Gamma Ray-Induced Gelation of Carboxymethylcellulose

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In order to clarify the mechanism of gelation of aqueous solutions of sodium carboxymethylcelullose (NaCMC) irradiated with gamma ray, we have measured viscoelasticity, dynamic light scattering (DLS), and microwave dielectric spectrum of the solutions with varying dose of gamma ray and concentration of NaCMC. NaCMC was a commercial product obtained from Daicel Co. The degree of carboxymethyl substitution and the weight-average molecular weight were 2.2 and 5.2 × 10^5, respectively. Elastic modulus and viscosity were measured by a coaxial cylinder-type torsional viscoelastometer. The curve of elastic modulus versus dose has a minimum and the dose at the minimum decreased with the concentration of NaCMC. This suggests that the elastic properties could be determined by a competitive effect of degradation and crosslinking. This effect was also recognized in behaviors of the relaxation time obtained from dielectric measurements and the diffusion coefficient determined by DLS.
Key words: cellulose, hydrogel, gamma ray, viscoelasticity, dielectric relaxation, biodegradable

1. INTRODUCTION

It is of vital importance to prepare environmentally friendly useful products by environmentally preferable processes. Hydrogels made from water-soluble polymers are one of environmentally friendly materials which are used for wound dressing, contact lens and so on. Recently, Fei et al. showed that concentrated aqueous solutions of sodium carboxymethylcellulose (NaCMC) are crosslinked with irradiation of gamma ray to yield a hydrogel [1]. Since NaCMC is easily degraded by cellulase [2], the hydrogel thus obtained belongs to a class of biodegradable materials. Furthermore, no organic solvents are required to prepare the hydrogel by the gamma ray irradiation method, so that the preparation process is environmentally preferable. Thus, it is quite interesting to study the mechanism of the gelation process of NaCMC solutions and control the physicochemical properties of the product.

On the other hand, the irradiation of gamma ray is known to degrade various polymers including polysaccharides [3]. In fact, the relative viscosity of dilute solutions of NaCMC was shown to decrease with increasing dose of gamma ray and no gelation was observed in the solutions [1]. These results suggest that at least two reactions, i.e., crosslinking and degradation, occurs in concentrated NaCMC solutions.

In this paper, we report on rheological, hydrodynamic, and dielectric properties of aqueous NaCMC solutions as a first study to clarify such a complex mechanism of gamma ray-induced gelation. The shear modulus, the viscosity coefficient, and the diffusion coefficient were measured as a function of dose of gamma ray at various concentrations. For rheological and hydrodynamic properties, NaCl aqueous solution was used as the

solvent instead of pure water because these properties of NaCMC aqueous solutions depend on the ionic strength of the solvent, especially in dilute regime [4,5]. On the contrary, pure water was used as the solvent for dielectric measurements in order to avoid a large ionic relaxation process induced by the DC conductivity.

2. EXPERIMENTAL

2.1 Preparing solutions and irradiation

A previously investigated sample [1,2], CMC 2.2 whose chemical structure is illustrated in Figure 1, was chosen for this study. This sample is a commercial product obtained from Daicel Co., Ltd. and the degree of carboxymethyl substitution was indicated to be 2.2 by the manufacturer. The intrinsic viscosity $[\eta]$ of this sample in 0.1 M aqueous NaCl at 25°C had been determined to be 590 cm^3 g^{-1} from viscometry and the weight-average molecular weight M_w was estimated to be 5.2 × 10^5 from a known relation for $[\eta]$ and M_w [6]. The sample dried in vacuum for 12 hours was dissolved in deionized water or 0.01 M aqueous NaCl. The solutions were transferred into a cylindrical tube with 14.4 mm i.d. and irradiated with gamma rays generated from a ^{60}Co source at a dose rate of 10 kGy / h. Then the solutions were centrifuged at 1200 – 2000 × g for 60 min in order to remove bubbles generated under irradiation of gamma ray. Some solutions with high concentration and dose were not used for the measurements because the bubbles could not be removed completely.

2.2 Rheological measurements

Rheological measurements were made for 4, 7, 12, and 20wt% NaCMC solutions with different dose using a Rhesca Model RD-100 AD coaxial cylinder-type

torsional viscoelastometer [7]. The cylindrical tube containing an NaCMC solution was set into an air bath of the apparatus and the inner cylinder (stainless cylinder with 3 or 8 mm) was inserted into the solution. Rotating the inner cylinder up-to the shear angle less than 1°, a damped oscillation was induced by elastic restoring force of the sample and the piano wire supporting the inner cylinder. The shear modulus G and the viscosity coefficient η for each solution were determined at 25°C as functions of dose and concentration of NaCMC. The measured range of the angular frequency was between 1.4 and 1.7 rad s^{-1}. For the data processing, consult ref [8].

