ELSEVIER

PII: S0144-8617(96)00083-5

Carbohydrate Polymers **30** (1996) 141–144

0144-8617/96/$15.00 + .00

Water structure in gellan gum–water system

S. Mashimo,[1] N. Shinyashiki & Y. Matsumura

Department of Physics, Tokai University, Hiratsuka-shi, Kanagawa 259-12, Japan

Gellan gum shows a gel–sol transition at a temperature of 50°C. Two relaxation peaks were definitely observed both in gel and in solution. The high frequency peak observed at about 10GHz could be easily attributed to free water. It is a surprising result that free water exists even in the gel phase and most of water included is the free water. The low frequency peak around 10MHz would be due to orientation of bound water. Relaxation strength shows a drastic change at the gel–solution transition point. It is far greater in gel phase than in solution. No other relaxation process could be found in the frequency range concerned. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Dielectric properties of gel have not been clarified yet, since the gel has usually a big dc conductivity which prevents accurate measurements of the properties. In the case where the gel has a lot of water, the structure of water inside of the gel network has not been examined sufficiently to give an appropriate model for the structure. It is doubtless that water inside forms a cluster. It does not leak from the gel, even when the gel has a lot of water. If water molecules do not construct a cluster and each molecule exists independently inside of the network, then some water molecules could pass through the network. In addition, the possibilty is quite interesting that water molecules in the vicinity of the net form a special structure and play a peculiar role in stabilizing the network.

A gellan gum–water system shows a gel–sol transition at a temperature depending on the concentration of gellan gum (Miyoshi *et al.*, 1994a, b). The system has relatively a low dc conductivity. Therefore it is thought that the system is suitable for dielectric measurements. However, even though gellan gum has a low dc conductivity, accurate dielectric measurements at frequencies lower than 100kHz are quite difficult. Therefore if there is a relaxation peak at a frequency lower than 100kHz, this peak cannot be extracted accurately from the total absorption. Usually the relaxation strength of the relaxation process due to molecular motion is small and the dispersion and absorption for the process are hardly distinguishable from the total dispersion and absorption.

It has been well established that microwave dielectric measurement is available to examine water structure in polymers and biomaterials (Mashimo *et al.*, 1987, 1989; Shinyashiki *et al.*, 1990; Kuwabara *et al.*, 1988; Umehara *et al.*, 1990; Miura *et al.*, 1994). Most biosystems contain three kinds of water structure: the first shows an absorption peak at about 10GHz, which has the same structure as the bulk water; the second shows a peak at 10–100MHz and is thought to be bound to the biopolymers or biomaterials; the third has an intermediate structure between the first and the second. This intermediate structure exists between the first and the second layers. Recently, measurements in a region from MHz to GHz have been performed on the systems by employing time domain reflectometry (TDR). This TDR method is available to measure biosystems with dc conductivity. In this work the TDR method was employed to examine dielectric properties of gellan gum–water system in a frequency range of 100Hz–10GHz. At the phase transition temperature, it is expected that the relaxation process due to water shows a change since the gel structure disappears and the amounts of the bound water associated with the network disappear at this temperature too.

EXPERIMENTAL

Gellan gum was the same as that used in the previous works (Miyoshi *et al.*, 1994a, b). It is a microbial polysaccharide derived from *Pseudomonas elodea*. The contents of the inorganic ions Na^+, K^+, Ca^{2+} and Mg^{2+} are: Na, 3.03%; K, 0.19%; Ca, 0.11%; and Mg, 0.02%. No further purification was performed before use. Distilled and dechlorinated water was purchased from Wittaker Bioproducts Inc.

