Novel Applications of the QCM Technique in Biomaterials Science

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ABSTRACT

A quartz crystal microbalance (QCM) has been used to investigate polymer samples. The vapor sorption of three different polymer samples (poly(vinyl acetate), polybutadiene and polydimethylsiloxane) was studied. The change in resonance frequency of the quartz sensor uniformly coated with polymer films was measured as a function of the film thickness and water absorption at different temperatures. The range of linear frequency vs. mass response was determined in the absence of absorbed water. The glass transition temperature of thin poly(vinyl acetate) films (10 nm <thickness< 1000 nm) was found to be in reasonable agreement with published values for macroscopic samples.

INTRODUCTION

The capability of precisely measuring the water absorption from the environment is of great importance in a variety of applications. The physical properties of both synthetic and biopolymers are significantly affected by the hydration of the macromolecules. Furthermore, in many biological applications, it is important to know the relation between water content and function [1, 2].

Sauerbrey [3, 4] showed that, for rigid thin films attached to the quartz crystal, the resonant frequency of the crystal (ΔF) decreases as the mass deposited per unit area (Δm) increases:

$$\Delta F = - C \cdot \Delta m / n \qquad (1)$$

where C is dependent on resonant frequency, density and shear velocity of sound waves in the crystal, and n is the overtone number. The interest in models to explain the deviation from the ideal Sauerbrey regime is vast [5-8], but not investigated in this work.

While the QCM technique has been used extensively to investigate adsorption from solution [9] only a few studies have utilized its ability to detect controlled changes in the vapor pressure of the surrounding environment [10-13]. Recently, we developed a high sensitivity vapor pressure osmometer [10] that allows us to determine the water absorption of very small (>1 microgram) samples. In the present work we report experimental results obtained by this QCM technique for the hydration of polymer films.

EXPERIMENT

Sample Preparation

Gold electrode quartz crystals were used in all QCM measurements. They were cleaned under UV light for 10 minutes, then rinsed first in a 2% SDS solution for 30 minutes and then in distilled water for 10 minutes before drying in a N_2 flow. Finally, the crystals were exposed to UV light for 10 more minutes before being used.

The polymer samples: poly(vinyl acetate) (PVAc), polybutadiene (PBu) and polydimethylsiloxane (PDMS) were purchased from Sigma-Aldrich. The molecular weights of the polymers were: 113,000 (PVAc), 60,900 (PBu), and 95,000 (PDMS).

PVAc and the PDMS were dissolved in toluene and PBu in cyclohexane. The polymers were uniformly deposited on the surface of the quartz crystal and air dried before being placed in the measurement chamber.

QCM Experiment

A QCM with dissipation monitoring capability [14] was used. The range of linear behavior of the QCM was determined using different concentrations of poly(vinyl acetate) solutions in toluene (from 0.02% to 2% (w/w)). They were uniformly deposited on quartz crystals (at 27°) and ΔF was measured until all the solvent was evaporated.

Experiments were performed to determine the sensitivity of the instrument to temperature by first monitoring the response of bare quartz crystals and then of quartz crystals coated with the three different polymers studied here. These temperature dependence experiments were done with no water vapor flow, in the range of 27°C to 40°C, at different heating/cooling rates.

Finally, the swelling/deswelling experiments on the polymers were done at fixed temperature (27°C). The swelling was induced by constant flow of water vapor in the sample chamber.

RESULTS AND DISCUSSION

Determination of the range of linearity

Figure 1 shows the dependence of ΔF as a function of the mass of the polymer film deposited on the surface of the crystal. The data clearly indicate that ΔF decreases linearly with increasing mass over the range $0 < \text{mass} < 0.15$ mg cm^{-2}. Above m = 0.15 mg cm^{-2} the deviation from the linear response becomes pronounced. In this paper we report data measured in the linear range, in which the Sauerbrey equation provides a satisfactory description of the data.
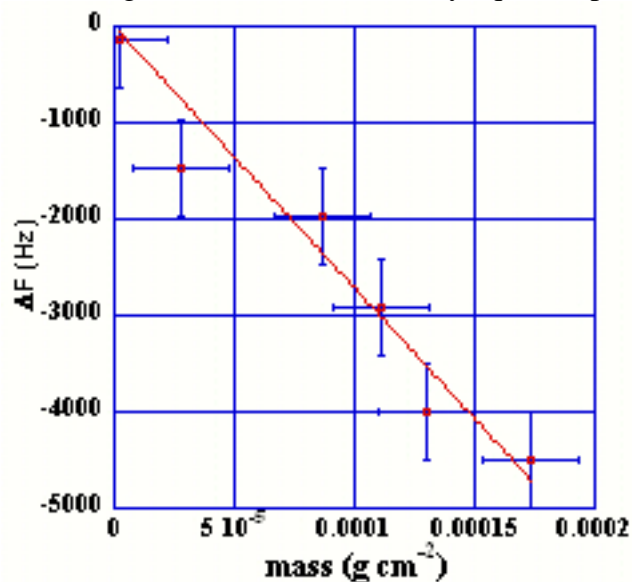
Figure 1: ΔF as a function of mass/unit area of the crystal.