2.3 Dynamic light scattering

Dynamic light scattering experiments at 25°C were carried out for 4wt% and 7wt% NaCMC solutions with or without irradiation using a laboratory-made light scattering apparatus [9] with a Brookhaven BI-9000 correlator. Vertically polarized incident light of 532 nm wavelength (green diode laser, BWT-50, B&W) was used. The normalized autocorrelation function $g^{(2)}(\tau)$ was measured at two scattering angles of 40 and 60°. It is related to the first cumulant Γ by

$$\frac{1}{2}\ln\left[g^{(2)}(\tau)-1\right] = -\Gamma\tau + O(\tau^2)$$

The (cooperative) diffusion coefficient D is determined from the extrapolated Γk^{-2} value to 0 angle. Here k is the magnitude of scattering vector. In the present work, D was determined to be the average value measured with two scattering angles because Γk^{-2} values were independent of the scattering angle in our experimental error.

2.4 Dielectric relaxation measurements

Dielectric relaxation measurements on 1–7wt% irradiated NaCMC in water at 25°C were performed by a time domain reflectometry (TDR) system (main frame: Hewlett-Packard, 54121B) and an Impedance/Material Analyzer (Hewlett-Packard, 4291A). A flat-end cell with the electric length of 0.15 mm and the geometric capacitance of 0.010 pF was used for the both measuring systems. Details of TDR measurements with the flat-end cell are described in our papers [10,11]. The investigated NaCMC sample had been dissolved in deionized water and crosslinked by irradiation with gamma rays of 10, 20 and 30 kGy.

## 3. RESULTS AND DISCUSSION

3.1 Rheological properties

Figure 2 shows the dose dependence of G for the NaCMC solution except the irradiated 4wt% solution because they are too small. The shear modulus of 4wt% solution decreases with increasing dose, whereas that of 20wt% increases. For middle two solutions (7 and 12wt%), each fitted by a smooth curve, decreases gradually in the range of dose < 30 kGy and turns to increase. Though the shear modulus generally increases with gelation [12], each G value for these two solutions irradiated at a dose of 50 kGy is little different from the unirradiated value. However, it had been
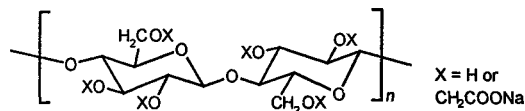
Figure 1. Chemical structure of sodium carboxymethylcellulose. X represents a hydrogen atom or a CH₂COONa group. About 73 % of X for CMC 2.2 are substituted by the latter group.
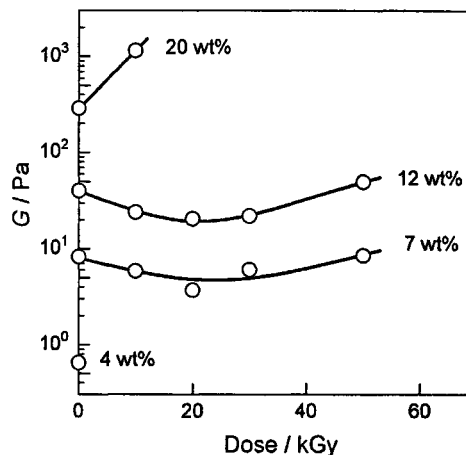
Figure 2. Dose dependence of the shear modulus G at indicated concentrations for 0.01 M aqueous NaCl solutions of NaCMC at 25°C.
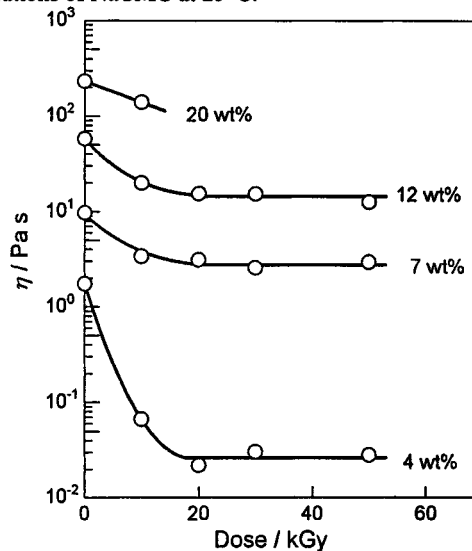
Figure 3. Dose dependence of the viscosity coefficient η at indicated concentrations for 0.01 M aqueous NaCl solutions of NaCMC at 25°C.

shown that the gel fraction of the 10wt% solution increases rapidly with dose and reaches about 50% at a dose of 50 kGy [1]. Therefore, it is reasonable to suppose that thus complex behavior is attributed to simultaneous reactions, scission and crosslinking.

