Quartz Crystal Microbalance Monitoring of Poly(Vinyl Alcohol) Sol during the Freeze–Thaw Process

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Abstract

A quartz crystal microbalance (QCM) working under cryo-conditions was applied to analyzing the gelation and/or phase behavior of poly(vinyl alcohol) (PVA) sol during repeated freeze–thaw processes. The development of a porous structure with the gelation of PVA sol during the freeze–thaw cycle was examined in terms of the thermal behavior of the water in the sol and the viscoelastic behavior of the sol through thermal and QCM analyses. Water was liberated from the hydrophilic PVA during the freeze–thaw process through the aggregation of PVA. The water decreased the freezing temperature and increased the melting temperature because of the development of the porous structure with gelation by the thermal treatment. The state of the water during the gelation was estimated from the phase transition temperature and enthalpy change of the water during the thermal scan by using water-saturated silica gels with a series of pore size distributions. The viscoelasticity of the PVA sol during the freeze–thaw process was measured by cryo-QCM using admittance analysis (QCM-A). The free water and/or porous structure in the PVA sol was found to increase from the viscoelastic point of view by QCM measurements showing a shift in the resonance parameters (f_s , R_1). A hard gel was confirmed to form by the decrease in f_s and the increase in R_1 with the thermal scan treatment. The cryo-QCM was found to be an effective probe for clarifying the gelation and phase behavior of PVA sol in detail with high resolution.

Keywords: hydrogel, quartz crystal microbalance, poly(vinyl alcohol), freeze-thaw, gelation, pore water

1. Introduction

The quartz crystal microbalance (QCM) is used in biological, medical and industrial fields as a molecular probe because of its fine spatiotemporal resolution of several tens of nanometers to sub-microns and its economic advantages (Janshoff, Galla, & Steinem, 2000; Marx, 2007; Iniewski, 2012; Diethelm, 2015). Modern QCMs realize a stable resonator by using a network analyzer with a sufficient power supply. This development has inspired the application of QCMs to large loading system associated with solid phases of samples and soft materials. The physical properties of soft/wet materials in a cryo-environment and/or at low temperature are also of interest. The shear-mode megahertz oscillation of the quartz in a QCM works as a probe for the rheological measurement of viscous samples. Thus, a QCM can be applied to observing the structural changes in soft materials from a viscoelastic point of view. QCMs have been applied in measuring the phase behavior of crosslinked thermo-responsive hydrogels, which are a typical soft material (Nakano, Kawabe, & Seida, 1998; Nakano, Seida, & Nakano, 2007; Seida, 2007; Seida, 2013). Viscoelasticity changes significantly depending on hydration behavior in hydrogel and hydration behavior is temperature-responsive in general. Thus we have investigated a temperature controllable QCM as a tool observing a change in hydration with high resolution based on the viscoelastic sensing function of OCM in the previous study. The use of OCM for the analysis of soft materials has several advantages. The shear-mode dynamic viscoelastic behavior of a micro-volume sample can be observed. Because a OCM has a high resonant frequency of several megahertz, the viscoelasticity of a small sample can be observed with high sensitivity. The QCM allows the hydration behavior of a thermo-responsive hydrogel to be observed in its collapse phase at higher temperature than the volume phase transition temperature (i.e., 306 K). The QCM is effective at identifying the phase behavior of a hydrogel and/or the temperature dependence of the hydration behavior at polar sites of the hydrogel, which is difficult with other more conventional techniques during the collapse phase of the gel.

