Relaxation Dynamics of Sugar Glasses[1]

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Summary

We studied the relaxation dynamics of sugar glasses by using dielectric loss spectroscopy and dynamic light scattering spectroscopy methods. First, we studied dielectric relaxation phenomena of glucose-water and galactose-water mixtures in the supercooled and glassy states at frequencies ranging from 0.1 Hz to 10 MHz. In this frequency range, the monosaccharide-water mixture systems show both α and the secondary relaxation processes. We observed that as the water content or temperature decreased the relaxation time difference between the α and the secondary relaxations increased and the relative relaxation strength between the α and the secondary relaxation decreased. Therefore, the effect of adding water or increasing temperature on the secondary relaxation process was the same and was qualitatively similar to the effect of decreasing rotational-translational(RT) coupling constant in the schematic mode-coupling theory with RT coupling. Second, we studied density correlation functions of disaccharide sugars at different temperatures by using the Brookhaven(BI-9000AT) photon correlator. We found that trehalose glass showed a compressed exponential relaxation function at temperatures higher than 140^{o}C. Based on the results from X-ray diffraction and Raman spectroscopy experiments, we strongly speculate that the observed compressed exponential relaxation function in trehalose may originate from the change of glycosidic bond in trehalose sugars.

1. Introduction

Dynamics in the liquid-glass transition of glass forming molecules with many experimental techniques has been intensively studied to test theories of the liquid-glass transition. Molecular glass forming material that have received relatively little attention is the sugars. The dynamics in the liquid-glass transition in sugars is important for several reasons. First, sugar glasses are very effective materials for cryopreservation and anhydrobiosis. Some organisms can survive in very cold or dry condition because they contain sucrose or trehalose and can reversibly glassy. Second, biochemists commonly use sugars to suspend biomaterials in a glassy matrix for spectroscopic studies. They suspend proteins or membrane vesicles in aqueous solutions of disaccharides and then remove water by evaporation or freeze-drying to immobilize the biomaterials. Third, sugars are also useful material to study the glassy dynamics such as the secondary relaxation process and the aging phenomena. Since many sugars have glass transition temperatures above the room temperature[1], experiments on aging effects can be carried out without cryogenic equipment, facilitating rapid temperature quenches. Also, sugar-water mixtures are known to reveal well pronounced secondary relaxation in dielectric loss spectra[2, 3].

In the present paper, we studied the relaxation dynamics of sugar glasses by using dielectric loss spectroscopy and dynamic light scattering methods. We studied dielectric relaxation phenomena of glucose-water and galactose-water mixtures in the supercooled

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and glassy states and found that the effect of adding water or increasing temperature on the secondary relaxation are qualitatively similar to that of decreasing the rotation-translation (RT) coupling constant in the schematic mode-coupling theory(MCT)[4]. We also studied density correlation functions of sugar glasses at different temperatures and found that different from other sugar glasses, trehalose glasses showed a compressed exponential relaxation function at temperatures higher than 140^{o}C which may originate from the change of glycosidic bond in trehalose sugars.

2. Experimental Tools

2.1 Sample preparation The samples used in this study were monosaccharide-water mixtures (glucose-water and galactose-water mixtures) for dielectric spectroscopy study and a trehalose for light scattering studies. A α-D glucose or D-galactose (Aldrich Chemical Company, Inc. USA) and deionized distilled water were used to make a monosaccharide-water mixture. The weight percent of the water was measured by using moisture analyzer (Sartorius MA100, Germany) with 0.1 wt. % precision. The glass transition temperature, T_g, of the different mixtures were determined by using a differential scanning calorimetry(DSC: MAC science, DSC3100, Japan). The measured T_g were highly consistent with the results from Brillouin scattering method[5].

α, α-Trehalose dihydrate was sponsored by Cargill Corporation and dried by using moisture analyzer(Sartorius MA100, Germany) at 130 ^{o}C for 5 hours to remove waters inherently stayed in trehalose dihydrate. The trehalose glass was made by using microwave oven because the microwave oven is an effective method to heat the trehalose quickly and uniformly without caramelization process during the heating[6].

