Behavior of QCM in Response to Heavy Loading of Polystyrene under Ambient Condition

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Yoshimi Seida [*]

Abstract

QCM resonance oscillation in response to heavy mass loading was examined using polystyrene（PS）as an elastic mass load. The behavior of QCM was observed with admittance analysis of the QCM oscillation. The mass effect was monitored by f_2 (the frequency independent of viscosity influence) as well as resonance frequency f_s. The dynamics of QCM behavior in response to the heavy loading was investigated based on the phenomenological process occurring on the QCM.

Keywords: QCM-A, Viscoelasticity, Mass Effect, Heavy loading

1. INTRODUCTION

Heavy load on QCM and temperature drift are the major factors inducing unstable drift of resonance frequency of QCM. Under the heavy loading, classical QCM was not able to keep its stable oscillation due to lack of enough electric power supply for its stable oscillation. Modern quartz crystal microbalance maintains its stable oscillation even under condition contacting rather heavy loading media [1-5]. Heavy load induces discontinuous red-shift of resonance frequency departing from the load mass *vs*. frequency shift relation (Saubray's equation) [6]. It will be due to a stress induced in quartz by the heavy load. Goka *et al*., observed the stress distribution in quartz during its oscillation [7]. This behavior is obviously observed when QCM measurement is applied to identify viscoelastic phase behavior of water during its freezing-thawing process [8,9]. The red-shift of resonance frequency also occurs when loading mass increases due to liquid-solid transition (freezing of water). The red-shift under heavy loading is completely opposite phenomena to the conventional knowledge of frequency shift Δf_s *vs*. loading mass change Δm linear relation (Sauerbrey's equation). The shift of resonance frequency Δf_s of QCM proportionally depends on the Δm within a range of small loading. When the load exceeds beyond the range of Δf_s *vs*. Δm linear relation, the

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red-shift of resonance frequency occurs at some amount of large loading.

In the present study, influence of heavy mass loading on the response (resonance behavior) of QCM was examined using polystyrene (PS) as an elastic load. The resonance frequency f_s and the resonance resistance R_1 (=1/G) of the QCM oscillation in response to heavy load application were measured. The dynamics of QCM response by the application of polystyrene dissolved in toluene (volatile good solvent of PS) was investigated in relation to the process occurring on the QCM from the instillation to drying of the loading sample. This study was performed by two analyzes. The resonance frequency and the resistance were measured via a step-wise loading of the polymer beyond the range of Δf_s *vs*. Δm linear relation at first. Then, monitoring of dynamic behavior of QCM in response to the heavy mass loading was carried out.

2. QCM MEASUREMENT AND ANALYSIS

QCM-A was used in this study. Details of QCM-A are reported elsewhere [10,11]. Mathematical equivalency between mechanical model of the QCM and LCR electric circuit model under forced oscillation enables viscoelastic measurement of loading sample on QCM by means of admittance analysis of the oscillation system based on the LCR model (Fig.1). The admittance analysis was carried out using network analyzer. The parameters L_1, C_1, and R_1 in the LCR model correspond to the loading mass (m), inverse of elasticity (C_m) and viscosity (r) in the mechanical model of QCM, respectively. The resonance frequency f_s defined by the frequency at maximum conductance G_{max} was determined from the G profile shown in Fig.2. The R_1 was evaluated from the inverse of G_{max}. The frequency f_2 at minimum suseptance (B_{min}) and half maximum of conductance ($G_{max}/2$) is known to be independent from the viscosity influence of contacting media in some cases [12,13]. Thus, the f_2 was also monitored in this study.
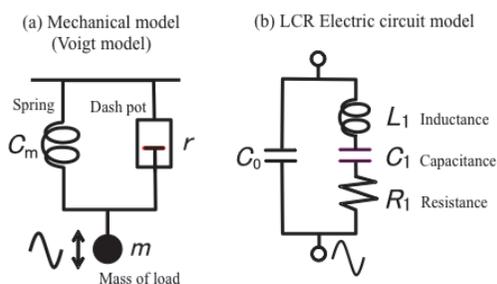
Fig. 1   Comparison between the model of QCM and the LCR model