The system and the apparatus of TDR measurement have been reported previously (Miura *et al.*, 1994; Cole *et al.*, 1980, 1989). If a known sample with known

---

[1] Deceased.

permittivity ε^*_S is used as a reference sample, the unknown permittivity ε^*_X is given as

$$\varepsilon_X^*(\omega) = \varepsilon_S^*(\omega)\frac{1 + \{(cf_S)/[j\omega(\gamma d)\varepsilon_S^*(\omega)]\}\rho f_X}{1 + \{[j\omega(\gamma d)\varepsilon_S^*(\omega)]/(cf_S)\}\rho f_S} \tag{1}$$

where

$$\rho = \frac{r_S - r_X}{r_S + r_X}$$

$$f_X = Z_X\cot Z_X \, Z_X = (\omega d/c)\varepsilon_X^*(\omega)^{1/2}$$

$$f_S = Z_S\cot Z_S \, Z_S = (\omega d/c)\varepsilon_S^*(\omega)^{1/2}$$

where $r_X(\omega)$ is the Fourier transform of the reflected wave from the unknown sample, $r_S(\omega)$ is that from the known sample, γd is an electric length of the cell, d is the geometric cell length, c is the speed of propagation, and ω is the angular frequency.

In this work, two kinds of aqueous solutions of gellan gum (2.5 and 5.0wt%) were prepared as follows. The powdered sample was dispersed by stirring to swell at 40°C for several hours and then heated at 95°C for several hours before each dielectric measurement to prevent gelation.

RESULTS

Two relaxation peaks can be seen in absorption curve as shown in Fig. 1 where contribution of dc conductivity is eliminated. The same trend was found for all solutions tested. Frequency dependence of the complex permittivity is thus expressed by

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon_l}{(1 + j\omega\tau_l)^{\alpha_l}} + \frac{\Delta\varepsilon_h}{1 + (j\omega\tau_h)^{\beta_h}} \tag{2}$$

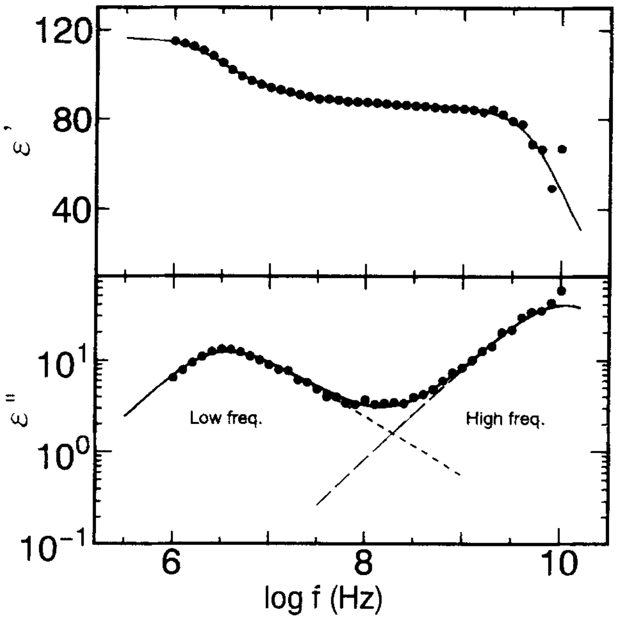

Fig. 1. Dielectric dispersion and absorption curves for gellan gum–water system with a gellan concentration of 5wt% at 5°C.

where ε_∞ is the limiting dielectric constant at high frequency, $\Delta\varepsilon$ is the relaxation strength, τ is the relaxation time, and α and β are the relaxation parameters describing the distribution of relaxation times, respectively. Suffix h indicates the high frequency process and l indicates the low frequency process, respectively. The high frequency process is well described by the Cole–Cole representation (Cole & Cole, 1941) and the low frequency one is described by the Cole–Davidson representation (Davidson & Cole, 1951).

The experimental dispersion and absorption curves can be fitted well by Equation 2 employing appropriate values to the parameters, which are listed in Table 1. Relaxation time for the high frequency process is in good accordance

Table 1. Dielectric relaxation parameters of gellan gum–water systems.