2.2 Dielectric loss spectroscopy The frequency dependent dielectric constants at different temperatures were carried out by using a parallel-plate assembly consisting of two thin copper plates. Two different measurement schemes were employed depending on the frequency range under consideration. For the frequency range of 0.1 Hz to 10 kHz, the in-phase and out-of-phase currents through the capacitor were measured by using a dual phase lock-in amplifier(Stanford SR 830, U.S.A.). For the frequency range of 100 Hz to 10 MHz, an impedance analyzer (HP 4194A, Hewlett-Packard U.S.A.) with a standard four-terminal pair configuration was used to measure the capacitance and conductance of the sample. The data obtained from the two methods were in excellent agreement where they overlapped. The temperature of the sample was controlled by using a closed-cycle He refrigerator and a temperature controller (Lakeshore 330, U.S.A.) with 0.01 K precision. The temperature of the sample was monitored by a platinum sensor and a silicon diode sensor.

2.3 Light scattering spectroscopy In a photon correlation spectroscopy(PCS) experiment, the Brookhaven BI-9000AT digital correlator (Brookhaven Instruments Corp., U.S.A.) was used to measure the correlation function, *G(t)*, of trehalose glass. The Brookhaven correlator can cover ten decades of time($10^{-1}\mu s \sim 10^{9}\mu s$). The incident beam was a vertically polarized 514.5 nm green light of Ar-ion laser (I90-C, Coherent, USA) with 200 mW power and single mode fiber optic was used for detecting the scattered light. The depolarized (VH) components of the scattered light were selected by using the Glan-Thompson Analyzer with a leakage factor of less than 1%. A scattering geometry was 90^o.

In a Raman spectroscopy measurement, the back-scattering geometry was used. The incident beam was a vertically polarized 514.5 nm green light of Ar-ion laser (I90-C, Coherent, USA) with 100 mW power. The scattered light was measured by using monochromator (Acton Research, Spectra Pro-750, USA) and charge coupled device (AndorMCD, USA) in the range of 1000~1200 cm^{-1}.

3. Results and discussion

3.1 Dielectric loss spectroscopy Figures 1(a) - 1(c) show the frequency dependent dielectric loss spectra of glucose-water mixtures in the temperature range which covers the glassy and the supercooled states. In these figures, we can clearly observe the α and the secondary relaxations. As the temperature increased, both the α-relaxation and the secondary relaxation progressively shifted to higher frequencies. However, the α relaxation moved faster than the secondary relaxation, therefore two relaxations were superposed at high temperatures. We also observed that the relaxation strengths of the α process were almost constant but those of the secondary relaxation increased as the temperature increased.

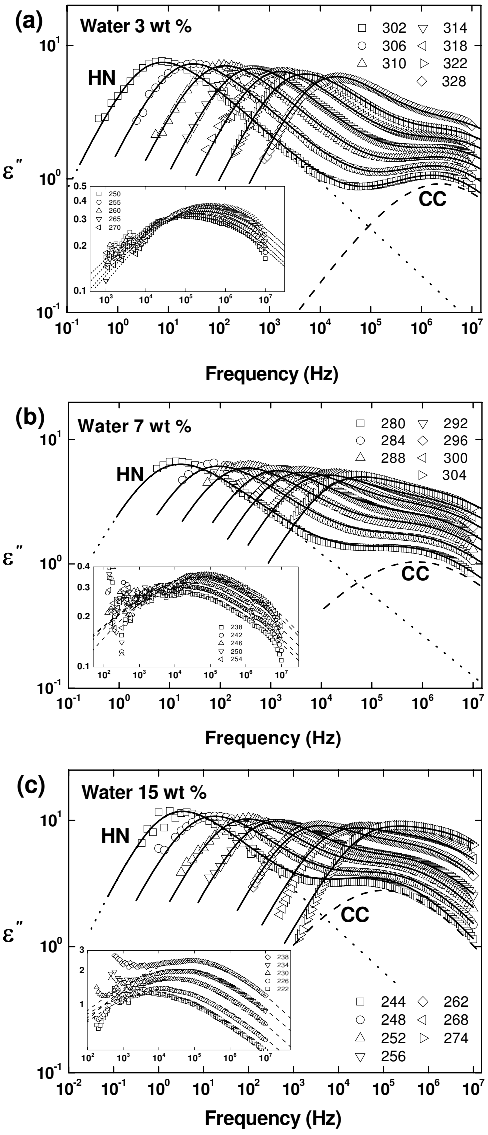

Fig.1 Frequency dependent dielectric loss spectra in glucose-water mixtures at different temperatures with water contents of (a) 3 wt.%, (b) 7 wt.%, and (c) 15 wt.%.

