crystal resonator. The measurements are compared with the DSC results, and the performance of the proposed device is evaluated with polyethylene.

2. Experimental

2.1 Chemicals

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.

2.2 Analytical instruments

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

2.3 Resonator and frequency counter

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. 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 digital signals of the resonant frequency, resonant resistance and temperature were provided to a PC for data analysis.

2.4 Experimental procedure

The cell module illustrated in Figure 1 is prepared with two glass holders, two o-rings, two bakelite brackets and four screws. The resonator is 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 is assembled, fine particles of polyethylene is obtained by sieving the powder with a

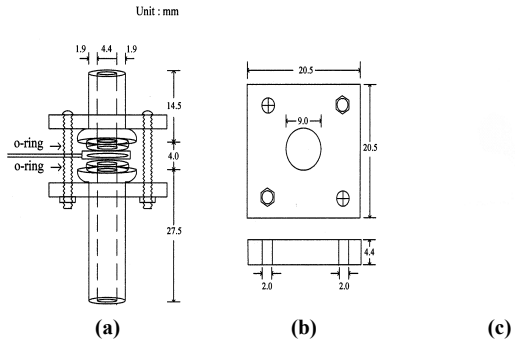

Figure 1. A schematic diagram of resonator cell module (a), holding bracket (b) and quartz crystal resonator.

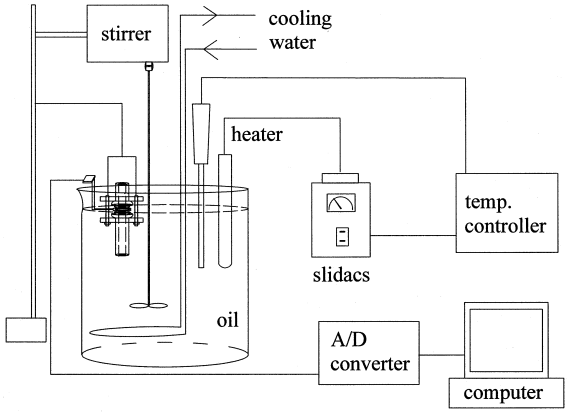

Figure 2. A schematic diagram of experimental setup.

sieve of 250 μm. About one third of 0.1 mg of the polyethylene powder is placed on the top electrode of the resonator. The module is put in an oil bath demonstrated in Figure 2. For the better control of resonator temperature, the module is immersed until the upper o-ring levels with the oil surface. The bath temperature is adjusted by electric heating, and water cooling is also provided for the cooling cycle of experiment. The electric heater is controlled with a programmable temperature controller (Hanyoung Electronic Co., Korea, Model NP-200).

The experiment begins at a temperature of 40 ℃. The setup is stabilized for an hour. The temperature is raised at a rate of 1.5 ℃/min. up to 100 ℃, and is lowered at a rate of 0.5 ℃/min. In two separate runs, the cooling cycles are conducted with rates of 1 ℃/min. and 2 ℃/min., respectively. A PC collects the data of resonant frequency, resonant resistance and bath temperature during the experiment, and the data is analyzed after the experiment.

3. Results and Discussion

While the temperature of oil bath was raised from 40 ℃ to 100 ℃ at a rate of 1.5 ℃/min. and reduced to 40 ℃ at a rate of 1 ℃/min., the variations of the resonant frequency and resonant resistance and temperature are shown in Figure 3. During the temperature elevation up to 90 ℃ no significant change of the frequency is observed, while a slow reduction of resonant resistance is detected. The reduction is from the surface softening of sample due to the temperature increase. When the sample begins to melt, the frequency also decreases until all the sample melts. Initially the solid sample particle is put on the electrode surface, and the contact area is limited. During the melting of the sample the area continuously broadens to reduce the frequency and to raise the resistance. After completion of the melting, the frequency and resistance are stable until melt crystallization starts. As the crystallization proceeds, the frequency steadily drops and the resistance rises. The frequency decrease and the resistance elevation are due to the solidification of the melt.

For the close examination of the frequency variation along with the temperature change, the two are plotted in Figure 4. The steady frequency at the top of the plot suddenly drops at the temperature of 93.3 ℃, at which the melting of polyethylene sample begins.

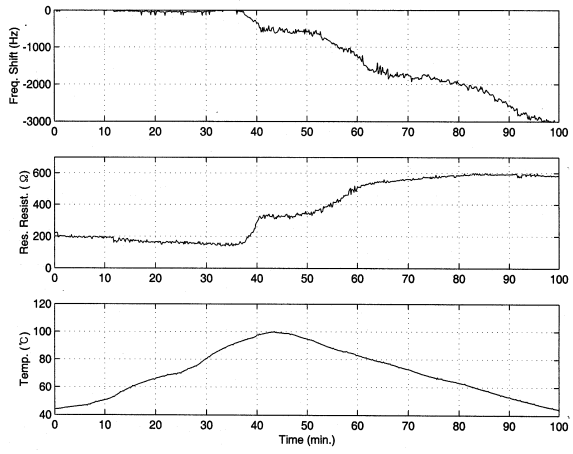

Figure 3. Variations of resonant frequency, resonant resistance and temperature with a cooling rate of 1 ℃/min.

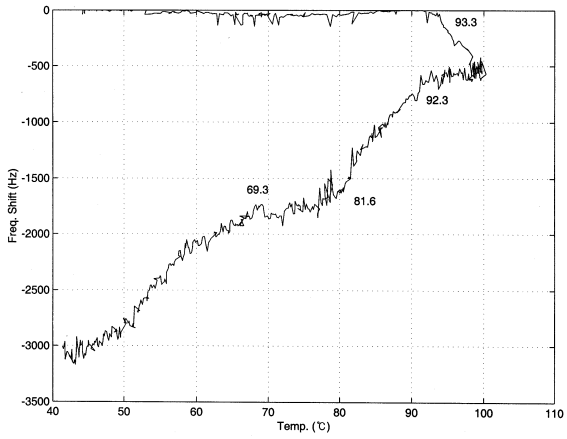

Figure 4. Variation of resonant frequency with temperature. The numbers are the temperatures at the moment of pattern change of the frequency variation.

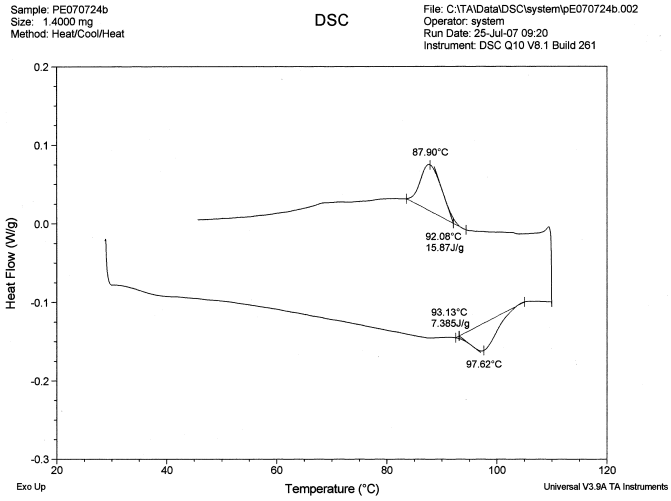

Figure 5. Plot of DSC thermoanalysis.

The frequency decrease stops at 100 ℃ when the melting completes and slowly lowers when the temperature decreases. At the temperature of 92.3 ℃ the frequency reduction is faster due to the crystallization of the melt. In the process of temperature reduction two irregular points of frequency variation are observed at the temperatures of 81.6 ℃ and 69.3 ℃. These are presumed to be phase transition points.

The observation of the proposed device of a quartz crystal resonator was compared with the DSC analysis shown in Figure 5. The beginning temperatures of melting and crystallization are 93.13 ℃ and 92.08 ℃, respectively, and the observed results are quite comparable to the DSC analysis. Two distinct observations of phase transition are not clearly indicated in the DSC outcome.

4. Conclusion

A monitoring device to observe phase transition of a polymer sample was proposed, and its performance was examined with polyethylene sample. The proposed device utilizes a quartz crystal resonator and its resonant frequency was implemented in the analysis of monitoring process. The experimental results indicate that the device shows the temperatures of polymer melting and crystallization, and the temperatures of phase transition between monoclinic and hexagonal phases are also determined. The comparison with the outcome of DSC analysis demonstrates the effectiveness of the proposed device.

Acknowledgement

Financial supports from the Korea Science and Engineering Foundation and the Korea Energy Management Corporation are gratefully acknowledged.

References

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[2] Maeda, K.; Kim, B. C.; Kim, Y. H.; Fukui, K. Anal Chim Acta 2006, 558, 337-344.