The present study examined the potential of cryo-QCM for observing the gelation process of soft materials, where poly(vinyl alcohol) (PVA) sol was used as a representative soft material. In PVA, gelation occurs with a change in viscoelasticity, so it can be observed by using QCM with high-resolution. A QCM with admittance analysis (QCM-A) was applied to observing the viscoelasticity of PVA sol during its freeze-thaw process. An aqueous solution of PVA with a large degree of saponification is known to develop a strong and physically crosslinked hydrogel through repeated freeze-thaw thermal scan cycle treatments (Peppas & Stauffer, 1991) due to the formation of dense polymer aggregates and/or bundled polymers (micellar crystalline). A porous network structure is created with repeated freeze-thaw treatments of PVA sol. The morphology and viscoelastic properties of the hydrogel depend on the molecular weight, saponification, concentration of PVA, freeze-thaw temperature, time, and number of the thermal scan cycles (Peppas & Stauffer, 1991). The micellar crystallization and/or bundle formation of PVA via hydrogen bonding plays an important role in the formation of hydrogel through freeze-thaw cycles. There have been no reports of in situ mechanical measurements of PVA sol during its freeze-thaw process. The gelation process of PVA sol includes a phase change and is performed under cryo-conditions so that the mechanical measurement of the gelation itself is difficult to perform with conventional methods. QCM-A was applied to the mechanical measurement of the gelation of PVA sol through repeated freeze-thaw thermal scan cycles. The QCM response in the repeated thermal cycle process was examined from a viewpoint of hydration behavior of PVA obtained through thermal analysis of water in the PVA, referring to a pore structure-hydration behavior relationship obtained from thermal analysis of a series of water saturated porous silica gels with controlled pore size distributions. The silica gel had a hydroxyl group on its surface that was similar to that of porous PVA gel. Thus, silica gels with a series of pore size distributions were employed in the thermal analysis to investigate the influence of the pore structure on the state of water and to identify the gelation mechanism observed by the QCM in terms of the phase behavior of water in the sol.

2. Experimental

2.1 Samples

2.1.1 PVA Sample

PVA (molecular weight: 2000, saponification: 98%) purchased from Wako Pure Chemicals Co. Ltd. (Japan) was used as received. A 15 wt% aqueous PVA solution was prepared by dissolving the PVA in pure water at 371 K under vigorous stirring. The prepared viscous solution was gently stirred for 1 day to remove bubbles that were produced during the preparation stage. The sol showed gelation when it was kept at 253 K for 1 h in a freezer followed by thawing at room temperature.

2.1.2 Silica Gel

Silica gels with a series of pore size distributions d_p were supplied from Fuji Silysia Chemical Ltd. The N₂ adsorption/desorption method was used to characterize the porous structure of the silica gels at 77 K. The Brunauer–Emmett–Teller (BET) method was used to determine the specific surface area S_{BET} from the N₂ desorption isotherm of each silica gel. The Barrett–Joyner–Halenda (BJH) method was used to determine the pore size distribution and pore volume V_p by using the N₂ desorption isotherms (Gregg & Sing, 1982). Figure 1(a) shows the pore size distribution of each silica gel. The silica gels used in this study had relatively narrow pore size distributions: sharp with a single peak. Figure 1(b) shows the specific surface area as a function of the pore diameter. The water absorption capacity of each silica gels was determined based on the mass balance between water-saturated and dry samples. The water for 48 h with ultrasonication for 10 min in the initial stage of immersion. The water content of the series of the silica gels was a simple linear function of the pore volume of the samples as shown in Figure 1(c). Table 1 summarizes the structural characteristics of the series of silica gels.

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Sample	А	В	С	D	Е	F	
$d_{\rm p}$ (nm)	3.3	6.2	10.6	16.0	32.6	51.1	
$V_{\rm p}~({\rm ml/g})$	0.27	0.66	1.01	1.02	0.97	0.88	
$S_{\rm BET} ({\rm m}^2/{\rm g})$	511.0	370.0	309.7	198.0	101.0	69.8	
Water content (%)	35.9	55.0	63.3	64.9	60.7	61.1	

Table 1. Characterized structural parameters of the silica gels



Figure 1. (a) The pore size distribution, (b) the relationship between the pore size and the specific surface area and (c) the relationship between the pore volume and the water content for the series of silica gels used in the present study