We fitted our data to the superposition of the Havriliak-Negami(HN)[7] function for the α-relaxation and the Cole-Cole(CC)[8] function for the secondary relaxation. The fitting function used is as follows

$$\epsilon^*(\omega)=\frac{\Delta\epsilon_\alpha}{[1+(i\omega\tau_\alpha)^{a_\alpha}]^{b_\alpha}}+\frac{\Delta\epsilon_{2nd}}{1+(i\omega\tau_{2nd})^{a_{2nd}}} \qquad (1)$$

where, $\Delta\epsilon_\alpha$ and $\Delta\epsilon_{2nd}$ are the relaxation strengths, τ_α and τ_{2nd} are the relaxation times, and exponents a_α, b_α and a_{2nd} are parameters reflecting the width and shape of the relaxation spectra. As can be seen in Figs. 1(a)-1(c), good fits to the experimental data were achieved in this way for all glucose-water mixtures. The insets in Figs. 1 show the secondary relaxation process in the frequency range of 100 Hz to 10 MHz. We can see that the CC function fits the data very well.

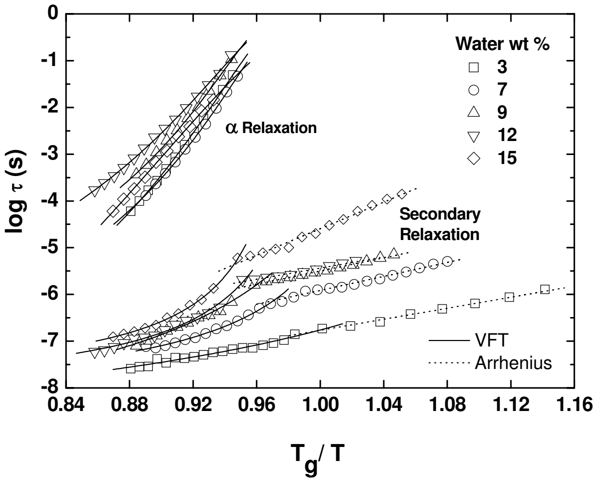

Fig.2 Temperature dependent α- and the secondary relaxation times of glucose-water mixture with different water contents. The reciprocal temperature was re-scaled by T_g.

Figure 2 shows the temperature dependent relaxation times for both the α and the secondary processes with different water contents. The relaxation times are plotted logarithmical against the reciprocal temperature scaled by T_g. Usually, the temperature dependent α-relaxation times in glass forming materials can be described by the Arrhenius law at low temperatures and the VFT law[9] at high temperatures. These two different temperature regions are separated by the Fisher-Stegel temperature T_{FS}, which appears to be very close to the crossover temperature T_c in the MCT[10].

The temperature dependent secondary relaxation time still remains as an open question even though it has been intensively studied. It has been generally accepted that the secondary relaxation times obey the Arrhenius law. Recently, Blochowicz and Rössler[11] studied the secondary relaxation process in 2-picoline in tri-styrene and found that the temperature dependent secondary relaxation time can be the combination of two different forms. They reported that the temperature dependent secondary relaxation time follows the Arrhenius law at low temperatures and deviates from the Arrhenius law at high temperatures.

We can observe in Fig. 2 that α-relaxation times for all water concentrations seem to exhibit the VFT temperature dependence when $0.85 < T_g/T < 0.95$. This is different from what we expected since the temperature dependent α-relaxation time usually obeys the Arrhenius law at temperatures close to the glass transition temperature. However, we do not want to emphasize this result too much, since our relaxation time measurement only covers 3 decades of time.

In the case of the secondary process, the relaxation times show two different behaviors which are very similar to the results in Ref.[11] by Blochowicz and Rössler. We fitted relaxation times to the VFT law or the Arrhenius law and the results are shown in Fig. 2. as solid or dotted lines. Relaxation times for all water concentrations clearly obey the Arrhenius law at low temperatures and the VFT law at high temperatures. We can also observe in Fig. 2 that the secondary relaxation time increased as the water content increased at a fixed T_g/T.