	Low frequency process			High frequency process				
T(°C)	α	$\Delta\varepsilon_l$	$\log\tau_l$(s)	β	$\Delta\varepsilon_h$	$\log\tau_h$(s)	ε_∞	σ(s)
2.5wt%								
0	0.741	12.1	−7.44	0.987	83.7	−10.78	6.14	0.200
5	0.720	9.72	−7.61	0.995	82.3	−10.84	5.72	0.228
15	0.744	5.03	−8.08	0.997	77.8	−10.94	5.96	0.281
25	0.897	3.32	−8.42	0.981	69.6	−11.04	7.43	0.324
35	0.811	2.41	−8.55	0.982	68.8	−11.12	5.52	0.363
45	0.706	1.86	−8.89	0.982	64.2	−11.25	5.39	0.414
5.0wt%								
0	0.554	53.5	−6.82	0.981	82.0	−10.77	5.67	0.250
5	0.643	30.6	−7.21	0.979	81.8	−10.83	4.60	0.286
15	0.519	26.6	−7.34	0.999	74.2	−10.93	5.66	0.390
25	0.478	28.0	−7.25	0.984	69.0	−11.03	5.28	0.464
45	0.523	26.6	−7.57	0.981	61.2	−11.24	5.09	0.604
50	0.579	3.58	−8.65	0.859	58.8	−11.31	5.54	0.640
55	0.495	2.39	−9.23	0.839	58.8	−11.31	6.55	0.672

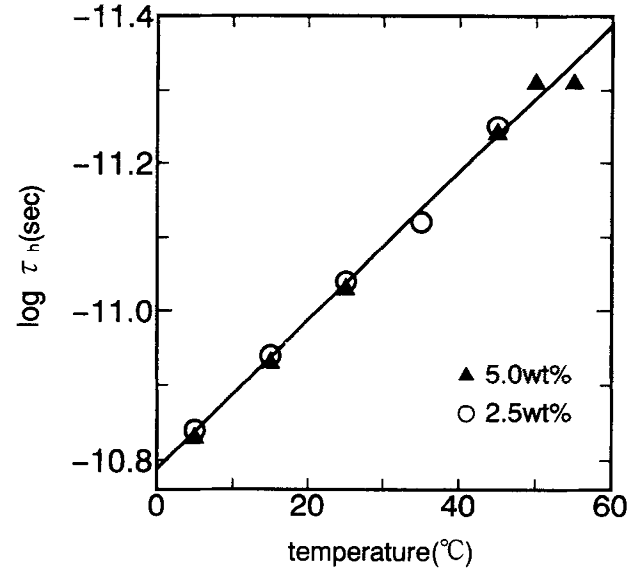

Fig. 2. Temperature dependence of $\log\tau_h$ for gellan gum–water systems.

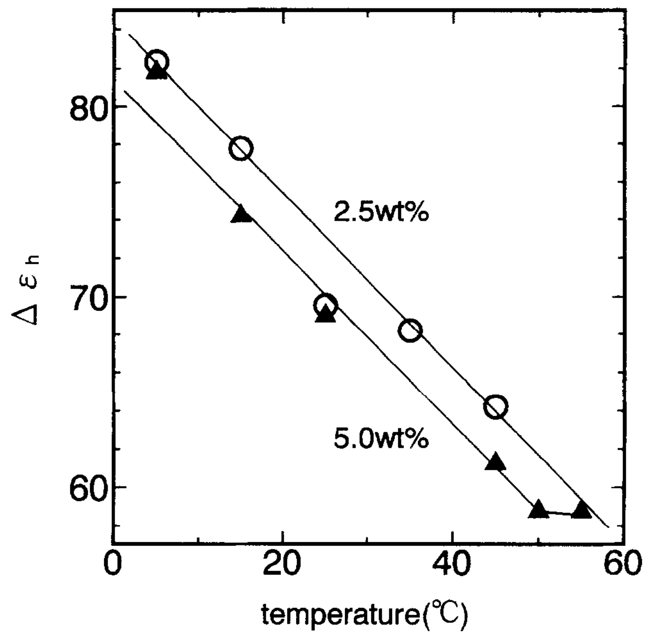

Fig. 3. Temperature dependence of $\Delta\varepsilon_h$ for gellan gum–water systems.