2.2 Thermal Analysis

The thermal analysis of the series of water-saturated silica gels was performed with a differential scanning calorimeter (DSC) to understand the phase behavior of pore water in the silica gels during a freeze–thaw operation as a function of the pore size in the silica gel. The freezing and thawing temperatures $T_{\rm f}$, $T_{\rm m}$ and freezing and melting enthalpies of water $\Delta H_{\rm f}$, $\Delta H_{\rm m}$ in each water-saturated silica gel were determined from DSC cooling and heating charts, respectively. The water-saturated silica gels were packed in an aluminum DSC sample cell, and cooling and heating charts were recorded with a DSC200 (Seiko Corporation Instrument). The scanning temperature range and rate in the DSC measurement were 293–243 K and 1 K/min, respectively. Thermal analysis was also performed on the 15 wt% PVA sol sample. The DSC measurements were performed under the same analytical conditions as the case of silica gels. The PVA sample was cooled and heated for five cycles with data acquisition to identify changes in the water behavior (hydration structure) of the PVA.

2.3 Principle of QCM-A

Based on the mathematical equivalency between the mechanical model of the QCM oscillation and LCR electric circuit model under forced oscillation (Figure 2), the viscoelastic property of the viscoelastic soft samples on the QCM were evaluated by admittance analysis of the QCM oscillation. Details of the admittance analysis have been reported elsewhere (Muramatsu, Tamiya & Karube, 1988). The resonance frequency f_s at the maximum conductance G_{max} and the resonance resistance R_1 (i.e., inverse of the G_{max}) of the QCM oscillation were obtained from the admittance analysis through a frequency scan around the resonance frequency. f_s depends on a substantial loading mass and/or elasticity of the load on the QCM (Sauerbrey 1959). R_1 is used as an index for the viscosity of a load. In a QCM, f_s and R_1 shift when the viscoelastic property of the sample changes. f_s also shifts for a viscous sample due to the influence of viscosity on the oscillation of QCM, so f_s is not a simple function of the loading mass in the case of a viscous sample (Kanazawa & Gordon, 1985). Martin, Granstaff, and Frye (1991) reported the independence of f_2 (i.e., the frequency f_2 was also measured in this study to evaluate the mass effect that is free from the influence of the sample viscosity.





2.4 QCM Measurement

The viscoelasticity of the PVA sol during its freeze-thaw process was measured by QCM-A. A 5 MHz QCM with a gold electrode (φ 10 mm diameter) purchased from Mitadenpa Co. (Japan) was used in this study. Figure 3 shows a schematic diagram of the QCM system used in this study. The temperature dependence of the frequencies f_s and f_2 and the resonance resistance R_1 of the bare OCM were measured first. Then, 1 uL of the PVA sol sample was dropped onto the surface of the QCM within an area of 1 mm². The QCM was installed in a thin cryo-cell with a Peltier device at the bottom of the cell. To reduce the loss of the aliquot PVA sol sample by drying and to avoid condensation from moisture in the atmosphere on the QCM, the PVA sol sample was covered with a thin polymer film made of poly(propylene), and the entire QCM electrode was covered with a silicon sheet. The film had a reverse dimple with a φ 1 mm diameter and 1 mm depth at its center to hold the sample sol. The influence of the thin film on the QCM oscillation was examined in advance and was found to be negligible compared to the changes in f and R_1 induced by the sample on the QCM. The sample temperature was measured by using a $\varphi 1$ mm thermocouple placed near the edge of the quartz of the QCM. The sample temperature was controlled by using the Peltier device with a proportional-integral-derivative (PID) controller. The sample was cooled from 283 K to 243 K and then heated to 283 K in a stepwise manner. This temperature swing was repeated three times. The cooling and heating rates were 1 K/min. The admittance of the QCM oscillation during the thermal scan cycle was analyzed at each temperature to collect the f_s , f_2 , and R_1 data with a network analyzer.