Determination of the temperature response of the quartz crystal

Since the water sorption of materials varies with the temperature it is important to know the temperature dependence of the resonance frequency. It is also necessary to know if there is any temperature related contribution from the uncoated quartz crystal, in the range of 27°C to 40°C, so the data may be corrected. In Figure 2, data obtained by different heating/cooling rates are displayed. It can be seen that ΔF increases with increasing temperature and the area of the hysteresis loop decreases as the heating rate decreases. Hysteresis was found to be negligible below 0.02°C/min. These findings are consistent with the known temperature dependence of AT quartz crystals [15]. These quartz crystals are cut to show almost no frequency-temperature change at around 20°C, but the frequency changes considerably when the temperature is below or above 20°C.
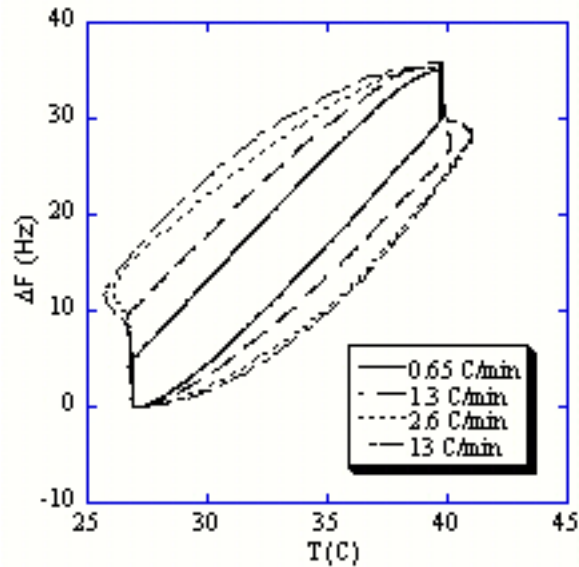
Figure 2: Frequency response of the bare quartz crystal at different heating/cooling rates. The area of the hysteresis loop increases with the heating rate.

Temperature dependence of the mechanical response of polymers

The physical properties of polymers depend on the temperature and the time allotted to perform the experiment. In general, amorphous polymers are glassy and brittle below the glass transition temperature (Tg). Above Tg the segments of the polymer molecules move relatively freely and the polymer becomes rubbery.

Table I shows the Tg for the three polymers studied here. The temperature dependence of ΔF was measured over the range 27°C to 40°C, at 0.65ºC/min for each polymer (Figure 3). The experimental swelling/deswelling data reported here were corrected for the temperature dependence of the quartz crystal determined independently for each sample.

Table I: Tg for different polymers.

| Polymer	Tg	Molecular Weight
PVAc	29°C[16], 28°C[17], 32°C[18].	113,000
PDMS	-123°C[16]	95,000
PBu	-85°C[16]	60,900

Figure 3 reveals important differences between the three samples. For both PDMS and PBu ΔF is practically independent of the temperature since the experimental temperature range was well above their glass transitions. However, in the case of PVAc, ΔF first decreases and then increases (between 31.5ºC and 34ºC) with increasing temperature. We attribute this behavior to changes in the segmental mobility as PVAc undergoes a glass-rubber transition at about 32°C (see Table I).
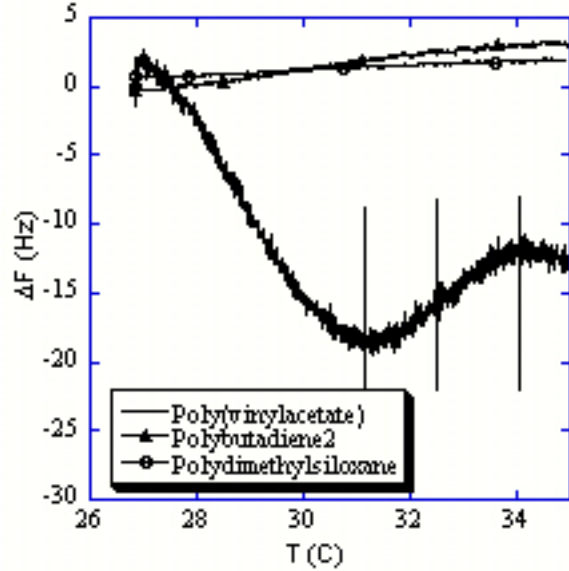

Figure 3: Temperature dependence of the QCM response for different polymers.

Measurement of water sorption of polymer films

Figure 4 a-c, show the results of swelling/deswelling experiments made on the three polymers at 27°C. The water uptake of PVAc significantly exceeded that of PDMS and PBu. PVAc absorbed 8.6 µg/cm^2 of water vapor, while PDMS and PBu absorbed 68.8 ng/cm^2 and 11.6 ng/cm^2, respectively. It is important to note that the swelling/deswelling process was reversible and the amount of water vapor absorbed by each of the polymers was reproducible.

(a)

(b)

(c)
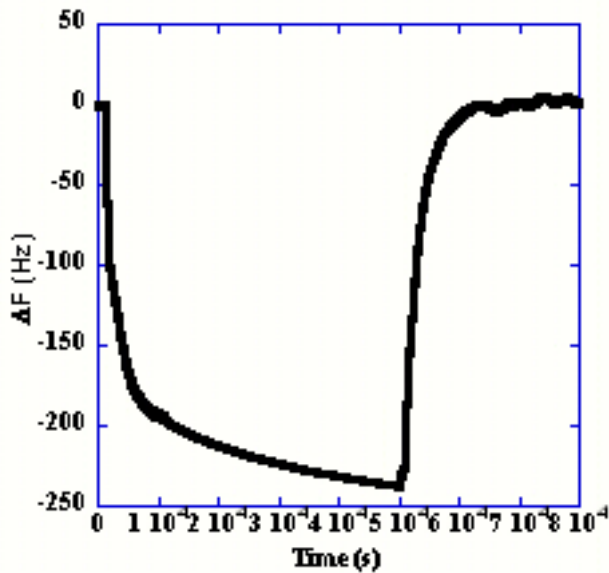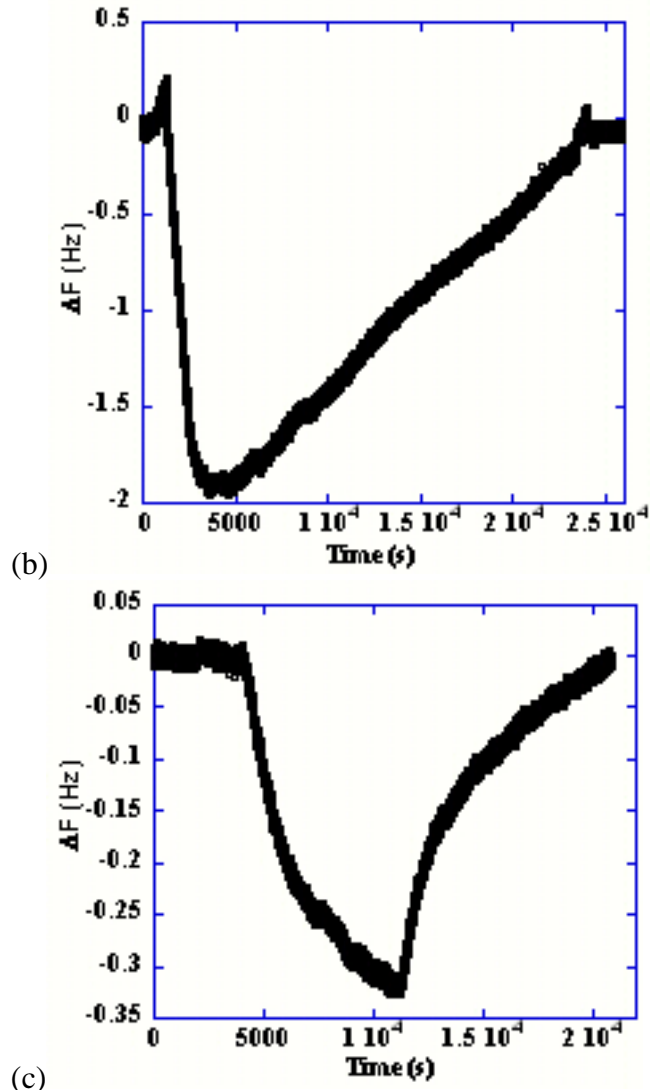
Figure 4: Results of the swelling/deswelling experiment for: (a)PVAc, (b) PDMS and (c) PBu.

CONCLUSIONS

Two applications of the QCM technique were demonstrated here for polymers. Corrections have also been suggested to improve the accuracy of mass data from QCM measurements at different temperatures and heating rates. It is important to obtain the temperature response of the quartz crystal alone before performing the experiment with the sample.

It was demonstrated that the QCM technique can be used to determine the amount of water absorbed by thin polymer films and that the swelling/deswelling process is reversible. The bare quartz crystals did not contribute to the water absorption of the polymers. Furthermore, QCM detects changes occurring in the vicinity of the glass transition temperature of polymer films. It was possible to estimate the Tg for PVAc, with good agreement compared with published values obtained for macroscopic samples.

The QCM technique proved to be appropriate for observing small samples, making it well suited to the study of biological specimens (e.g., biological tissues, cells) at different osmotic swelling pressure and at body temperature.

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