

# Effect of Water Content on Dielectric Relaxation of Gelatin in a Glassy State

Hitoshi Kumagai,\* Takashi Sugiyama, and Satoshi Iwamoto

Department of Applied Biological Chemistry, Division of Agriculture and Agricultural Life Sciences,  
The University of Tokyo 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan

The dielectric properties of gelatin in the glassy state were measured from 100 Hz to 1 MHz over a temperature range of  $-20$  to  $60$  °C. Samples with different water contents were prepared by varying the drying time for desalted gelatin solution; they were confirmed to be in the glassy state from DSC measurements. The dielectric relaxation (the decrease in dielectric constant,  $\epsilon'$ , and the maximum of the dielectric loss,  $\epsilon''$ ) was observed for each sample; the relaxation time  $\tau$  was evaluated from the peak of  $\epsilon''$ . The activation energy  $E$  obtained from an Arrhenius plot of  $\tau$  decreased with increasing water content. On the basis of the order of magnitude of  $E$ , the dielectric relaxation observed was considered to be  $\beta$ -relaxation reflecting the local motion of molecules.  $E$  and  $\tau$  seem to describe the enhancement effect of water on the mobility of gelatin molecules in the glassy state;  $\tau$  and  $E$  are considered to be suitable parameters for the characterization of the plasticizing effect of water on a glassy material.

**Keywords:** Dielectric relaxation; gelatin; water; plasticizer; glass

## INTRODUCTION

When the temperature of a glassy material is increased, the material changes to a rubbery state at the glass transition temperature,  $T_g$ . The glass transition has attracted great interest from food scientists in recent years because food materials maintain their physical and chemical stability better in a glassy state than in a rubbery state. The glass transition temperature  $T_g$  is influenced by food components; in addition, water is known to act as a plasticizer and depress  $T_g$  (Levine and Slade, 1988). It is therefore important to determine  $T_g$  for predicting food properties and stability. The glass transition temperature  $T_g$  for many foods has been determined by thermal analysis such as differential scanning calorimetry (DSC) and state diagrams ( $T_g$  versus water content plots) reported (Levine and Slade, 1993; Orford et al., 1989). Such data have contributed to the prediction of food properties and storage stability (Levine and Slade, 1993; Borchard et al., 1980).

On a molecular level, a glassy material is considered to be stable because the micro-Brownian motions of the main chains of the polymers are immobilized. Local segmental motions, however, remain even in a glassy state. Polymers in a glassy state approach an equilibrium state over an extended period; the volume, enthalpy, and entropy of a glassy material consequently decrease, that is, isotropic annealing or physical aging (Johari, 1982; Noel et al., 1993). The process of physical aging appears to be an important aspect of food properties and stability (Shelly and Amy, 1996). Information on molecular mobility in the glassy state is therefore also important as well as  $T_g$  data. Thermal analysis,

however, does not provide information about the motions of the molecular chain.

Dielectric spectroscopy is widely used to study molecular dynamics in dispersed systems, especially for synthetic polymers (Maxwell, 1873; Debye, 1929; McCrum et al., 1967; Johari, 1973, 1985, 1986; Boyd, 1985; Dorfmueller and Williams, 1987; Johnson and Cole, 1951; Adachi and Kotaka, 1983; Neagu et al., 1997). With increasing frequency, the dielectric constant,  $\epsilon'$ , often decreases, and the dielectric loss,  $\epsilon''$ , shows a peak due to the delay in dipole moments, this phenomenon being the so-called dielectric relaxation (Maxwell, 1873). From dielectric relaxation data, one can obtain parameters reflecting chain mobility: the relaxation time,  $\tau$ , which corresponds to the time needed for electric dipoles to orient in the direction of an electric field, and the activation energy  $E$  evaluated from the Arrhenius plot of  $\tau$ . In a glassy state (below  $T_g$ ), dielectric relaxation, which arises from the rotation of the side chain of a gelatin molecule and/or the local segmental motion of the backbone chain (McCrumb et al., 1967; Boyd, 1985; Dorfmueller and Williams, 1987; Tatsumi et al., 1992) is observed; this dielectric relaxation is called  $\beta$ - (or secondary) relaxation. The physical aging of a glass explained before causes a decrease in the number of molecules contributing to  $\beta$ -relaxation (Johari, 1985). The values of activation energy  $E$  are evaluated to be  $\sim 100$  kJ/mol for synthetic polymers such as poly(methyl methacrylate) (PMMA) and poly(ethylene terephthalate) (McCrumb et al., 1967). Dielectric relaxation has also been observed for concentrated sugar–water systems (Nishinari et al., 1985; Mariastella et al., 1991; Noel et al., 1992, 1993, 1996; Montes et al., 1997; Murthy et al., 1994). Dielectric relaxation of proteins or peptides has, however, not been investigated in concentrated systems.

Gelatin is a useful fibrous protein, produced from collagen (Djabourov et al., 1988; Pezron et al., 1991),

\* Author to whom correspondence should be addressed (telephone +81-3-5841-5167; fax +81-3-5841-8031; e-mail akumah@mail.ecc.u-tokyo.ac.jp).



and is used as a food supplement. Some researchers have reported on the glass transition of gelatin (Fakirov et al., 1997; Fraga and Williams, 1985; Marshall and Petrie, 1980). On the other hand, dielectric relaxation data have been reported for gelatin solution and gels (Fricke and Jacobson, 1939; Ikeda et al., 1997; Iwamoto and Kumagai, 1998), but there are few studies on the dielectric properties of glassy gelatin. Khutorsky and Lang (1997) measured the pyroelectric and dielectric properties of triglycine sulfate–gelatin films to examine the stability of the films during aging. They presented the frequency dependence of permittivity ( $\epsilon'$ ) in the frequency range of  $10^0$ – $10^5$  Hz. The values of  $\epsilon'$  in their study seem to be apparent ones due to the polarization of the counterion atmosphere in the electric double layer surrounding the colloidal particles or electrical polarization at the electrode–electrolyte interface; quantitative discussion such as the behavior of  $\tau$  and  $E$  has not been done.

In this study, prior to the investigation of the behavior of molecular motions in glassy gelatin involving physical aging, the water content dependence of the dielectric properties of desalted gelatin in the glassy state was analyzed without aging.

## THEORY

**Measurement of the Dielectric Constant,  $\epsilon'$ , and Loss,  $\epsilon''$ .** The dielectric constant,  $\epsilon'$ , and loss,  $\epsilon''$ , are defined by

$$\epsilon' = C/C_0 \quad (1)$$

$$\epsilon'' = G/\omega C_0 \quad (2)$$

where  $C$  is the capacitance of the sample,  $C_0$  is the capacitance of the empty cell,  $\omega$  is the angular frequency ( $=2\pi f$ ;  $f$  = frequency), and  $G$  is the conductance of the sample. A decrease in the  $\epsilon'$  versus  $f$  plot or a peak in the  $\epsilon''$  versus  $f$  plot is called the dielectric relaxation.

The parameters  $C$  and  $G$  are expressed using the admittance,  $Y$ , and the relative phase shift,  $\theta$ , as follows:

$$C = |Y| \sin \theta / \omega \quad (3)$$

$$G = |Y| \cos \theta \quad (4)$$

By substituting eqs 3 and 4 into eqs 1 and 2, respectively, one can obtain

$$\epsilon' = |Y| \sin \theta / \omega C_0 \quad (5)$$

$$\epsilon'' = |Y| \cos \theta / \omega C_0 \quad (6)$$

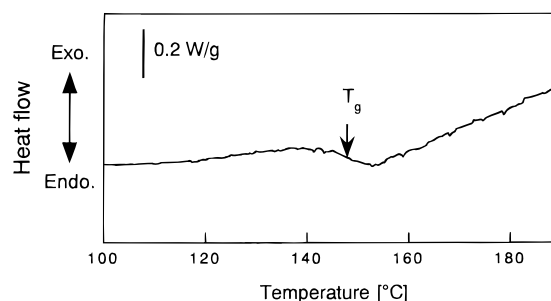
**Evaluation of the Relaxation Time  $\tau$  and the Activation Energy  $E$ .** The relaxation time  $\tau$  is related to  $f_{\max}$ , the frequency that gives the maximum magnitude of dielectric loss  $\epsilon''$  as follows:

$$\tau = 1/2\pi f_{\max} \quad (7)$$

If the temperature dependence of  $\tau$  is described by the following Arrhenius type equation, the activation energy  $E$  is calculated from the slope of a semilogarithmic plot of  $\tau$  versus  $1/T$  (Arrhenius plot)

$$\tau \propto \exp(E/RT) \quad (8)$$

where  $R$  is the gas constant.



**Figure 1.** DSC heat flow curves of gelatin–water systems. Water content = 0.038 kg/kg; heating rate = 10 °C/min.

## EXPERIMENTAL PROCEDURES

**Preparation of Gelatin Films.** Gelatin (Nitta Gelatin, Osaka, Japan; type B, from calf bone, 205 Bloom) was suspended in water and allowed to swell for 10 min at room temperature. The sample was then dissolved at 60 °C by stirring with a magnetic bar for 60 min. The salt was removed by electrodialysis with a Micro Acilyzer S1 (Asahi Chemical Industry Co., Tokyo, Japan) at 25 °C. The desalted gelatin solution was then freeze-dried. The  $\text{Na}^+$  content in the desalted gelatin samples was reduced to <1 ppm.

Desalted gelatin films were prepared by “hot-drying” (Marshall and Petrie, 1980) to prevent the formation of structural order (helix structure or crystallites). A 10% (w/w) aqueous solution was prepared by dissolving the required amount of the desalted gelatin and then heating at 60 °C in a polyethylene Petri dish. The gelatin solution was then kept at 60 °C for several days until it formed an aqueous film. By varying the drying days, four samples with different water contents were obtained; hereafter, the samples are referred to as samples A–D. Immediately after each sample was prepared, DSC and dielectric measurements were carried out. The water contents of samples A–D were determined to be 0.116, 0.0470, 0.0400, and 0.0380 kg/kg of samples, respectively, from the decrease in weight on drying under vacuum at 60 °C with  $\text{P}_2\text{O}_5$ .

**Determination of Glass Transition Temperature,  $T_g$ , by DSC.** The glass transition temperature,  $T_g$ , was determined using a DSC7 (Perkin-Elmer Japan Co., Ltd., Kanagawa, Japan) calibrated with indium and *n*-octane. The gelatin samples prepared were placed in a stainless pan, and the pan was hermetically sealed. An empty stainless pan was used as the reference.

The heating rate was 10 °C/min. In this study, the midpoint between the onset and end temperatures was taken as the glass transition temperature,  $T_g$ .

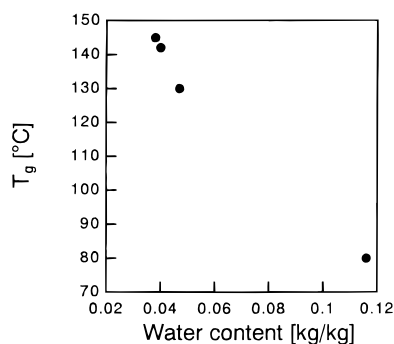
**Dielectric Measurement of Gelatin Films.** The temperature of a sample was varied from –20 to 60 °C at intervals of 10 °C. The temperature was raised to a selected value and then maintained for 30 min; thereafter, the electrical measurement was carried out. The magnitude of the admittance,  $|Y|$ , and the relative phase shift,  $\theta$ , of the sample were measured in the frequency range from 100 to  $10^6$  Hz with LCR meters (Hewlett-Packard Japan, Tokyo, Japan; 4284A and 4285A) equipped with a parallel plate type of cell (Ando Electric Co., Tokyo, Japan; SE-70) at the selected temperature. The dielectric constant  $\epsilon'$  and the loss  $\epsilon''$  were calculated using eqs 5 and 6.

As a preliminary test, the experimental system was calibrated using a poly(ethylene terephthalate) film, confirming that the measured values of  $\epsilon'$  and loss  $\epsilon''$  coincided with those measured by Tatsumi et al. (1992) within the error of 5%.

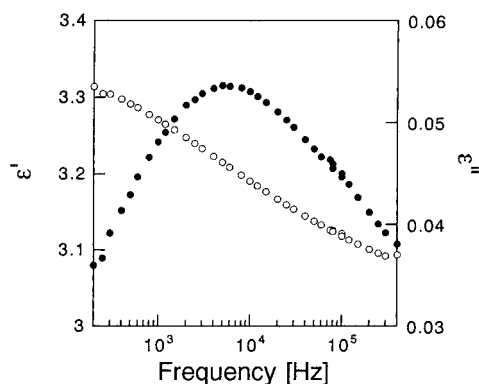
## RESULTS

As an example, a DSC heating curve for sample D is illustrated in Figure 1. The glass-transition temperature  $T_g$  is shown by an arrow; the value of  $T_g$  for sample D was determined to be 145 °C from the midpoints of the DSC curve. The contour of a DSC diagram of sample D





**Figure 2.** Dependence of the glass transition temperature  $T_g$  on water content.



**Figure 3.** Frequency dependence of the dielectric constant  $\epsilon'$  (○) and loss  $\epsilon''$  (●) for gelatin–water system at 0 °C. Water content = 0.038 kg/kg (sample D).

at the second run (the same sample was cooled rapidly in the DSC pan, and then the DSC measurement was carried out again) was similar to that in Figure 1; the value of  $T_g$  at the second run agreed well with that shown in Figure 1. If the specific heat change observed in Figure 1 is ascribed to helix–coil transition, the peak for helix–coil transition would be lost at the second run (Marshall and Petrie, 1980). Therefore, the specific heat change observed in Figure 1 is considered to be associated with glass transition of the gelatin film and not with an endothermic peak for helix–coil transition. The gelatin films prepared by hot drying as described before would contain little helix structure. The values of  $T_g$  for the samples examined in this study are shown in Figure 2. In this study, electrical measurements were carried out over a temperature range of  $-20$  to  $60$  °C. From the DSC data in Figure 2, samples A–D were confirmed to be in a glassy state in this temperature region. The dependence of  $T_g$  on water content shown in Figure 2 is similar to that for calf bone gelatin reported by Levine and Slade (1988). According to their data,  $T_g$  was independent of water content above a water content of 0.35 kg/kg of sample, whereas the value of  $T_g$  increased with decreasing water content for samples of water content of  $<0.35$  kg/kg of sample. They concluded, consequently, that an amount of water of  $<0.35$  kg/kg of sample functioned as an effective plasticizer of the amorphous regions of the gelatin polymer. For the gelatin examined in the present study, water is also considered to act as a plasticizer below a water content of 0.12 kg/kg of sample.

Typical spectra of the dielectric constant  $\epsilon'$  and the dielectric loss  $\epsilon''$  for a gelatin are shown in Figure 3. With increasing frequency,  $\epsilon'$  decreased and the dielectric loss showed a maximum; that is, the dielectric

relaxation was observed for the gelatin in a glassy state. The relaxation time  $\tau$  is given not only as the peak of the  $\epsilon''$  versus  $f$  plot but also as the inflection point of the  $\epsilon'$  versus  $f$  plot (Debye, 1929). It was, however, more feasible to evaluate  $\tau$  from the  $\epsilon''$  versus  $f$  plot than from the  $\epsilon'$  versus  $f$  plot in this study because an inflection point was difficult to detect, as shown in Figure 3. Therefore, only the frequency dependence of  $\epsilon''$ , not that of  $\epsilon'$ , will be examined in the subsequent part of this study.

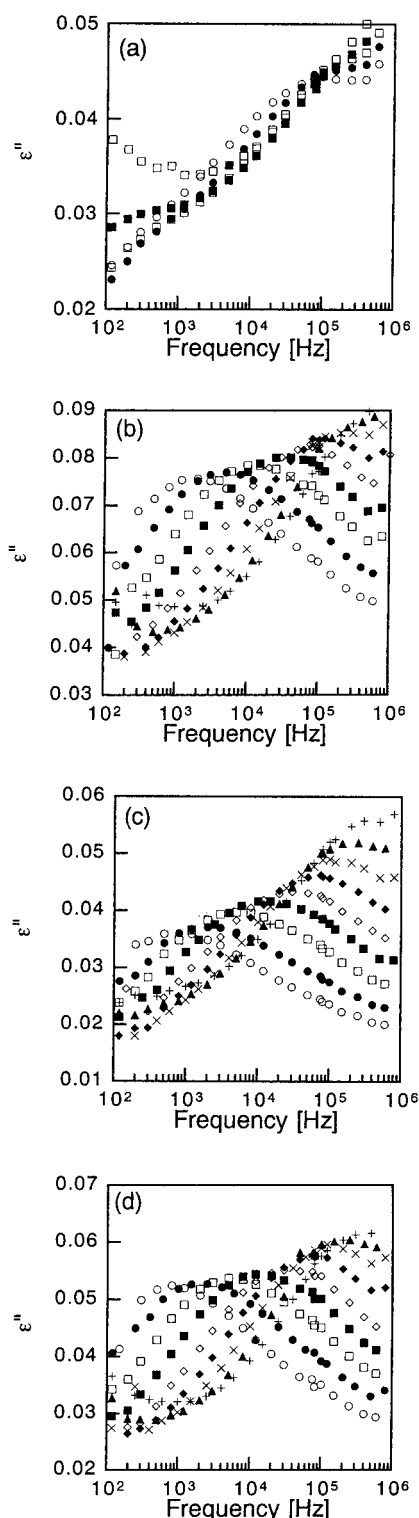
Figure 4 shows the frequency dependence of dielectric loss  $\epsilon''$  for samples A–D at various temperatures; the peaks of  $\epsilon''$  (dielectric relaxation) were observed for each sample. The peaks of  $\epsilon''$  shifted to higher frequencies with increasing temperature and were not observed at high temperature (see panels a–c of Figure 4). At such a high temperature, the peak of  $\epsilon''$  would have shifted to  $>10^6$  Hz and consequently would not have been observed in the frequency range examined in this study. The relaxation time  $\tau$  was therefore calculated according to eq 7 only in the temperature range where the peaks of  $\epsilon''$  are observed. Figure 5 shows the dependence of  $\tau$  on water content. The value of  $\tau$  was larger for lower temperature at an identical water content and decreased sharply with increasing water content.

Figure 6 presents Arrhenius plots of  $\tau$  for samples A–D. For all of the samples, a linear relationship was observed, and the activation energies  $E$  were obtained from eq 8. Figure 7 shows the dependence of activation energy  $E$  on water contents. The value of  $E$  decreased from 64.5 to 34.0 kJ/mol with increasing water contents from 0.0380 to 0.116 kg/kg of sample.

## DISCUSSION

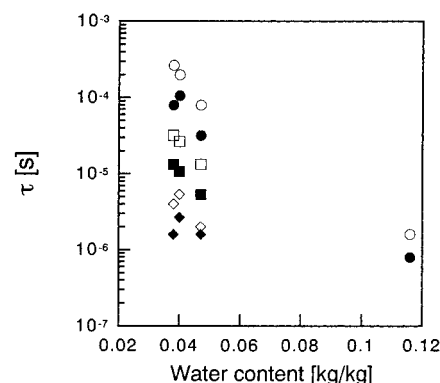
As shown in Figure 5, the peaks of  $\epsilon''$ , that is, dielectric relaxation, were observed for each glassy gelatin. As explained before,  $\beta$ -relaxation is an intrinsic property of the glassy state (Johari, 1985), and the value of its activation energy  $E$  is  $\sim 100$  kJ/mol. On the other hand, the dielectric relaxation observed in a rubbery state (at temperatures around and above  $T_g$ ) is ascribed to the micro-Brownian motions of the main chains (McCrum et al., 1967; Boyd, 1985). This relaxation is called  $\alpha$ - (or the primary) relaxation, and the value of its apparent activation energy  $E$  are 100–700 kJ/mol for synthetic polymers and sugars (Nishinari et al., 1985; Mariastella et al., 1991; Noel et al., 1992, 1993, 1996; Montes et al., 1997; Murthy et al., 1994). As shown in Figure 7, the value of  $E$  varied from 64.5 to 34.0 kJ/mol; on the basis of the order of the magnitude of  $E$ , the dielectric relaxations observed for the samples examined were considered to be  $\beta$ -relaxation reflecting the local motion of molecules (McCrum et al., 1967; Boyd, 1985; Dorfmueller and Williams, 1987). It is generally thought that  $\beta$ -relaxation in amorphous polymers results from rotations of side groups attached to the main chain and/or from limited motions within the chain backbone. The relaxation would be ascribed to the rotation of the side chain of a gelatin molecule and/or the local segmental motion of the backbone chain (Johari, 1985; McCrum et al., 1967; Murthy et al., 1994), although we cannot identify the part of a gelatin molecule that the relaxation reflects.



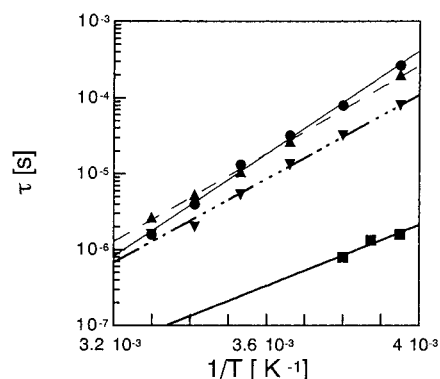


**Figure 4.** Frequency dependence of the dielectric loss for a gelatin–water system: (a) sample A; (b) sample B; (c) sample C; (d) sample D. Temperature: ○, −20 °C; ●, −10 °C; □, 0 °C; ■, 10 °C; ◇, 20 °C; ◆, 30 °C; ×, 40 °C; ▲, 50 °C; +, 60 °C.

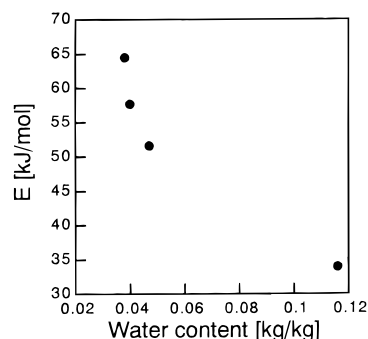
In Figure 5, the value of  $\tau$  was larger for lower temperature at an identical water content. The relaxation time  $\tau$  can be the time needed for electric dipoles to orient in the direction of the electric field and increases as the local viscosity increases (Noel et al., 1993). A temperature increase would make the local viscosity decrease, resulting in a decrease in  $\tau$ . Moreover, as shown in Figure 5, the value of  $\tau$  decreased



**Figure 5.** Dependence of the relaxation time  $\tau$  on water content. Temperature: ○, −20 °C; ●, −10 °C; □, 0 °C; ■, 10 °C; ◇, 20 °C; ◆, 30 °C; ×, 40 °C; ▲, 50 °C; +, 60 °C.



**Figure 6.** Arrhenius plots of  $\tau$  for a gelatin–water system. Sample: ■, sample A; ▼, sample B; ▲, sample C; ●, sample D.



**Figure 7.** Dependence of the activation energy  $E$  on water content.

sharply with increasing water content. Water is the most important plasticizer for food, and, as discussed before, water is also considered to act as a plasticizer for gelatin examined in the present study below a water content of 0.12 kg/kg of sample. Plasticization, on a molecular level, leads to increased intermolecular space or free volume and decreased local viscosity (Levine and Slade, 1993). Local viscosity would be decreased by the plasticizing effect of water, causing the value of  $\tau$  to be reduced, as shown in Figure 5. The relaxation time  $\tau$  seems to describe the enhancement effect of water on the mobility of gelatin molecules in the glassy state. Of course, the relaxation time  $\tau$  reflects the movement of electric dipoles in the electric field. However, a difference in the mobility of molecular chains among materials could be relatively compared.

As can be seen from Figure 7, the value of  $E$  decreased with increasing water contents from 0.0380 to 0.116 kg/



kg of sample. The activation energy  $E$  is the energy barrier for the movement of electric dipoles in a system (Fröhlich, 1958; Kirkwood, 1941; McCrum et al., 1967). Water would have decreased the local viscosity of the gelatin films and reduced the value of  $E$ . As discussed before and here, both  $\tau$  and  $E$  can describe the enhancement effect of water on the mobility of gelatin molecules in the glassy state. The relaxation time  $\tau$  is influenced not only by water content but also by temperature, as shown in Figure 5. On the other hand,  $E$  takes an intrinsic value for a sample at a selected water content; in addition, the relaxation type ( $\alpha$  or  $\beta$ ) can be discriminated from the order of the magnitude of  $E$ .

Water content dependence of the activation energy  $E$  evaluated from dielectric measurement has been investigated only on a limited basis. Starkweather and Barkley (1981) investigated the dielectric properties of Nylon 66 at frequencies from 10 to  $10^5$  Hz and at temperatures from  $-70$  °C to room temperatures and reported that moisture increased the frequency for the  $\beta$ -relaxation and reduced its activation energy; this result is similar to that of the present study.

In conclusion, dielectric relaxation was observed for glassy gelatin. From the order of the magnitude of  $E$ , the relaxation observed was  $\beta$ -relaxation, which is ascribed to the rotation of a side chain of a gelatin molecule and/or the local segmental motion of the backbone chain. The relaxation time  $\tau$  and activation energies  $E$  seemed to describe the enhancement effect of water on the mobility of gelatin molecules in the glassy state; they are considered to be suitable parameters for characterizing the plasticizing effect of water on a glassy material.

#### ACKNOWLEDGMENT

We express our thanks to Mr. Y. Hayashi for his help in DSC measurements.

#### LITERATURE CITED

- Adachi, K.; Kotaka, T. Dielectric normal mode in dilute solutions of poly(2,6-dichloro-1,4-phenylene oxide). *Macromolecules* **1983**, *16*, 1936–1941.
- Borchard, W.; Bremer, W.; Keese, A. The state diagram of the water-gelatin system. *Colloid Polym. Sci.* **1980**, *258*, 516–526.
- Boyd, R. H. Relaxation processes in crystalline polymers: experimental behaviour—a review. *Polymer* **1985**, *26*, 323–346.
- Debye, P. *Polar Molecules*; Chemical Catalogue Co.: New York, 1929.
- Djabourov, M.; Leblond, J.; Papon, P. Gelation of aqueous gelatin solutions. I. Structural investigation. *J. Phys. (Fr.)* **1988**, *49*, 319–332.
- Dorfmueller, T.; Williams, G. Eds. *Molecular Dynamics and Relaxation Phenomena in Glasses*; Springer Verlag: Berlin, Germany, 1987.
- Fakirov, S.; Sarac, Z.; Anbar, T.; Boz, B.; Bahar, I.; Evstatiev, M.; Apostolov, A.; Mark, J. E.; Kloczkowski, A. Mechanical properties and transition temperature of cross-linked-oriented gelatin. *Colloid Polym. Sci.* **1997**, *275*, 307–314.
- Fraga, A. N.; Williams, R. J. Thermal properties of gelatin films. *Polymer* **1985**, *26*, 113–118.
- Fricke, H.; Jacobson, L. E., A dielectric study of the gelatin-water system: Anomalous dispersion in bound (oriented) water. *J. Phys. Chem.* **1939**, *43*, 781–796.
- Fröhlich, H. *Theory of Dielectrics; Dielectric Constant and Dielectric Loss*; Clarendon Press: Oxford, U.K., 1958.
- Ikedda, S.; Kumagai, H.; Nakamura, K. Dielectric analysis of interaction between polyelectrolytes and metal ions within food gels. *Food Hydrocolloids* **1997**, *11*, 303–310.
- Iwamoto, S.; Kumagai, H. Analysis of dielectric relaxation of a gelatin solution. *Biosci., Biotechnol., Biochem.* **1998**, *62*, 1381–1387.
- Johari, G. P. Intrinsic mobility of molecular glasses. *J. Chem. Phys.* **1973**, *58*, 1766–1770.
- Johari, G. P. Effect of annealing on the secondary relaxations in glasses. *J. Chem. Phys.* **1982**, *77*, 4619–4626.
- Johari, G. P. Low-frequency molecular relaxations in disordered solids. *J. Chim. Phys.* **1985**, *82*, 283–291.
- Johari, G. P. Dielectric relaxations in the liquid and glassy state of poly(propylene oxide) 4000. *Polymer* **1986**, *27*, 866–870.
- Johnson, J. F.; Cole, R. H. Dielectric polarization of liquid and solid formic acid. *J. Am. Chem. Soc.* **1951**, *73*, 4536–4540.
- Khutorsky, V. E.; Lang, B. Very strong influence of moisture on pyroelectric and dielectric properties of triglycine sulfate-gelatin films. *J. Appl. Phys.* **1997**, *82*, 1288–1292.
- Kirkwood, J. G.; Fuoss, R. M. Anomalous Dispersion and Dielectric Loss in Polar Polymers. *J. Chem. Phys.* **1941**, *9*, 329–340.
- Levine, H.; Slade, L. Water as a plasticizer: physico-chemical aspects of low-moisture polymeric systems. In *Water Science Reviews*. 3; Franks, F., Ed.; Cambridge University Press: New York, 1988; pp 79–185.
- Levine, H.; Slade, L. The glassy state in applications for the food industry, with an emphasis on cookie and cracker production. In *The Glassy State in Foods*; Blanshard, J. M. V., Lillford, P. J., Eds.; Nottingham University Press: Leicestershire, U.K., 1993.
- Mariastella, S.; Giuseppina, C.; Maria, P. Molecular motions of polysaccharides in the solids state: dextran, pullulan and amylose. *Int. J. Biol. Macromol.* **1991**, *13*, 254–260.
- Marshall, A. S.; Petrie, S. E. B. Thermal transitions in gelatin and aqueous gelatin solutions. *J. Photogr. Sci.* **1980**, *28*, 128–134.
- Maxwell, J. C. *A Treatise on Electricity and Magnetism*; Clarendon Press: London, U.K., 1873.
- McCrumb, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Wiley: London, U.K., 1967.
- Montes, H. M.; Mazeau, K.; Cavaille, J. Y. Secondary mechanical relaxations in amorphous cellulose. *Macromolecules* **1997**, *30*, 6977–6984.
- Murthy, S. S. N.; Sobhanadri, J.; Gaqngasharan. The origin of  $\beta$  relaxation in the organic glasses. *J. Chem. Phys.* **1994**, *100*, 4601–4606.
- Neagu, E.; Pissis, P.; Apekis, L.; Ribelles, G. Dielectric relaxation spectroscopy of polyethylene terephthalate (PET) films. *J. Phys. D: Appl. Phys.* **1997**, *30*, 1551–1560.
- Nishinari, K.; Shibuya, N.; Kainuma, K. Dielectric relaxation in solid dextran and pullulan. *Makromol. Chem.* **1985**, *186*, 433–438.
- Noel, T. R.; Ring, S. G.; Whittam, M. A. Dielectric relaxations of small carbohydrate molecules in the liquid and glassy states. *J. Phys. Chem.* **1992**, *96*, 5662–5667.
- Noel, T. R.; Ring, S. G.; Whittam, M. A. Relaxations in supercooled carbohydrate liquids. In *The Glassy State in Foods*; Blanshard, J. M. V., Lillford, P. J., Eds.; Nottingham University Press: Leicestershire, U.K., 1993.
- Noel, T. R.; Parker, R.; Ring, G. S. A comparative study of the dielectric relaxation behavior of glucose, maltose, and their mixtures with water in the liquid and glassy states. *Carbohydr. Res.* **1996**, *282*, 193–206.
- Orford, P. D.; Parker, R.; Ring, G. S.; Smith, A. C. Effect of water as a diluent on the glass transition behaviour of malto-oligosaccharides, amylose and amylopectin. *Int. J. Biol. Macromol.* **1989**, *11*, 91–96.
- Pezron, I.; Djabourov, M.; Leblond, J. Conformation of gelatin chains in aqueous solutions: 1. A light and small-angle neutron scattering study. *J. Polym.* **1991**, *32*, 3201–3210.



- Scandola, M.; Ceccorulli, G.; Pizzoli, M. Molecular motions of polysaccharides in the solids state: dextran, pullulan and amylose. *Int. J. Biol. Macromol.* **1991**, *13*, 254–260.
- Shelly, J. S.; Amy, M. L. Physical aging of maltose glasses. *J. Food Sci.* **1996**, *61*, 870–875.
- Starkweather, Jr., H. W.; Barkley, J. R. The effect of water on the secondary dielectric relaxations in Nylon 66. *J. Polym. Sci: Polym. Phys. Ed.* **1981**, *19*, 1211–1220.
- Tatsumi, T.; Ito, E.; Hayakawa, R. Study of the dielectric  $\beta$ -relaxation in poly(ethylene terephthalate) and ethylene isophthalate terephthalate copolyesters. *J. Polym. Sci. B: Polym. Phys.* **1992**, *30*, 701–706.

Received for review October 1, 1999. Revised manuscript received March 15, 2000. Accepted March 23, 2000. Part of this work was financially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan and the Salt Science Research Foundation, Japan.

JF991081P