Figure 3. Schematic diagram of the QCM system used in this study

3. Results

3.1 Thermal Behavior of Pore Water in the Silica Gels

Figure 4 indicates the relationship between the pore size of the silica gels and the change in enthalpy with freezing $\Delta H_{\rm f}$ obtained from the cooling charts in the DSC analysis. The water in the silica gels showed supercooled freezing with a single exothermic peak. The freezing temperature $T_{\rm f}$ decreased monotonically with increasing pore size. $\Delta H_{\rm f}$ in Figure 4 was obtained from DSC time charts because the temperature drift occurred at the freezing point due to the exothermic heat process of the freezing. $\Delta H_{\rm f}$ increased with the pore size and reached near the value for pure water in the silica gel with a pore size of more than 30 nm. This indicates the existence of a large amount of non-freezable bound water in the silica gel with small pores of less than 16 nm. This was because of the increase in the surface area relative to the pore volume with the decreasing pore size. The ratio between the specific surface area $S_{\rm BET}$ and water content in sample A was three times greater than that in sample C, as indicated in Table 1. $T_{\rm f}$ for pure water obtained by the same method was lower (253 K) than the temperature observed in the silica gels with large pores. Increasing the pore size of the silica gels was found to decrease $T_{\rm f}$ and increase $\Delta H_{\rm f}$.



Figure 4. T_f and ΔH_f of water in each silica gel obtained from the cooling charts of DSC. \Box : weight basis enthalpy, \blacksquare : water content basis enthalpy, \times freezing temperature T_f



Figure 5. (a) DSC heating charts for the series of silica gels saturated with water. (b) $T_{\rm m}$ and $\Delta H_{\rm m}$ of water determined from the heating charts of DSC. \blacksquare : $\Delta H_{\rm m}$ /water content, Δ : $T_{\rm m1}$ and \times : $T_{\rm m2}$

Figure 5(a) indicates the DSC heating charts for the series of water-saturated silica gels. The silica gels frozen at 243 K revealed characteristic endothermic peaks depending on the pore size in the heating process. The endothermic peaks below 273 K indicate the existence of freezable bound water in the silica gels. The ice of strongly bound water starts melting at temperatures below 273 K depending on the strength of the binding. The enthalpy was calculated from the peak area above and below 273 K enclosed by the DSC heating curve and the interpolated baseline as referenced from the peak area of pure water (Watase, Nishinari, & Hatakeyama, 1988; Seida & Nakano, 1996). The melting enthalpy of freezable bound water ΔH_{m2} was calculated from the peak area below 273 K. The melting enthalpy of free water ΔH_{m1} was determined from the area above 273 K. As shown in Figure 5(a), the peak due to melting of the bound water shifted toward a higher temperature with increasing pore size. The endothermic peaks below 273 K indicate the existence of freezable bound water, as mentioned above.

 T_{m1} was defined as the melting temperature of free water. T_{m2} was defined as the melting temperature of bound water that could be observed in the DSC analysis. T_{m1} was determined from the inflection point around 273 K in the case of the multi-peak sample. T_{m2} was determined by a conventional method as indicated in Fig.5(a). The endothermic peak attributed to the freezable bound water disappeared in Sample A. Figure 5(b) indicates the melting temperatures T_{m1} , T_{m2} and the melting enthalpy of water ΔH_m (= $\Delta H_{m1} + \Delta H_{m2}$) as a function of the silica gel pore size. T_{m2} and ΔH_m were found to decrease with the pore size of silica gel. The results indicate the existence of some amount of non-freezable bound water in the silica gels with small pores. In the silica gels with pore sizes larger than 30 nm, the total ΔH_m reached close to the melting enthalpy of pure water. This indicates that free water was dominant in the pores larger than 30 nm. The fraction of water that was free from the influence of polar sites on the pore surface was large in the large pores, so T_{m2} and ΔH_{m1} were found to increase with the pore size. The melting temperature T_{m2} of freezable bound water and the melting enthalpy ΔH_m of freezable water can be associated with the pore structure in the case of silica gels. Slight decrease of T_{m1} occurred with the thermal cycle treatment due to a overlapping of the melting peak of bound water in the definition of T_{m1} . The DSC heating charts are a better way to clearly represent the state of water in the present system.

3.2 Thermal Behavior of PVA Sol

Figure 6(a) presents the DSC heating charts of the PVA sol obtained in the freeze-thaw measurements. An endothermic melting peak appeared from around 253 K, which indicates the existence of freezable bound water in the PVA sol. A slight shift in the endothermic peak was observed with the thermal scan cycle. Figure 6(b) summarizes $T_{\rm f}$, $T_{\rm m}$, and $\Delta H_{\rm m}$ obtained from each DSC chart. The supercooled freezing temperature $T_{\rm f}$ of the PVA sol shifted toward a lower temperature with the thermal scan cycle. In contrast, the melting temperature T_m determined based on the conventional slope method, as described above, decreased very slightly with the thermal scan cycle. This was due to the tail overlapping of the endothermic melting peak of freezable bound water with the melting peak of free water. Figure 6(b) shows $\Delta H_{\rm m}$ at each freeze-thaw cycle normalized by $\Delta H_{\rm m}$ of the first freeze-thaw cycle $\Delta H_{m,1st}$. The increase in $\Delta H_m / \Delta H_{m,1st}$ indicates the increase in free and freezable bound water with each repetition of the thermal scan cycle treatment. Thus, the melting temperature of the freezable bound water increased because of the decrease in non-freezing bound water with the gelation of PVA. Based on the thermal behavior of water observed in the silica gels, the decrease in $T_{\rm f}$ of the PVA sol with the thermal scan cycle indicates an increase in free water. The partial densification and/or aggregation of PVA as a result of repeated thermal scan cycle treatment produces a pore structure along with gelation of the sol (Peppas & Stauffer, 1991, Watase, Nishinari, & Nanbu, 1983). The formation of bundled polymers (micellar crystalline aggregates) via hydrogen bonding among hydroxyl groups in PVA results in pore formation with gelation. Based on the knowledge obtained from thermal analysis of the silica gels, the results in Figure 6 indicates the formation and development of a porous structure in the gelling PVA sol by the freeze-thaw thermal scan cycle.



Figure 6. (a) DSC heating charts of the PVA sol, (b) $T_{\rm f}(\Delta)$, $T_{\rm m}(\circ)$ and $\Delta H_{\rm m}/\Delta H_{\rm m, 1st cycle}$ (**■**) obtained by the DSC analysis for the PVA sol

3.3 QCM Response in the PVA Sol during the Freeze-Thaw Thermal Swing

The f_s and R_1 values showed a slight dependence on the temperature within several hertz in the considered temperature range (243–283 K) for the case of a bare QCM. The thermal shifts in the f_s and R_1 values were negligible compared to the varying ranges of f and R_1 observed in the PVA sol. The use of a thin film to hold the

PVA sol did not significantly affect the oscillation of the QCM. The change in oscillation due to the application of the thin film was within several hertz in the considered temperature range.

Figures 7 (a), (b), and (c) indicate temperature dependences of f_s , f_2 , and R_1 , respectively, in the QCM analysis of the PVA sol during the freeze-thaw thermal scan cycle. During the cooling process, f_s decreased and R_1 (=1/*G*) increased with decreasing temperature. In contrast, f_2 slightly decreased, which indicates that the viscosity R_1 change has a significant influence on f_s (Kanazawa & Gordon, 1985). The increase in R_1 during the cooling process was due to the increased density of water with temperature. A drastic shift in f_s , f_2 , and R_1 occurred at the freezing temperature of the PVA sol after some supercooling. A large change in the effective load (i.e., penetration depth of the shear wave of the QCM) induced by the phase transition of the water from a liquid to solid (i.e., freezing) caused the behaviors of f_s and R_1 . The transition temperature (i.e., point at which the red-shift of f_s occurred) shifted down closer to the freezing temperature of pure water with the thermal scan cycle.