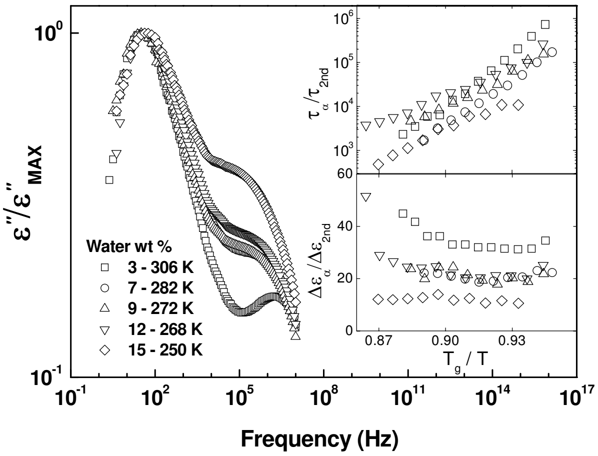

Fig.3 The effect of water on secondary relaxation process. Selected spectra have the same α-peak positions. The temperatures of selected spectra are 300K, 296K, 268K, and 258K for 3, 5, 10, and 15 wt% water contents, respectively.

The effect of water on the secondary relaxation in the glucose-water mixtures can be seen in Fig. 3. Figure 3 shows a group of data which have the same α peak position with different water contents and at different temperatures. The data was re-scaled with the α peak amplitude in order to compare the relative characteristics of the secondary relaxation to the α relaxation. The α-relaxations of all glucose-water mixtures have similar spectra at the same peak position. However, it is clear that there exists a large variation of the relative position and strength of the secondary relaxations. As can be seen in Fig. 3, the secondary relaxation of 3 wt.% glucose-water mixture is well separated from the α-relaxation, and the peak width seems to be small. By contrast, the secondary relaxation of 15 wt.% glucose-water mixture is not well separated from the α-relaxation, and the peak width seems to be large. Also, it seems that the effect of adding water on the secondary relaxation is the same as increasing the temperature. Indeed, as can be seen in Figs. 1(a)-1(c), we observed the same trend of the secondary relaxations with the temperature.

The two insets in Fig. 3 show the relaxation time and relaxation strength ratios between α and the secondary relaxations at different temperatures for each water content. We can observe in these insets that the addition of the water clearly results in the increase of the secondary relaxation amplitude and causes the secondary relaxation to merge with the α-relaxation.

In a dielectric study of galactose-water mixtures, to be described in more detail in another publication, we found that the water contents and the temperature dependent dielectric relaxation behaviors are very similar to those in glucose-water mixtures. Figures 4(a)-4(c) show the frequency dependent dielectric loss spectra of galactose-water mixtures above the glass transition temperature with different water contents. Similar to the dielectric data of glucose-water mixtures, we can clearly observe the α- and the secondary relaxations. As the temperature decreased, both the α- and the secondary relaxation progressively shifted to lower frequencies. The observed dielectric loss spectra of galactose-water mixtures were very similar to those of glucose-water mixtures because the chemical structure of glucose and galactose are very similar[12].

We fitted our data to the superposition of the power law function for dc part, the Havriliak-Negami(HN) [7] function for the α-relaxation and the Cole-Cole(CC) [8] function for the secondary relaxation. The fitting function was shown in Eq. (1). In the case of galactose-water mixtures, the dc conduction part was included in the fitting function. Good fits to the experimental data were achieved in this way for all galactose-water mixtures.

Figure 5 shows the temperature dependent relaxation times for both the α and the secondary processes