$$L_1 = \frac{R_1}{2\pi(f_2 - f_1)} \,,\; C_1 = \frac{1}{(2\pi f_s)^2 L_1} \,,\; R_1 = \frac{1}{G_{max}}$$
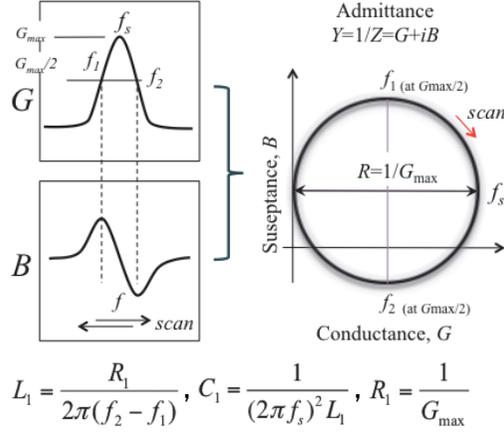
Fig. 2   Schematic diagram of the admittance analysis

3. EXPERIMENTAL

3.1   Sample and apparatus

   5MHz AT-cut QCM with gold electrode was used. Temperature of the QCM was controlled precisely via peltier device with resolution ±0.1K. Network analyzer R3755A (Advantest Co.) was used for the admittance analysis. In the case of overlapping peaks, peak position and its intensity were determined by multi-peak fitting tool installed in Origin software. Reagent grade chemicals were used without further purification.

3.2   Approach

   At first, observation of QCM behavior in response to the step-wise instillation of polystyrene was carried out. The loading was carried out step by step until a red-shift of resonance frequency appeared. Polystyrene (PS) dissolved in toluene (20mg/5mL) was used in this study. The use of polymer dissolved in volatile good solvent accompanies evaporation of the solvent after the instillation of polymer solution on the QCM so that the dynamics of QCM will necessarily be complicated. Then, monitoring of QCM behavior in response to the instillation of the polymer solution was performed to investigate the dynamics of QCM response after the instillation of the sample until reaching stable state of the QCM oscillation.

3.3   Procedure of analysis

   Behavior of QCM in response to the heavy loading of elastic polymer was observed as follows. The PS obeys the Sauerbray's Δf_s *vs*. Δm linear relation within the range of small

loading on QCM. 1µl of instillation of the PS solution prepared in this study results in 1000ng-PS loading on the QCM. Each 1µl sample was loaded step by step with a time interval that was enough to evaporate the solvent toluene under ambient condition. The admittance was monitored during the experiment to collect the f_s, f_2 and G_{max} (=1/R_1) data in each sample loading to identify the influence of loading mass on both the f_s, f_2 and R_1. Dynamic behavior of QCM response during the sample instillation ~ the drying process was monitored carefully until reaching a stable resonance frequency.

4. RESULTS AND DISCUSSION

4.1 QCM behavior in response to the stepwise loading of the PS

Fig.3 indicates the relationship between the loading mass and the frequencies (f_s, f_2). In the case of small amount of loading, the resonance frequency f_s obeys the Sauerbrey's equation that is well known ordinary $\Delta m - \Delta f_s$ linear relation. When the load exceeds more than the linear range of the Sauerbrey's equation, another resonance peak gradually appeared with the increase of loading mass at frequency that is higher than the fundamental one of the QCM. The frequency of the 2nd peak was also monitored.
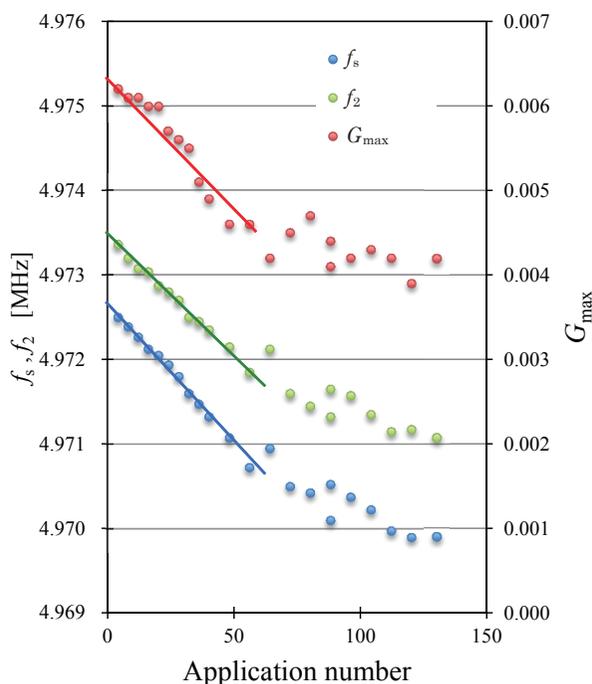
Fig. 3 Relationship between the loading mass and the resonance frequency.