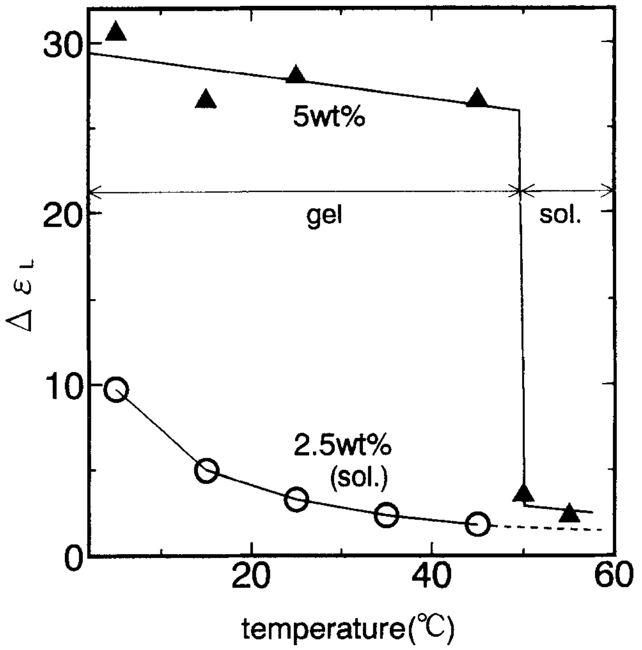

Fig. 4. Temperature dependence of $\Delta\varepsilon_l$ for gellan gum–water systems.

with that for pure water. Furthermore its relaxation strength is nearly the same as that of pure water. The Cole–Cole parameters β_h are very close to unity except for the solution with 5.0wt% gellan gum at 50 or 55°C where it takes a much smaller value than unity.

DISCUSSION

The solution with 2.5wt% gellan gum without salt was a typical solution in the temperature range 50–55°C used in this work. On the other hand, the solution with 5.0wt% gellan gum shows a gel–sol transition at 50°C. Below 50°C, it takes a gel phase.

The high frequency relaxation process can be attributed to reorientation of water molecules in bulk water, judging from the relaxation time τ_h and the relaxation strength $\Delta\varepsilon_h$. No apparent transition could be observed in the plot of $\log\tau_h$ against T or that of $\Delta\varepsilon_h$ against T for the 2.5wt% solution as shown in Figs 2 and 3, respectively. On the other hand, for the low frequency process of the solution with 5.0wt% gellan gum, the plot of $\Delta\varepsilon_l$ against T shows a drastic change at the gel–sol transition temperature. In the gel phase $\Delta\varepsilon_l$ has a considerably large value below the transition temperature. Such a big difference of $\Delta\varepsilon_l$ suggests that the low frequency process is mainly related to the gel phase. At a sufficiently low temperature, gellan gum constructs a double helix and in the gel phase, such double helices gather to form a network structure (Robinson *et al.*, 1991). The double helix of polysaccharide undoubtedly has water molecules bound to the polymer. This type of water is often found in biopolymers such as DNA (Kuwabara *et al.*, 1988; Mashimo *et al.*, 1989; Umehara *et al.*, 1990), globular protein (Miura *et al.*, 1994) and collagen (Shinyashiki *et al.*, 1990). The 2.5wt% solution shows an absorption peak (due to the bound water) at nearly the same frequency as those for the biopolymers. Undoubtedly, the low frequency peak for the 2.5wt% solution is also due to bound water.

No correlation between the dc conductivity σ and the relaxation strength $\Delta\varepsilon_l$ could be found in this work (see Table 1). This suggests that the low frequency process is not due to counter ion migration along the polymer

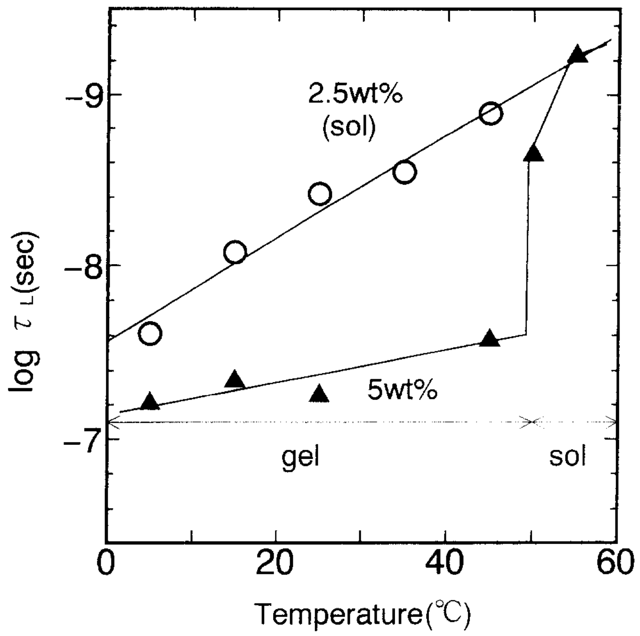

Fig. 5. Temperature dependence of log τ_l for gellan gum water systems.

chain. Furthermore the counter ion process usually produces a fairly large absorption peak at a far lower frequency than the frequency used in this work.