Viscosity coefficients η for irradiated NaCMC solutions are illustrated in Figure 3. It is seen that η decreases with increasing dose in the range of dose < 20 kGy and reaches an asymptotic value at higher doses.

Especially, η for 4wt% solution decreases by two orders only with irradiation of 20 kGy. On the other hand, for higher concentration solution, η decreases much more gently. Indeed, the ratio of the asymptotic value to the initial value is about 0.5 both for 7 and 12wt% solutions. This difference of viscosity behavior between dilute (4wt%) and concentrated solutions could also be explained by taking consideration of not only scission but also crosslinking reaction because it is expected that the viscosity of the concentrated solutions becomes much smaller when the crosslinking reaction occurs.

3.2 A hydrodynamic property

Dose dependence of the diffusion coefficient D for 4wt% and 7wt% NaCMC solutions is shown in Figure 4. The diffusion coefficient for 4wt% increases by about two orders with irradiation of 50 kGy, while D for 7wt% increases initially and turns to decrease. This result resembles the dose dependence of the shear modulus in the range measured.

3.3 Dielectric properties

Dielectric dispersion and absorption curves for irradiated NaCMC aqueous solution (20 kGy) of 5wt% at 25°C were shown in Figure 5. We reported that three relaxation processes, h, m, and l are often observed for aqueous solutions of polysaccharide in the present frequency range [13]. The h process is attributed to the rotational diffusion of water molecules interacting among six water molecules. The l process is the high frequency wing of an ionic process related to an electrode polarization and DC conductivity. The m process is considered to reflect the chain motion.

Recently KWW function is employed to express the frequency dependences of the complex dielectric constant for a relaxation process caused by polymer chain motions [14]. Thus relaxation parameters for the m process were obtained from fitting procedures using KWW function and also Cole-Cole equation for other two processes, l and h [11].

Dose dependences of relaxation parameters, $\Delta\varepsilon_m$, τ_m, and β_m were shown in Figure 6 for various polymer concentrations. Here τ_m is the relaxation time, $\Delta\varepsilon_m$ is the relaxation strength, and β_k is the parameter to describe the asymmetrical broadness of the dispersion and relaxation curves for the m process. These concentration dependences of relaxation parameters exhibit the typical features of polymer chain motions as discussed in another paper [11], except for the relaxation time at 3wt%. The concentration dependence of the relaxation time, τ_m, for the chain motions in polymer solutions has been often explained by the free volume theory. The free volume model explains the mobility of chains with a scaling concept of the free volume fraction affected by diluents. This idea is also consistent with rheological treatments on the dynamical behavior of chains in the viscous medium. Then, in the simplest case, it is easily expected that the relaxation time is proportional to the viscosity of the sample as described by the Stokes law and it follows the same dose dependence with the viscosity shown in Figure 3.

However the relaxation time at 3wt% shows an ambiguous behavior indicating smaller values than those for more dilute NaCMC solution of 1wt% in Figure 6.
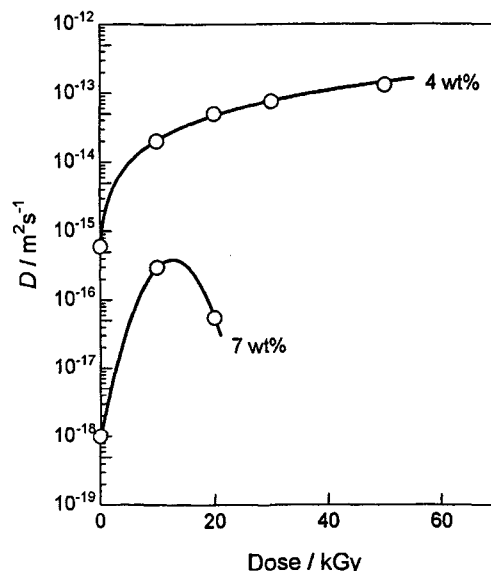
Figure 4. Dose dependence of the diffusion coefficient D at indicated concentrations for 0.01 M aqueous NaCl solutions of NaCMC at 25°C.
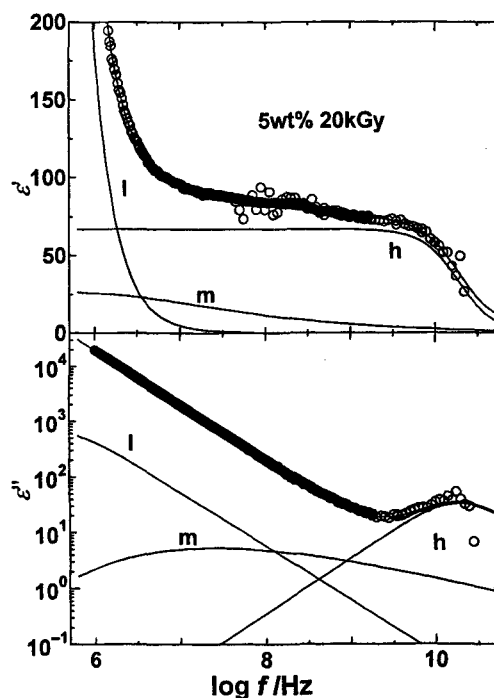
Figure 5. Dielectric dispersion and absorption curves for irradiated gel (20 kGy) of NaCMC 5wt% at 25°C. Solids lines were calculated from Eq. (1) in ref [11].