The 2nd peak also obeys the linear relationship of Sauerbrey's equation. The frequency of 2nd peak is much lower than overtone frequency of the QCM and is not spurious mode one of resonance but due to the heavy loading. X-ray topography of stress pattern on the QCM surface indicated the existence of various oscillation modes [7,14].

4.2   Dynamics of QCM response

Figs.4(a)~(c) indicate the conductance G profile, suseptance B profile and admittance plot during the instillation ~ dry process of the PS sample. The response of QCM was classified into three stages as shown schematic diagram in Fig.5. The schematic image of the G profile along with phenomenological event on the QCM was depicted in the figure.

Stage I: Just after instillation of sample solution onto the QCM, rapid increase of the peak intensity (the G_{max} value corresponding to the increase of diameter of admittance circle) is observed followed by red-shift of the peak with the increase of G_{max} value.

Stage II: Then rapid blue-shift of the resonance frequency f_s occurs with decrease of the peak intensity. Evaporation of solvent toluene becomes obvious in this stage
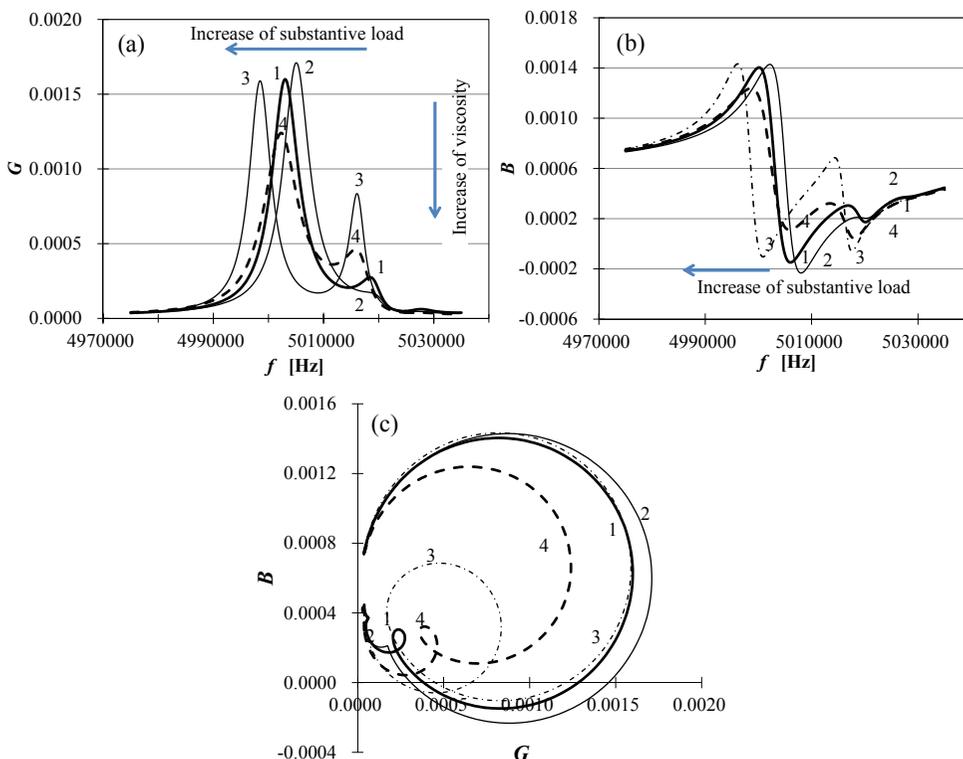
Fig. 4   Details of resonance behavior profile in response to the loading of PS dissolving in toluene (a) change of conductance G, (b) change of suseptance B profile and (c) admittance plot

causing the increase of penetration depth of QCM shear wave due to the decrease of solvent in the polymer, which resulted in the increase of substantive loading mass and viscosity of the load on the QCM. The load on the QCM increases after a major amount of evaporation of toluene that dissipated the shear wave propagation of QCM in the swollen phase.

