Broadband Dielectric Spectroscopy of Fructose-Water Mixture in Frozen State

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Freezing and glass transition phenomena of sugar-water mixtures are directly concerned with the preservation of dried foods and frozen foods. According differential scanning calorimetry to the (DSC) measurements for sugar-water mixtures, the glass transitions are observed at temperature below the melting temperature. Furthermore two glass-transition like behaviors have been also reported in sugar-water mixtures, and explained with two ideas. One idea is that one of the two transitions is the glass transition and another is the melting of part of the heterogeneous ice. Another idea is that the both two are the glass transitions. However, the mechanism based on the complexity of the frozen mixture is still the subject of a controversy. In order to make clear the glass transition from the molecular dynamics in the frozen state of sugar-water mixtures, broadband dielectric measurements were made for 5-40 wt% fructose-water mixtures. Dielectric measurements were performed in a frequency range from 2 mHz to 20 GHz, using a time domain reflectometry (TDR) (100 MHz-20 GHz), an impedance/material analyzer (Hewlett Packard 4291A) (1MHz-1.8 GHz), a precision impedance -1 kHz) in the temperature range between - 70 and 25 °C analyzer (Agilent Technologies 4294A)(40 Hz-110 MHz), an LCR meter (Hewlett Packard 4284A)(20 Hz-1 MHz), and an AC phase analysis (ACPA) method (2 mHz-1 kHz).

Figure 1 shows dielectric constant and loss for the frozen 40 wt% fructose-water mixture at -36 °C. The frequency dependence of dielectric constant and loss can be well described by assuming contributions of dc conductivity and three relaxation processes. The relaxation process "c-process" observed in a frequency range between 100 Hz and 1 kHz is a relaxation process of ice. Huge electrode polarization "d-process" and dc conductivity are observed around in frequency ranges below 100 mHz for the dielectric constant and below 1 Hz for the dielectric loss. In addition to these relaxation processes, two relaxations "a- and b-processes" are observed around 1 Hz and 1kHz respectively. The relaxation times for the a- and b-processes increase with decreasing temperature, and temperature dependences are larger than ice. On the other hand, the relaxation times of the a- and b-processes are independent of the fructose concentration. The two glass-transition like changes of the specific heat were observed by DSC in the vicinity of -50°C and -40°C for the fructose-water mixture. The relaxation times for the a- and b-processes are 100-1000s at the vicinity of these two glass-transition temperatures determined by DSC. These results suggest that the molecular motions concerned with the a- and b-processes are the origins of the two glass transitions. The a-process and b-process seem to be caused by the motion of fructose and water molecules in a freeze-concentrated phase in the frozen mixture.

We will present more detailed discussions for the contributions of fructose and water molecules to the relaxation processes.



Fig1. Dielectric constant and loss for 40wt% fructose-water mixture at -36 .