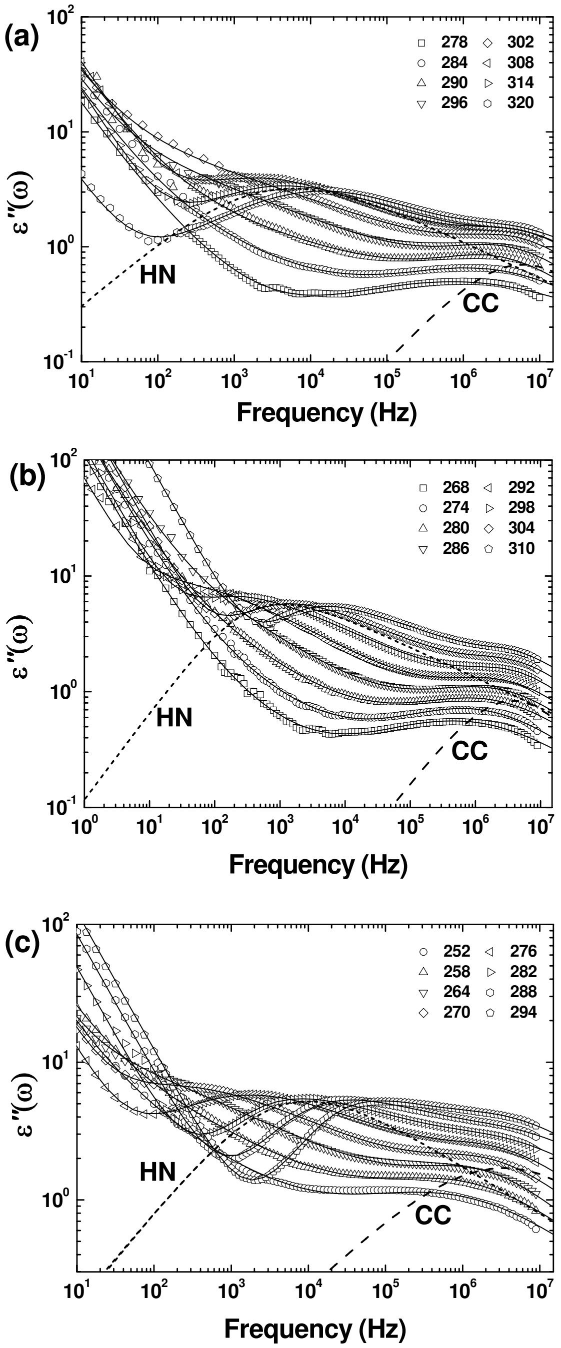

Fig.4 Frequency dependent dielectric loss spectra in galactose-water mixtures at different temperatures with water contents of (a) 3 wt.%, (b) 5 wt.%, and (c) 10 wt.%. The solid line is the fitted results with superposition equation of power law, HN, and CC equations. The short dashed lines and dashed lines are the fitted results of the the Havriliak-Negami and the Cole-Cole equations at 314K, 304K, and 282K for 3 wt.%, 5 wt.%, and 10 wt.%, respectively.

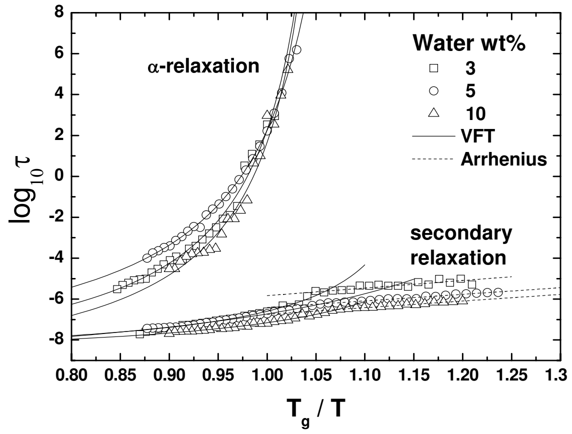

Fig.5 Temperature dependent α- and the secondary relaxation times of galactose-water mixtures with different water contents. The reciprocal temperature was re-scaled by T_g.

with different water contents. The relaxation times are plotted logarithmically against the reciprocal temperature scaled by T_g. Normally, the structural relaxation of glass forming materials followed the non-Arrhenius temperature dependence. We tried to fit the temperature dependent relaxation times of α-process with the Vogel-Fulcher-Tamman [9] law. All water concentrations exhibit the VFT temperature dependence when $0.8 < T_g/\mathrm{T} < 1$. In the case of the secondary process, the type of temperature dependent secondary relaxation time changed from the Arrhenius law to the VFT law at a certain temperature. The temperature dependence of the relaxation process of galactose-water mixture was very similar to that of glucose-water mixture shown previously. However, there are slight difference in the secondary relaxation. In the glucose-water mixture case, the crossover point where the temperature dependent changes from Arrhenius law to VFT law moved to higher temperatures with increasing water contents. However, in the galactose-water mixture case, the deviation temperatures were almost the same around $T_g/\mathrm{T} \simeq 1$.