Stage III: The G_{max} value increases gradually with a slight red-shift of the peak. This last process occurs taking a long period of several hours. After the major amount of evaporation, remaining toluene in collapse network of PS works as loading mass rather than the dissipation media of the shear wave, resulting in the large blue-shift (decrease) of resonance frequency f_s. The blue-shift means the increase of substantive load on the QCM. The solvent immobilized in the polymer network that would bind to the polymer then works as load with the collapse of polymer network. This results in the increase of substantive load and large blue shift of f_s. After that, increase of f_s again occurs due to decrease of loading mass by further evaporation of solvent from the polymer. At this third stage, increase of resonance frequency again occurs due to further evaporation of the toluene from the network of PS, resulting in the decrease of load with an increase of viscosity of polymer. The drying process in this stage was slow and took a long period. The f_s increased with increasing its intensity during the dry process indicating the decrease of mass load and viscosity. After the long period of drying, the f_s decreased below the value at the instillation, indicating the increase of load at last. The change of f_s, f_2, and G at each stage is shown in Fig.6
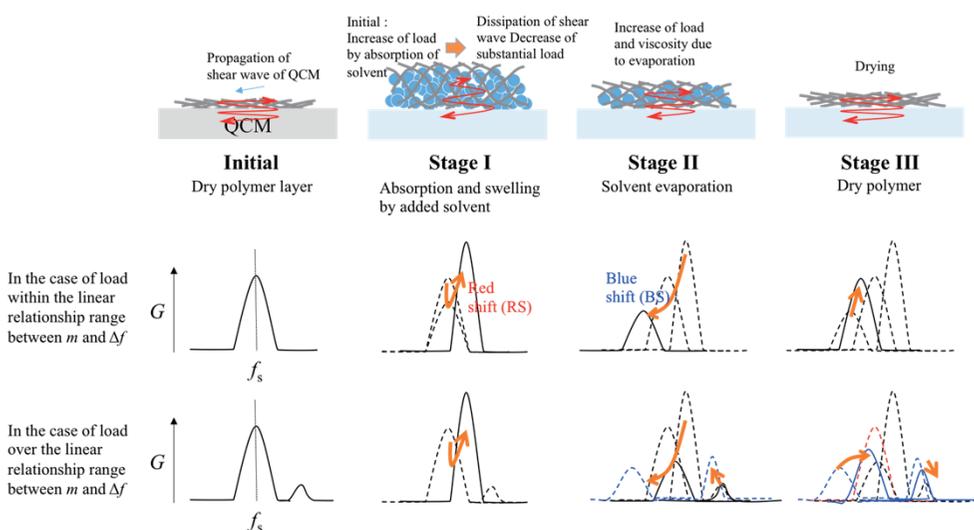
Fig. 5 Dynamics of QCM-A response until attaining stable resonance frequency after the application of sample on the QCM
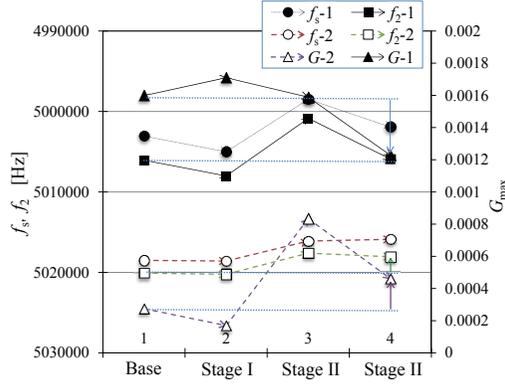
Fig. 6 The change of resonance frequency and conductance at each stage.

In the case of QCM that was pre-loaded some amount of PS, similar QCM behavior was observed. In the case of pre-loaded QCM, swelling of pre-loaded PS due to the toluene supplied with the PS instillation occurs at first in Stage I. Increase of resonance frequency f_s and the peak intensity occurs indicating the decrease of viscosity of loading material due to the swelling. Dissipation of shear wave of QCM in the swelling polymer results in the increase of f_s and G_{max} of the QCM response. The behavior of QCM depends on the balance between dissipation of energy by the swelling and the increase of loading mass due to evaporation. The f_2 also revealed the behavior similar to the f_s in response to the instillation of PS sample. The behavior at each stage is shown in Figs.5 and 7.

From the stepwise PS addition experiment, the dynamics of resonance frequency in response to the large loading was clarified. The red-shift of resonance frequency f_s is neither an appearance of so called spurious mode frequency nor over tone frequency. Q-factor of the main mode and the red-shifted mode were several ten thousands and several hundreds, respectively. The higher resonance frequency also obeys conventional mass-frequency shift relation.

The large load induces the resonance mode other than the fundamental main mode, resulting in the large red-shift of frequency beyond the fundamental one.