Furthermore, any conspicuous dose dependence of the relaxation time cannot be recognized, even if the same dependence with the viscosity is expected for the relaxation time.

Figure 3 indicates that the dose dependence of the viscosity at 4wt% is much larger than those obtained at higher concentrations. It is reasonable to assume the scission of NaCMC results in larger decreases in viscosity for more dilute solutions. This is consistent
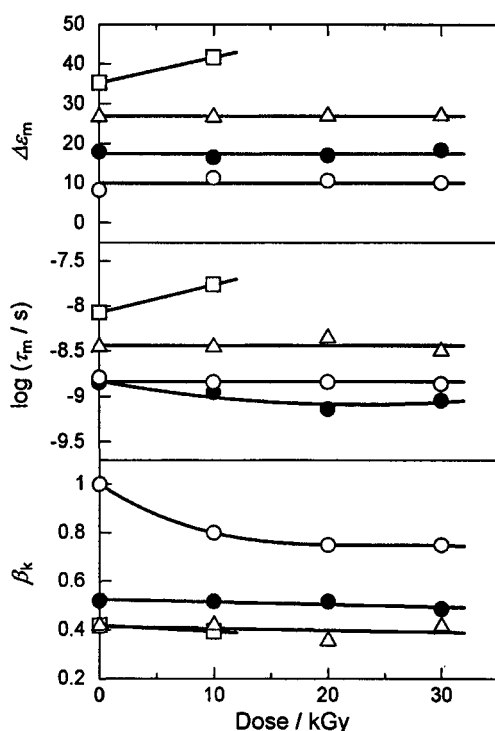
Figure 6. $\Delta\varepsilon_m$, τ_m, and β_m as a function of dose for aqueous solutions of NaCMC with or without irradiation: unfilled circles, 1 wt%; filled circles, 3 wt%; triangles, 5 wt%; squares, 7 wt%.

with the result of the dielectric measurements that the increase in the relaxation time with increasing dose was shown only at the highest concentration of 7wt%.

On the other hand, a decrease in the viscosity with increasing concentration often observed for dilute polyelectrolyte solutions was also reported in the case of NaCMC aqueous solutions with the low ionic strength [15]. Thus the present results on the larger value of the relaxation time for 1wt% NaCMC solution than that at 3wt% can be explained with corresponding viscosity, though the viscosity was not actually examined in the present case.

Therefore the ambiguity obtained for the relaxation time around 3wt% suggests a particular behavior of the polymer chain motion. The concentration dependence of the relaxation time for chain motions becomes smaller in the dilute concentration region [11]. This result means that the intermolecular interaction affecting chain motions is small in this concentration region. The larger relaxation time at 1wt% than that at 3wt% shown in Figure 6 suggests that the intermolecular interaction becomes larger again because of the extended chain structure with the low ionic strength. The cooperative mode of local chain motions makes the relaxation time larger with the large-scale intermolecular interaction.

4. CONCLUDING REMARKS

For gamma-ray-irradiated sodium carboxymethyl-cellulose samples in aqueous NaCl, we have examined change of the shear modulus, the viscosity coefficient, and the diffusion coefficient with concentration and dose. It follows from the consideration of obtained data that

the dominancy in these two reactions of scission and crosslinking depends on concentration, and the proportion of crosslinking / scission increases with increasing concentration. The effect of scission and crosslinking is also recognized in dielectric behaviors for the same sample in deionized water.

REFERENCES

[1] B. Fei, R. A. Wach, H. Mitomo, F. Yoshii, and T. Kume, *J. Appl. Polym. Sci.*, **78**, 278–83 (2000).

[2] R. A. Wach, H. Mitomo, F. Yoshii, T. Kume, *J. Appl. Polym. Sci.*, **81**, 3030–37 (2001).

[3] