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Dielectric Study on Polymer Gel in Frozen State

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Dielectric relaxation measurements were performed on various polymer gels in frozen state in the frequency range from 1MHz up to 18GHz. Though a higher frequency relaxation process reflecting free water observed in GHz region disappeared below the freezing temperature, another process for unfreezable water was still observed. The amount of unfreezable water determined from the relaxation strength and differential scanning calorimetry was discussed with glass transition phenomena observed below the freezing temperature.

Keywords: dielectric relaxation, time domain reflectometry, polymer gel, unfreezable water.

1. INTRODUCTION

Water is the most popular liquid existing anywhere on earth. Water molecule has a permanent electric dipole moment which rotational diffusion is observed as a dielectric relaxation process. The dielectric relaxation time of pure water is 8 ps at 25°C. When water coexists with hydrophilic polymers, the relaxation time of water increases because of the larger restriction of water molecules by the polymer chains. In the subzero temperature range, a part of water in polymer-water mixtures freezes and another part of water remains in the liquid state. The latter is called the unfreezable water. Water molecules surrounding the polymer chains should be observed as the unfreezable water. Recently it was suggested that the amount of unfreezable water in the aqueous solutions depends on the molecular structure of the polymer [1].

Dielectric spectroscopy is an effective tool to observe unfreezable water [2]. The amount of unfreezable water is estimated from the relaxation strength. We measured dielectric complex permittivity in the frozen state of various gels of hydroxypropylmethylcellulose (HPMC) and carboxymethylcellulose (CMC) in the present work. Differential scanning calorimetry (DSC) was also employed to determine the amount of unfreezable water and the glass transition temperature, T_g . A relationship between the amount of unfreezable water and the molecular weight of the repeat unit of the polymers is discussed. In addition we also discuss the relationship between T_g and the volume fraction of unfreezable water.

2. EXPERIMENTAL

HPMC was obtained from Shin-Etsu Chemical Co [3]. CMC was obtained from Daicel Co. Ltd., Japan.

HPMC and CMC were dissolved in deionized water. The aqueous solutions of CMC (7wt%) and HPMC (10wt%) were irradiated with gamma rays of 10kGy [4].

Dielectric relaxation measurements were performed by Time Domain Reflectometry (TDR) [2] and Impedance Material Analyzer HP4291A Agilent Technologies (IMA) measuring systems during the cooling process from 25°C to -60°C. The frequency range was 1MHz-18GHz. Electrodes employed for TDR and IMA measurements are a flat-end cell and a coaxial cell with the electric length of 0.15mm and 3.10mm, respectively.

Glass transition temperature and transition enthalpy of melting were obtained from DSC measurements for aqueous gels of poly(acrylamide) (PAAm), HPMC, and CMC.

3. RESULTS and DISCUSSION

Dielectric dispersion and absorption observed by IMA for 10wt% HPMC gel in cooling process from 25°C to -60°C were shown in Figure 1. When the HPMC gel was frozen at temperature between -6°C and -8°C, both ϵ' and ϵ'' values drastically decreased. The dielectric dispersion and absorption curves were explained by the summation of the two relaxation processes described by the Cole-Cole equation as shown in Figure 2.

$$\epsilon^*(\omega) = \frac{\Delta\epsilon_h}{1+(j\omega\tau_h)^\beta} + \frac{\Delta\epsilon_l}{1+(j\omega\tau_l)^\beta} + \epsilon_\infty + \frac{\sigma}{j\omega\epsilon_0} \quad (1)$$

where $\Delta\epsilon$ is the relaxation strength, τ is the relaxation time, ω is the angular frequency, j is the imaginary unit, ϵ_0 is the permittivity of vacuum, ϵ_∞ is the permittivity at limiting high frequency, β is the parameter to describe symmetrical broadness, σ is the dc conductivity, and h and l indicate the higher and lower relaxation processes, respectively.

Figure 3 shows temperature dependence of $\Delta\epsilon_h$ for aqueous gel of 10wt% HPMC. The $\Delta\epsilon_h$ abruptly decreased at the freezing temperature, T_f . The $\Delta\epsilon_h$ value is the relaxation strength for unfreezable water below T_f and that for free water above T_f . The number of the unfreezable water molecules per repeat unit of the polymer, n_{ufw} can be calculated by the following equation.

$$n_{ufw}(T) = \frac{\Delta\epsilon_h(T)}{\Delta\epsilon_{wat}(T)} \cdot \frac{100-C}{C} \cdot \frac{M_{rep}}{M_{wat}} \quad (2)$$

where $\Delta\epsilon_h$ is the relaxation strength for unfreezable water, $\Delta\epsilon_{wat}$ is the relaxation strength for pure water, C (wt%) is the polymer concentration, M_{rep}

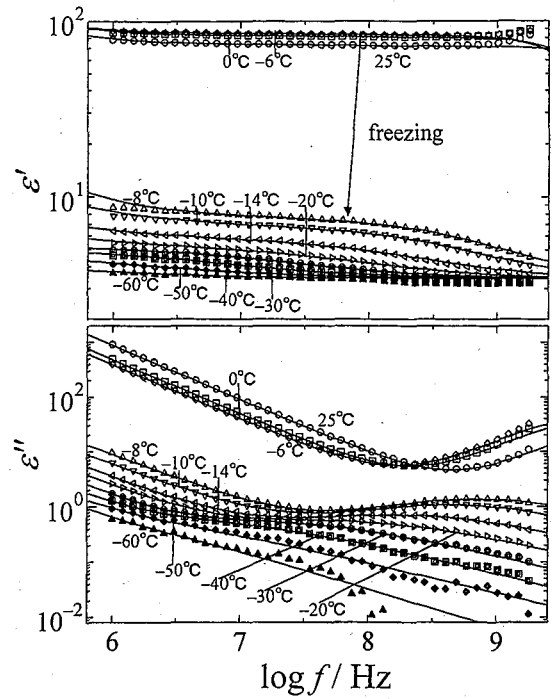


Fig.1 Dielectric dispersion and absorption for 10wt% HPMC aqueous gel irradiated at 10kGy in cooling process from 25°C to -60°C.

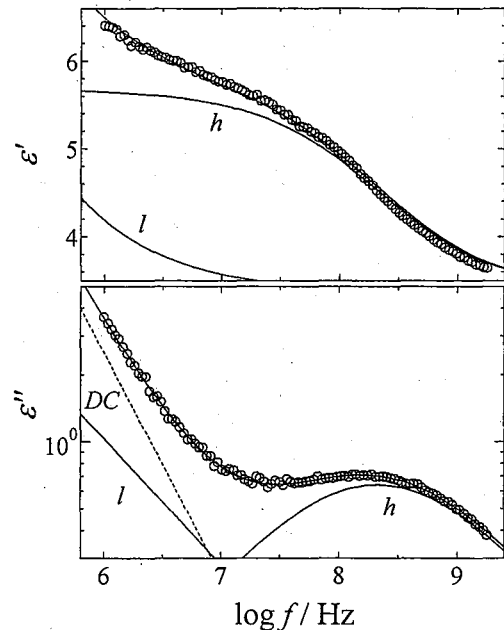


Fig. 2 Dielectric dispersion and absorption measured at -14°C for 10wt% HPMC aqueous gel irradiated at 10kGy. Lines were calculated from Eq. (1).

is the molecular weight of repeat unit, and M_{wat} is the molecular weight of water. Here the unfreezable water is assumed to take the same structure with pure water. n_{ufw} thus obtained were plotted against M_{rep} for various polymer aqueous systems in Figure 4. The n_{ufw} values increase in proportion to M_{rep} for the coiled polymer solutions of poly(vinyl pyrrolidone) (PVP) [1,5], poly(ethyleneglycol) (PEG) [1], poly(vinyl alcohol) (PVA) [1], poly(vinyl methyl ether) (PVME) [1], and amorphous gels of agarose [1], and hyaluronic acid [1], are shown on the same line. On the other hand, the n_{ufw} values for aqueous solutions of globular proteins of albumin [1,6] and trypsin [7], heat denatured gel of ovalbumin [1,8], and aqueous solution of schizophyllan [1,9] taking triplehelical structure were apparently smaller than that expected from the line, since water cannot exist inside those proteins and polysaccharide because of the hydrophobic interaction. In this work, we added more experimental data of aqueous solutions of CMC, HPMC, PAAm, and PAAm gel to the n_{ufw} - M_{rep} plot. The n_{ufw} value is smaller for the PAAm gel and is two times larger for the aqueous solution of CMC than each value expected from the straight line. The plots for HPMC and PAAm aqueous solutions are close to the straight line.

The n_{ufw} value for the PAAm gel is recognized to be smaller than that for PAAm aqueous solution. PAAm gel should have larger polymer density fluctuation in comparison with the aqueous solution. Then the condensed PAAm chains contact with smaller number of water molecules, and PAAm gel brings about a comparable result with the aqueous solutions of proteins and schizophyllan. The information of the microscopic structures of CMC and HPMC aqueous solutions have not been investigated enough. The present result suggests some difference in microscopic structures, for example, entanglements or the network structure of the polymer chains.

In the frozen state, polymer-water mixtures mainly contain three components as polymer, ice, and unfreezable water. The water molecules forming ice are fixed at the lattice of ice crystal. These molecules essentially remain at the lattice and cannot take a diffusive motion at least in the present frequency range. Therefore the ice acts as a restricted wall against the rotational and diffusive motions of the unfreezable water and the polymer chain. In the dynamical viewpoint, the dielectric loss peak of the primary relaxation process is observed around 1mHz at the glass transition temperature. Since the loss peak for

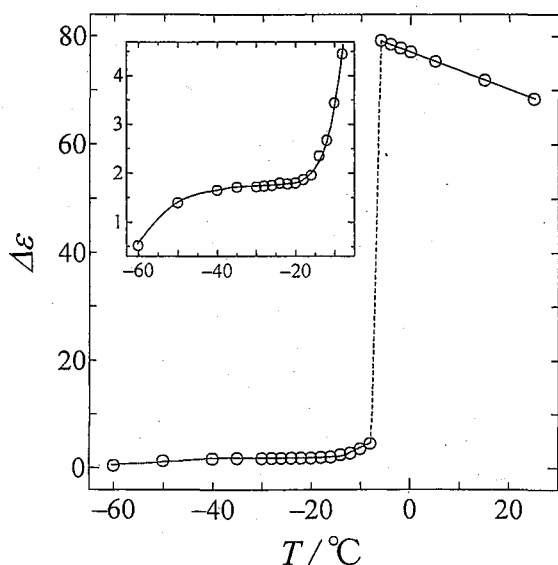


Fig.3. Temperature dependence of $\Delta\epsilon_h$ for 10wt% HPMC aqueous irradiated at 10kGy in cooling process from 25°C to -60°C.

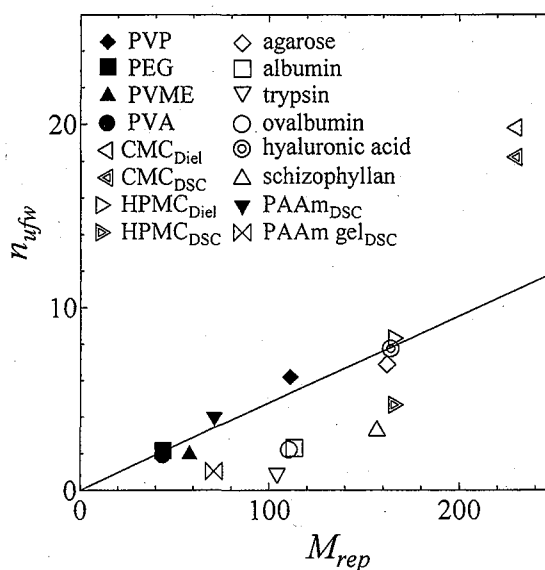


Fig.4. The number of unfreezable water per repeat unit, n_{ufw} vs. the molecular weight of repeat unit, M_{rep} , for various aqueous gels and solutions.

unfreezable water is observed in the MHz range of the frequency at the glass transition temperature, the unfreezable water itself should not exhibit the glass transition. In addition, according to our unpublished data of the glass transition observed by DSC and dielectric relaxation in a frozen state for poly(vinyl acetate) (PVAc)-benzene mixtures[10], the relaxation peak for PVAc was located in mHz range around the glass transition temperature, as well as those for the polymer-water mixtures. Then it is reasonable to consider that relaxation phenomena due to polymer chain motions restricted by the ice should cause the glass transition.

The polymer chain is surrounded by the unfreezable water molecules, whose relaxation time is quite smaller than that of the polymer chain. Therefore the space occupied by the unfreezable water behaves as the free space like the free volume for the polymer chain. Then glass transition temperature should be related to the amount of unfreezable water for a certain part of the chain. In this study, we tentatively examined the volume fraction of the unfreezable water, ϕ , against the repeat unit of the polymer chain by the following equation;

$$\phi = \frac{V_{H_2O} \cdot n_{ufw}(T)}{V_{ru} + V_{H_2O} \cdot n_{ufw}(T)} \quad (3)$$

where V_{H_2O} and V_{ru} are the van der Waals volumes obtained for water molecule and repeat unit of the

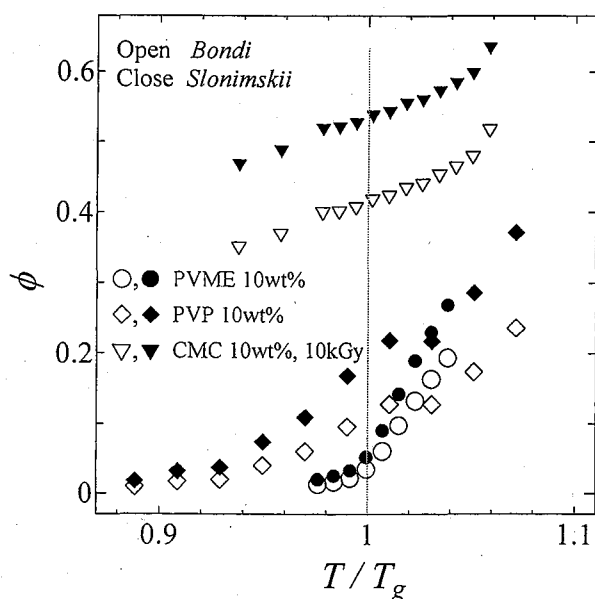


Fig.5 Plots of volume fraction of unfreezable water, ϕ , against scaled temperature, T/T_g .

polymer, respectively. These van del Waals volumes were obtained from literatures of Bondi [11] and Slonimskii [12] et al.

Figure 5 is the plots of the volume fraction of unfreezable water, ϕ , thus obtained for the aqueous solutions of PVP, PVME, and CMC against the scaled temperature. We already had both T_g and the amount of unfreezable water for these aqueous solutions.

The ϕ value decreases with decreasing temperature, since the unfreezable water gradually freezes and decreases with decreasing temperature. It is also shown that the ϕ value at T_g depends on the chain structure. The large value indicated by the CMC solution at T_g seems to suggest that more rigid polymers require larger ϕ for chain motions.

The dependency of the amount of unfreezable water is expected to provide important information for the liquid structure of polymer aqueous solutions in the frozen state. More systematic measurements should realize the discussion on the microscopic structure of water-polymer systems including gel in detail.

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