

Measurement of Toluene Solubility in PVAc Using a Quartz Crystal Microbalance

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PVAc에서 Quartz Crystal Microbalance를 이용한 톨루엔의 용해도 측정에 관한 연구

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ABSTRACT : The resistance and frequency change of a quartz crystal microbalance during toluene absorption was measured for poly(vinyl acetate) (PVAc) with 268 nm thickness. Solubility of toluene in PVAc were measured at temperatures from 25°C to 42°C and pressures up to 28.4 torr. The frequency of a quartz crystal microbalance increased with increasing temperature and decreased with an increase in toluene vapor pressure. The resistance of a quartz crystal microbalance increased with increasing toluene vapor pressure and decreased with an increase in temperature. A greater pressure of toluene results in a greater solubility of the toluene into the PVAc film. The change of solubility was calculated by Sauerbrey equation.

요 약 : 268 nm 두께의 PVAc가 코팅된 수정결정 미소저울(QCM)을 사용하여 저항과 진동수 변화를 측정하였다. 이를 이용하여 온도(25°C~42°C)와 톨루엔의 증기압(12.4~28.4 torr) 변화에 따른 톨루엔의 폴리비닐아세테이트에 대한 용해도를 측정하였다. 진동수는 온도가 증가함에 따라 증가하였으나 톨루엔의 증기압이 증가하면 감소하는 경향을 보였다. 톨루엔의 온도가 증가함에 따라 저항은 감소하였으며, 증기압이 증가하면 저항도 증가하는 경향을 나타내었다. Sauerbrey 식을 이용하여 온도와 압력변화에 따른 용해도 변화를 측정하였다.

Keywords : QCM, PVAc, frequency, solubility

I. Introduction

The solubility of vapors of low molecular weight substance in polymers is important in the design and operation of polymer plants. The removal of residual monomers, oligomers, and polymerization solvents from the produced polymers requires this know-

ledge. While vapor-liquid equilibria and solubility data have been measured for many years and are available in the literature, the data are limited in the number of systems and in the experimental conditions available.^{1,2}

The exploration of the properties of thin materials is a vital area of interest for the burgeoning field of technology, especially with regard to lubrication, adhesion, and biomaterials. The importance of un-

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derstanding the interaction of surfaces and interfaces of polymeric materials is now a critical necessity if the world wishes to advance its pursuit of reducing the size of modern technologies. With this understanding of the role of documenting these properties, the quartz crystal microbalance (QCM) was used to study thin films of polymer.

The QCM is a very sensitive tool to detect changes in weight and thus a helpful method to sense adsorption processes at solid/gas or solid/liquid interfaces. The basis of the QCM is a thin quartz exhibiting the inverse piezoelectric effect. Applying an alternating current excites a mechanical oscillation of the quartz plate. Using the specific resonance frequency of the quartz leads to a direct proportionality of the mass load and the frequency change. This effect was first found by G. Sauerbrey in 1959. Due to this property quartzes are for example used in evaporating chambers. Since the eighties the QCM is also applied as a biosensor. An advantage of this technique is the possibility to coat the quartz with thin layers of any material.

The application of QCM devices for sensing chemical vapor was first described by King and has remained an active research field.³ This technique has been applied by many researchers for the solubility measurement of organic vapors and high-pressure gases in polymers.^{4,11} The method has high sensitivity and offers the advantage of generating data much more rapidly than alternative gravimetric methods such as electronic and quartz spring microbalances as shown by Mikkilineni et al., French and Koplos, and Boudouris et al.¹¹⁻¹³

In this study, a QCM apparatus was used to determine the solubility of toluene in PVAc at various temperatures and pressures.

A 5.0 MHz crystal was initially coated and found to have a thickness of 268 nm. The solubilities of this coating in a toluene atmosphere were studied at varying temperatures using two different methods. The first included a constant toluene atmosphere while varying the temperature of the crystal chamber from 25°C to 42°C. The second method included

holding a constant crystal temperature while varying the toluene atmosphere. In addition to exploring solubilities of toluene in the PVAc thin film, the properties of the film were studied in a vacuum of much less than one torr.

II. Experimental

1. Materials

Poly(vinyl acetate) (PVAc, $T_g = 30^\circ\text{C}$, $M_n = 1.67 \times 10^5$) and Toluene (>99.5% purity) were purchased from Aldrich. Characteristic of the polymer was reported by the supplier.