Figure 7. QCM behaviors of the sample during the repeated freeze–thaw temperature scan cycle. (a) f_s , (b) f_2 and (c) R_1

During the heating process, f_s and f_2 decreased with the temperature followed by a large blue-shift after showing a broad peak. The trends were reproducible and depended on the number of thermal scan cycles. The peaks of f_s and f_2 just before the large blue-shift disappeared with the cycle. The formation of crystalline aggregates (bundled polymers) and gelation with the change in hydration structure in the PVA sol were the reasons for such characteristic trends. In contrast, R_1 increased gradually with temperature followed by a large drastic decrease. The *f* values decreased and the R_1 value increased with the increasing number of thermal scan cycles in the non-freezing phase above 273 K. This indicated the increasing viscoelasticity of the gelling PVA sample. The steep shift of f_s , f_2 , and R_1 due to the sample melting began at the temperature where the endothermic peak in the DSC analysis began. The change in viscoelastic property observed in the QCM measurement occurred with the melting of bound and

free water of the PVA sol during the thawing process. The changes below 273 K would reflect the melting of freezable bound water in the PVA. Figure 7 represents the first measurements of the soft/wet material during its freeze-thaw process with QCM.

4. Discussion

In the case of the aliquot of pure water on the QCM, the QCM behavior during the freezing and thawing processes of the water was reproducible, and the supercooled freezing temperature and melting temperature did not change with repeated temperature scan cycle measurements. The freezing and melting temperatures were determined from the points of drastic shifts in f_s and R_1 during the QCM measurement. The trend of heating chart for f_s and f_2 of ice from pure water was reproducible as a simple decreasing function of the temperature with a small peak just before the drastic blue-shift due to the ice melting (Seida 2016).

The size and/or amount of samples used in both the DSC analysis and QCM measurements were much larger than the size of the micellar crystalline aggregates of PVA (Hassan & Peppas, 2000) that are produced in the initial stage of the gelation of PVA sol and the pore sizes created in the PVA by the freeze–thaw cycle treatment. From this point of view, knowledge on the gelation mechanism for bulk PVA sol is applicable to this system (Watase & Nishinari, 1985; Peppas & Stauffer, 1991).

The pore size and thermal properties (hydration behavior) of water in the pores correlated well for the silica gels, as indicated above. Increasing the pore size decreased the freezing temperature T_f and increased both the melting temperature of freezable bound water T_{m2} and melting enthalpy of freezable bound water ΔH_{m1} in the silica gels. The freezing water excluded dissolved solutes from its ice crystal, which enhanced the bundle formation and/or micellar crystalline aggregates of PVA and resulted in the porous gel. The elasticity decreased near the melting temperature in the freezing phase of the PVA sample, as expected from the f_2 trend for the heating process shown in Figure 7(b). This would also enable the polymer molecule to be excluded from the ice crystal and enhance the aggregation of PVA. The fractional change in hydration of the PVA also occurred with the progress of the DSC analysis (Figure 6). Thus, the results shown in Figure 6 correspond to the development of a porous structure and gelation with repeated thermal scan cycles.

For the sol of 15 wt% PVA with 80% saponification and a small molecular weight, no obvious temperature shift with the freeze–thaw thermal cycle was observed (Seida, 2015). Bulk gelation does not occur in PVA sol with a small degree of saponification (~80%). Watase and Nishinari (1985) reported that acetate groups can inhibit the formation of gel in PVA. PVA with a small degree of saponification hardly shows bulk gelation even if crystalline PVA aggregates may be produced by the freeze–thaw thermal treatment. Thus, the change in the resonance parameters (i.e., f_s and R_1) during the freeze–thaw thermal scan cycle of the PVA sol, as observed in Figure 7, was attributed to the gelation of the PVA sol.