Gellan gum in gel phase exists mainly as a double helix structure and internal motions such as micro-Brownian motion of the chain are impossible. However, rotation of hydroxyl groups may be possible, but such rotation would give an absorption peak at much higher frequency than those used in this study.

If the low frequency process is due to bound water, its amount in gel phase is far greater than that in solution. The relaxation time observed in gel phase is several times longer than that in solution. These results may indicate that the water molecules are bound in a more stable manner to polysaccharide in gel phase than in solution. The double helix would be covered more easily and in a more stable way with the bound water.

It is a surprising result that most of the water included in the gel phase is free water, in other words, the bulk water. However, the free water molecules do not exude from the gel. This means that even this free water is shut in the mesh. The bound water may prevent the free water from passing through the mesh. Furthermore, the free water molecules cannot exist alone. It has recently been suggested that free water molecules construct a cluster consisting twenty to thirty molecules (Mashimo & Miura, 1993). A cluster of such a size cannot easily pass through the mesh.

Above the gel–sol transition temperature, most of the bound water molecules in the gel phase will be released and the free water increases in solution. This is in agreement with experimental results. The value of β_h has a fairly small value above the transition temperature. This means that water molecules around the polysaccharide adopt a complicated structure. It may be an intermediate structure between the bound water and the free water. However it should be noted that the relaxation time τ_h for the 5.0wt% solution at 55°C agrees completely with that for the 2.5wt% solution. The relaxation strength $\Delta\varepsilon_h$ for the 5.0wt% solution at 55°C is quite reasonable as compared to the extrapolated value at 55°C for the 2.5wt% solution.

REFERENCES

Cole, K.S. & Cole, R.H. (1941). *J. Chem. Phys.*, **9**, 341–351.

Cole, R.H., Mashimo, S. & Winsor IV, P.J. (1980). *J. Phys. Chem.*, **84**, 786–793.

Cole, R.H., Berberian, J.G., Mashimo, S., Chryssikos, G., Burns, A. & Tombari, E. (1989). *J. Appl. Phys.*, **66**, 793–802.

Davidson, D.W. & Cole, R.H. (1951). *J. Chem. Phys.*, **18**, 1417.

Kuwabara, S., Umehara, T., Mashimo, S. & Yagihara, S. (1988). *J. Phys. Chem.*, **92**, 4839–4841.

Mashimo, S. & Miura, N. (1993). *J. Chem. Phys.*, **99**, 9874–9881.

Mashimo, S., Umehara, T., Ota, T., Kuwabara, S., Shinyashiki, N. & Yagihara, S. (1987). *J. Mol. Liq.*, **36**, 135–151.

Mashimo, S., Umehara, T., Kuwabara, S. & Yagihara, S. (1989). *J. Phys. Chem.*, **93**, 4963–4967.

Miura, N., Asaka, N., Shinyashiki, N. & Mashimo, S. (1994). *Biopolymers*, **34**, 357–364.

Miyoshi, E., Takaya, T. & Nishinari, K. (1994a). *Food Hydrocoll.*, **8**, 505–527.

Miyoshi, E., Takaya, T. & Nishinari, K. (1994b). *Food Hydrocoll.*, **8**, 529–542.

Robinson, G., Manning, C.E. & Morris, E.R. (1991) *Food Polymers, Gels and Colloids*, E. Dickinson (ed.). Roy. Soc. Chem., Cambridge.

Shinyashiki, N., Asaka, N., Mashimo, S., Yagihara, S. 7 Sasaki, N. (1990). *Biopolymers*, **29**, 1185–1191.

Umehara, T., Kuwabara, S., Mashimo, S. & Yagihara, S. (1990). *Biopolymers*, **30**, 649–656.