The effect of water on the secondary relaxation in the galactose-water mixtures can be seen in Fig. 6. Figure 6 shows a group of data which have the same α-peak position with different water contents and at different temperatures. The data was re-scaled with the α-peak amplitude in order to compare the relative characteristics of the secondary relaxation to the α-relaxation. Similar to what we observed in Fig. 3, the α-relaxations of all galactose-water mixtures have similar spectra at the same peak position. However, it is clear that there exists a large variation of the relative position and strength of the secondary relaxations. As can be seen in Fig. 6, the secondary relax-

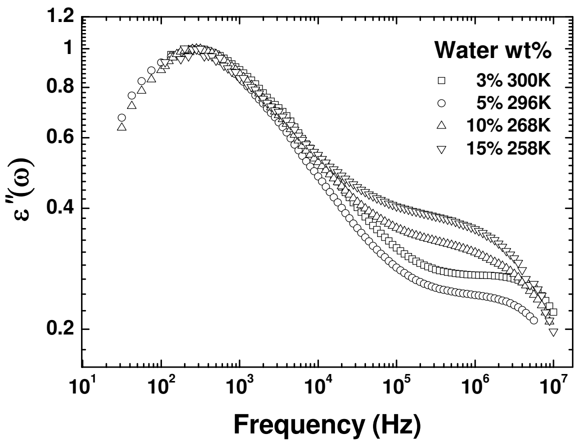

Fig.6 The effect of water on secondary relaxation process. Selected spectra have the same α-peak positions. The temperatures of selected spectra are 300K, 296K, 268K and 258K, for 3, 5, 10, and 15 wt% water contents, respectively.

ation of 3 wt% galactose-water mixture is well separated from the α-relaxation, and the peak width seems to be small. By contrast, the secondary relaxation of 10 wt% galactose-water mixture is not well separated from the α-relaxation, and the peak width seems to be large. The overall behavior of the secondary relaxation relative to the α-relaxation in galactose-water mixture is the same as that in glucose-water mixture.

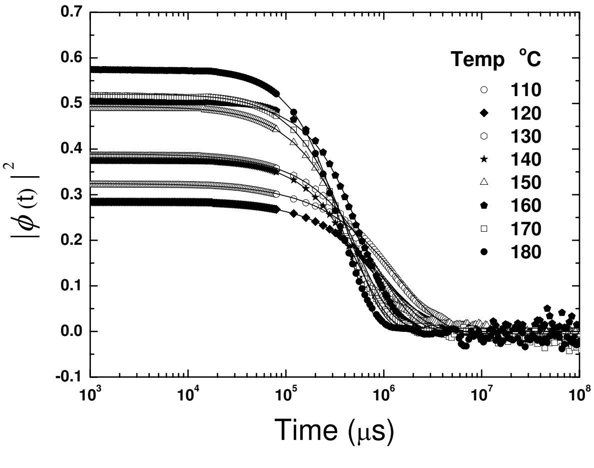

Fig.7 The $|\phi(t)^2|$ of depolarized components for different temperatures from 110 ^{o}C to 180 ^{o}C. The solid lines are the fits to the square of stretched-exponential function.

It is quite natural that the density dynamics is affected by the orientational dynamics as a consequence of the coupling effect between rotation and translation(RT). Recently, Götze and Sperl[4] showed that the schematic MCT model with RT coupling can successfully explain the nearly-logarithmic decay in the orientational correlation function observed in the optical Kerr experiment[13]. An interesting finding in their study is that the schematic MCT model with RT coupling can also produce the secondary relaxation process in the orientational correlation function. The correlation function showed that as the RT coupling strength decreased, the secondary relaxation strength increased and the relative position between the structural α-relaxation and the secondary relaxation decreased[14].

The quantitative behavior of the secondary relaxation with the RT coupling constant can be seen in the Fig. 5 in Ref. [14]. The properties of the secondary relaxation process with different RT coupling strengths are exactly the same as what we observed in the dielectric data of monosaccharide-water mixtures with different water contents or with different temperatures. Therefore, we propose a possibility that the origin of the secondary relaxation may relate to the RT coupling.

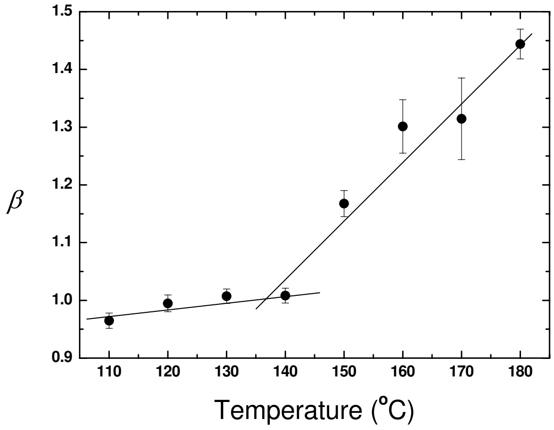

Fig.8 The stretched exponent β of trehalose glass with increasing temperature. The slope of β was changed around 140 ^{o}C and showed the bigger value than 1 above 140 ^{o}C.

3.2 Photon correlation spectroscopy

Figure 7 shows the $|\phi(t)|^2$ of VH components in trehalose glasses at temperatures ranging from 110 ^{o}C to 180 ^{o}C. The symbols are experimental results and the solid lines are the fits to the square of stretched-exponential function with fitting parameters, non-ergodicity parameter f_c, relaxation time τ, and stretched exponent β.

$$|\phi(t)|^2 = f_c^2 exp(-2(t/\tau)^\beta) \quad (2)$$

The obtained stretched exponent β of trehalose glass at different temperatures were shown in Fig. 8. As can be seen in Fig. 8., the stretched exponent β increased with increasing temperature and the slope was changed around 140 ^{o}C. Moreover, the stretched exponent β bigger than 1 above 140 ^{o}C. This result indicates that the relaxation process of trehalose glass changed from stretched- to compressed-exponential relaxations around 140 ^{o}C. The compressed exponential behavior has been observed in complex systems including colloidal gels[15], micellar polycrystals[16], and clays[17]. Recently, Bouchaud and Pitard[18] suggested a specific model about the compressed-exponential relaxation which associates with the local rearrangement or micro-collapse of particles.

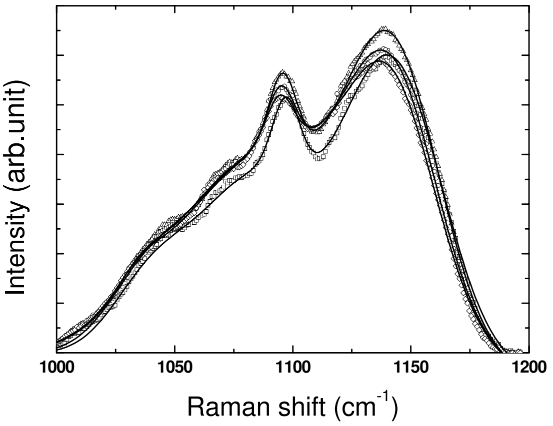

Fig.9 Raman peak shifts of trehalose glass. The slope of Raman shift was changed around 145 ^{o}C.

In this study, however, it seems that the observed compressed-exponential behavior in trehalose glasses might originate from a intra molecular structure change because we did not observe any intermolecular structure change in x-ray diffraction experiments at different temperatures. Figure 9 shows the Raman spectra of trehalose glass at different temperatures[20]. The Raman shift showed a constant value at the temperature range 40 ^{o}C $\sim$ 145 ^{o}C and started to decrease at the temperature around 145 ^{o}C. It indicates that the glycosidic bond of trehalose molecule was changed around 145 ^{o}C. From this result, we concluded that the unusual compressed-exponential relaxation in trehalose may be related to the change of the out-of-ring vibrations in trehalose molecule: i.e., the change of glycosidic linkage due to the coupling of C-O stretching(ν (C-O)), C-H bending(δ (C-H)), and C-O-H stretching(ν (C-O-H)) modes[19]. We also believe that the observed unique relaxation process in trehalose glasses might be related to the superior cell protection ability of trehalose.

4. Conclusion

The dielectric relaxations in the glucose-water mixture and galactose-water mixture with different water contents were studied in order to investigate the properties of the secondary relaxation process in the supercooled and glassy states. We could gradually changed the properties of the secondary relaxation by changing the water content or the temperature. As the water content or temperature decreased the relaxation time difference between the α and the secondary relaxations increased and the relative relaxation strength between the α and the secondary relaxation decreased. The effect of adding water or increasing temperature on the secondary relaxation process was qualitatively similar to the effect of decreasing RT coupling constant in the schematic MCT with RT coupling[14].

The relaxation times in Trehalose glasses were studied at different temperatures. We found that trehalose glasses showed a compressed exponential relaxation function at temperatures higher than 140^{o}C different from other sugar glasses which usually show the stretched exponential relaxation function. Based on the results from X-ray diffraction and Raman spectroscopy experiments, we strongly speculate that the observed compressed exponential relaxation function may originate from the change of glycosidic bond in trehalose sugars.

Acknowledgments

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