Rapid freezing produces an internal strain in the freezing phase and/or the interfacial strain between the ice and electrode surface of the QCM. Relaxing the strain would take a long time compared to the scan rate of the temperature in this study. Thus, the strain would affect the f and R_1 trends in the freezing phase of the temperature scan measurement. The scan rate of the temperature is also a potential factor for determining the f and R_1 behaviors in the freezing phase. The scan rate of the temperature in the present study was determined based on the conventional scan rate used in the DSC analysis.

The freezing temperature of the sample observed with the QCM decreased with the progress of gelation; this was associated with the increases in viscoelasticity and/or R_1 . The shift in the f_s and R_1 charts for the heating process were also associated with the increased viscoelastic properties with the thermal scan cycles. The increased melting temperature and temperature range of the melting peak of the freezable bound water on the PVA would indicate an increase in free water due to the development of the porous structure. The drastic shift of f_s was due to a large drastic change in the effective load (i.e., the product of the penetration depth δ of the shear wave of the QCM and the density of the load ρ (Kanazawa and Gordon, 1985)). The drastic change in f_2 indicated a drastic change in the penetration depth of the shear wave of QCM in the sample, which means a change in the effective load on the QCM. The steep increase in R_1 during the heating process indicated increased damping of the shear wave energy along with the increased penetration depth of the shear wave. The red-shift of f_s and f_2 with the freezing of the sample may seem to be quite different compared to the generally accepted relation between the loading mass and frequency shift (Sauerbrey, 1956). The large blue-shift of f_s occurred with increases in the water (liquid) phase and penetration depth of the shear wave. The increased effective load with small viscosity observed by the QCM decreased f_s , f_2 , and R_1 . Because the shear oscillation frequency of a QCM is very high, the freezing phase would behave like viscous body. In the case of a load with a much larger viscosity, f_s and f_2 increase in spite of the large R_1

(Seida, 2016). According to the pore structure-hydration behavior relationship obtained from the results in Figure 5, the decrease of red-shift temperature and the increase of blue-shift temperature of f_s and f_2 occur in the QCM response along with the increase of free water and/or formation of pore structure in the PVA. R_1 becomes large with the increase of free water in the PVA.

The findings obtained from the thermal analysis of the silica gels and the PVA sol with repeated freeze–thaw thermal scan cycles indicate that a QCM can be used to probe the structural formation of a PVA porous network during the gelation of PVA sol.

5. Conclusion

In the present study, the gelation process of PVA gel during repeated freeze–thaw thermal cycles was evaluated based on the thermal behavior of pore water and the viscoelastic behavior of the PVA sol obtained by the cryo-QCM developed in this study. The relationship between pore structure and hydration behavior of pore water was clarified based on the freezing temperature $T_{\rm f}$, melting temperature $T_{\rm m}$, and freezing and melting enthalpies $\Delta H_{\rm f}, \Delta H_{\rm m}$ of the pore water obtained from the thermal analysis using water saturated porous silica gels with a series of pore size distributions. The non-freezable and freezable bound water decreased with increasing pore size up to a diameter of 16 nm in the silica gels. $T_{\rm f}$ decreased and $T_{\rm m2}$ increased with the increase of pore size because of the increased amount of free water in the silica gel. The development of a porous structure in the PVA sol during the thermal scan cycle treatment was observed based on the parameters $T_{\rm f}$, $T_{\rm m}$, and $\Delta H_{\rm m}$ in the thermal analysis. The QCM response of the PVA sol in the repeated freeze–thaw thermal scan cycle was obtained fairly well. The QCM response was interpreted from the viewpoint of hydration behavior referring to the pore structure-hydration behavior relationship observed in the silica gels. The results obtained in this study indicate the viability of the cryo-QCM for clarifying the gelation as well as hydration behaviors of PVA sol during freeze–thaw process in detail from a viscoelastic point of view.

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