5. DISSCUSSION

Drastic red-shift of the resonance frequency is observed in the case of freezing of water [8,9,15]. The resonance frequency other than the main mode appears when the liquid-solid transition occurs in water. The red-shift is interpreted to be induced by large mass loading on QCM due to the liquid-solid transition. The red-shift is also observed in the measurement of phase behavior of thermo-responsive hydrogel when the gel collapse at
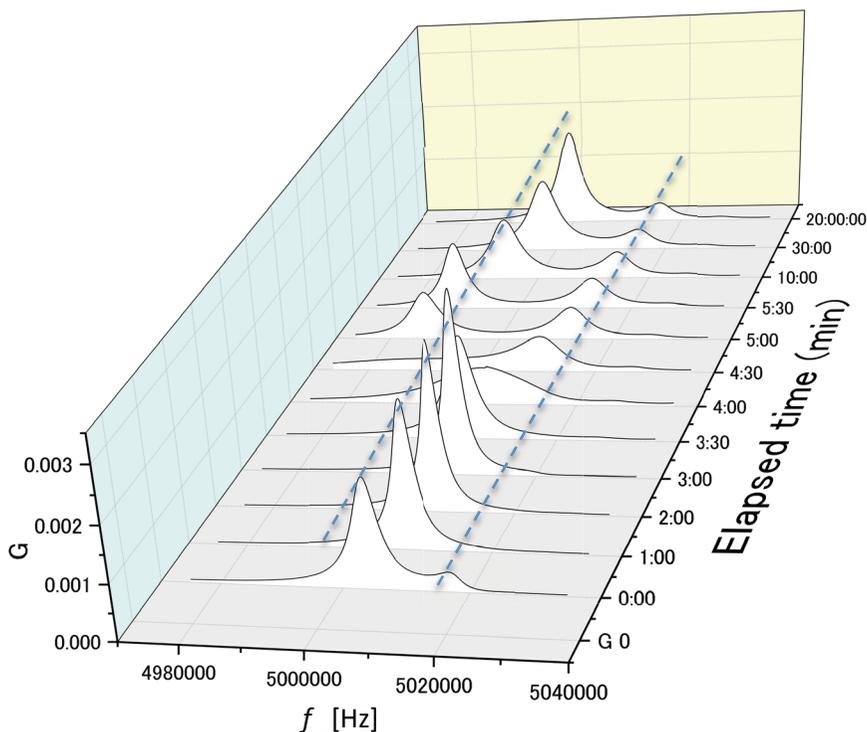
Fig. 7 The time course of *G* profile in response to the PS instillation in the case of QCM that was preloaded by some amount of the PS.

its phase separation temperature. Two reasons of the phenomena were considered. First is the emersion of another vibration mode due to large loading. Second is segregation of sample from the surface of QCM.

Temperature is also significant factor causing the drift of QCM oscillation. In the case of cooling process, the blue-shift of f_s occurs. The shift is obvious when the cooling rate is fast. On the contrary the red-shift occurs in the heating process. The drift during rapid heating or cooling is obvious and takes longer time to attain stable oscillation. The frequency shift will occur due to thermal stress induced in the quartz plate during the temperature swing.

6. CONCLUSION

QCM behavior in response to heavy load was investigated. Monitoring of QCM behavior by the stepwise instillation of polystyrene was performed. Relationship between the load and resonance frequency shift was observed. The influence of phenomena occurring on the QCM to the oscillation of QCM was clarified and the

phenomena was summarized into three stages. When the load exceeds the range of linear relationship between the change in loading mass Δm and resonance frequency shift f_s, other mode of resonance frequency appeared. The frequency also obeys Sauerbrey's relation. It is available to analyze phase behavior of samples with large mass load. This understanding indicates measurement of samples with large change of load such as samples with liquid-solid transition and soft material with huge molecular weight.

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和文要旨

ポリスチレン高負荷における水晶振動子マイクロバランス (QCM) の挙動解析

清 田 佳 美

　ポリスチレンを用いて、水晶振動子マイクロバランス (QCM) の過剰負荷試験を行った。過剰負荷と QCM の応答をアドミタンス法により解析した。その結果、電力供給が十分な状態では、高負荷時に安定に発振するもモードへの転移が起こる事が示された。そのダイナミクスについてアドミタンス解析をもとに視覚化した。本結果により、高負荷を伴う現象にも QCM が応用可能である事が示唆された。