2. Apparatus and methods

A diagram of the apparatus is shown in Figure 1. The sample chamber is a stainless steel pressure vessel that houses the holder for the quartz crystal. Sealed tubing goes from the crystal holder through one of the chamber ranges and carries wiring to instruments outside the chamber. The holder has gold leads that connect to the back side of the crystal when it is snapped into position. This provides connection to the electrical signal from the frequency oscilloscope. The output resonant frequency is collected on computer. A thermocouple wire is inserted into one of the sealed tubes going into the crystal holder. In this way, the temperature vary close to the crystal can be monitored during an experiment. This thermocouple is also connected to a PID temperature controller that powers heating tapes wrapped around the chamber. When insulating tape is mapped on the outside and fiberglass insulation is secured to the sides of the chamber flanges, the temperature inside was controlled to within $\pm 0.1^\circ\text{C}$. Tubing going through the other chamber flange connects to lines for vacuum, solvent source and argon. When the solvent is a liquid at ambient conditions, as in these PVAc/toluene experiments, it is placed in a glass boiler that is connected to the incoming line. The controlled temperature of the boiler determines the vapor pressure of solvent that will be

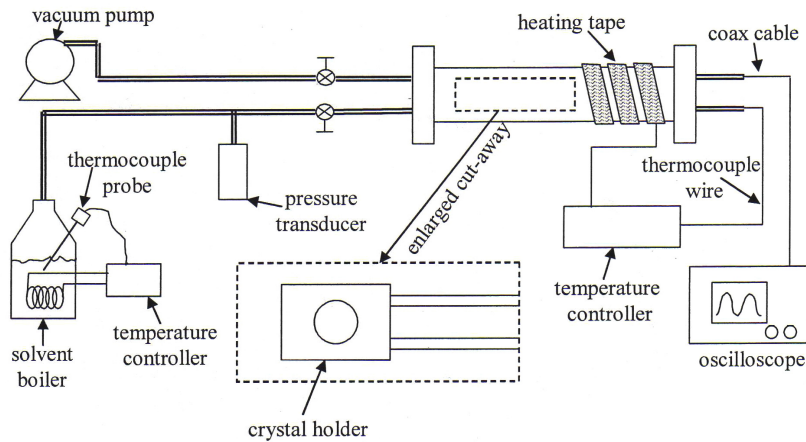


Figure 1. Schematic diagram of the quartz crystal microbalance apparatus.

maintained during the experiment. A pressure transducer in the solvent vapor line provides a check of the pressure and also monitors for leaks. The vacuum line is used to evacuate the chamber as well as degas the solvent in the boiler. The argon line is used to pressurize the system to check for the location of leaks.

6 MHz quartz crystals were used in the experiments. They were circular and approximately 1.4 cm in diameter. The first step was to measure the resonant frequency of the clean uncoated crystal. It is the frequency change after the coating is added that will determine the mass and thickness of polymer, which is too small to be measured by a microbalance. Once the bare crystal frequency is measured, the polymer coating is applied. A spin coater is used to rotate the crystal at high speed while a drop of dilute PVAc-toluene solution, on the order of 1% polymer concentration, is placed in the center. After two minutes of spinning, the majority of the solvent has evaporated. The remainder is removed by placing the crystal in a vacuum oven at 90°C for 30 minutes. The coated crystal is then placed in the QCM sample chamber at 40°C under vacuum and the frequency is recorded.

The difference in frequencies allowed for the determination of the mass of the thin film by the

Sauerbrey Equation. This equation shows the direct relationship of the change in frequency to the change in mass. This equation is only valid for rigid masses attached to the crystal and only in air. It has been determined from other works that when a coating of a polymer is sufficiently thin, the polymer coating is able to be considered a rigid mass, allowing for the use of this equation.

$$\Delta f = \frac{-2\Delta m f_0^2}{A \sqrt{e_g u_g}} \quad \text{Sauerbrey Equation} \quad (1)$$

A = Active Area of Crystal

ρ_q = Density of Quartz

μ_q = Shear Modulus of Quartz

f_0 = Resonant Frequency of the Crystal

Δf = Frequency Change

Δm = Mass Change

$$\log P = A - B/(T + C) \quad \text{Antoine Equation} \quad (2)$$

P = Vapor Pressure

T = Absolute Temperature

A, B, C = Coefficient

The crystal was then placed in the QCM and the computer was used to collect data which recorded

frequency and resistance. Data were collected a 1.0 °C intervals from 25 °C to 42 °C in a vacuum. This was done three times in order to ensure the trend was correct. These data were used as a background in order to calculate solubilities.

Once the vacuum data had been obtained, a toluene atmosphere was introduced. This was done using a temperature controlled boiler with high purity toluene. The pressure of toluene present was calculated using an Antoine equation. The pressures were low, ranging from 10 to 30 torr. The solubility of toluene was calculated using the Sauerbrey equation in terms of mass fraction.

III. Results and Discussions

1. Frequency and resistance of bare crystal

After coating the crystal, the first data that was collected was the vacuum frequency. This was done in order to explore how thin film responds to changes in temperature.

Figure 2 display the linear relationship between frequency and temperature of the crystal. This is also present for a bare crystal. As the temperature of the crystal increases, the modulus of the crystal increases and lowers the frequency.

A toluene atmosphere was then introduced into the QCM chamber in order that solubility could be investigated. The pressures of toluene introduced range from 12.4 to 28.4 torr which corresponds to toluene boiler temperatures of 10 °C to 25 °C. Higher pressures could not be explored because the temper-

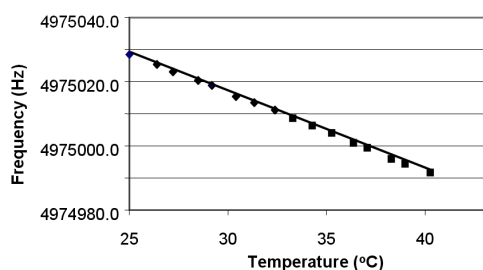


Figure 2. Relationship between frequency and temperature of the bare crystal.

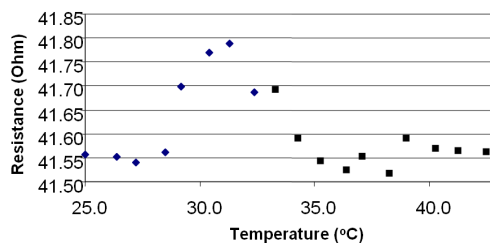


Figure 3. Relationship between resistance and temperature of the bare crystal.

ature of the boiler could not be higher than the temperature of the chamber. This would lead to condensation of the toluene in the chamber.

2. Frequency and resistance of PVAc coated crystal

As Figure 4 displays, the introduction of toluene reduced the frequency of the crystal. This is due to the mass adsorption of toluene into the thin film of PVAc. As the temperature increased, the difference between the vacuum and the toluene atmosphere leads to the conclusion that the solubility of toluene decreases with temperature. This trend was seen in all of the toluene atmospheres including 12.4, 16.5, 21.5, and 28.4 torr. Figure 5 displays the frequencies of all of the different atmospheres versus temperature. Figure 6 shows the resistance and temperature relationships. It appears that the

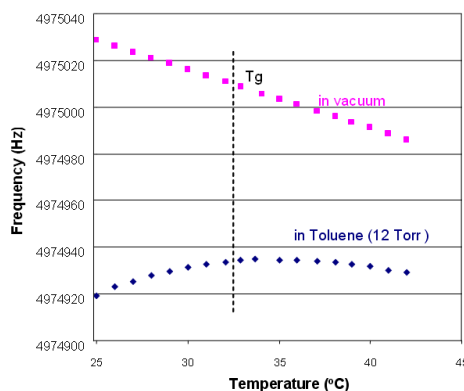


Figure 4. Relationships between frequency and temperature in vacuum and in 12 torr toluene atmosphere of PVAc coated crystal.

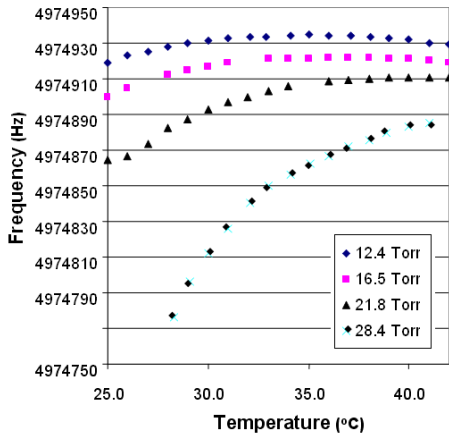


Figure 5. Relationships between frequency and temperature at various toluene atmospheres.

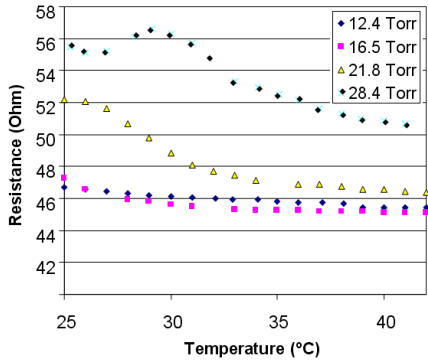


Figure 6. Relationships between resistance and frequency at various toluene atmospheres.

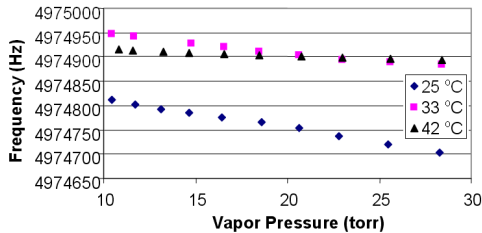


Figure 7. Relationships between frequency and vapor pressure at constant chamber temperature.

higher toluene pressures have a higher resistance with coated crystal. This may be due to the plasticizing effect of toluene which would increase the modulus and thus make it more difficult for the crystal

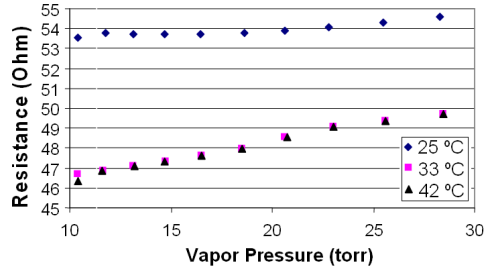


Figure 8. Relationships between resistance and vapor pressure at constant chamber temperature.

to resonate.

In addition to the constant toluene temperature and varying temperatures tests, the temperature of the chamber was held constant while varying the pressure. Figures 7 and 8 show the response of frequency and resistance to these variations respectively.

3. Solubility of PVAc coated crystal

The change in frequency of the crystal in the vacuum to the toluene atmosphere allows for the calculation in solubilities. The change in mass can be calculated using the Sauerbrey equation and thus the mass of the toluene is able to be calculated. Figure 9 is shown with the solubilities of the four different pressures. This data was collected with a constant toluene pressure and varying the temperature of the crystal. The solubilities increased with toluene pressure and decreased with an increase in temperature.

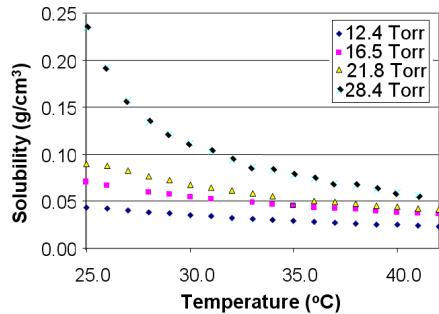


Figure 9. Relationships between solubility and temperature of toluene in PVAc.

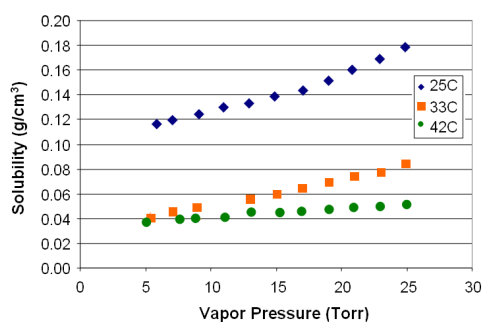


Figure 10. Relationships between solubility and vapor pressure of toluene in PVAc at constant chamber temperature.

Another method that was used to calculate solubilities included holding the temperature of the crystal constant while varying the toluene pressure. Figure 10 displays the calculated solubilities from this experiment. It should be noted that the solubilities of toluene in PVAc increased with increasing toluene vapor pressure and decreased with an increase in temperature.

The two methods used to determine solubilities had various advantages and disadvantages. The method of varying the pressure while holding the crystal temperature constant took only about half the time to perform. The method of varying the crystal temperature gives a broader range of data. Because they are both time consuming and yield basically the same information, only the test determined to be superior will be performed.

IV. Conclusions

The resistance and frequency change of a quartz crystal microbalance during toluene absorption was measured for poly(vinyl acetate) (PVAc) with 268 nm thickness. Solubility of toluene in PVAc were measured at temperatures from 25 °C to 42 °C and pressures up to 28.4 torr. The frequency of a quartz crystal microbalance increased with increasing temperature and decreased with an increase in toluene vapor pressure. The resistance of a quartz crystal microbalance increased with increasing toluene va-

por pressure and decreased with an increase in temperature. The higher temperatures result in lower solubility of toluene. Also a greater pressure of toluene results in a greater solubility of the toluene into the PVAc film.

Acknowledgement

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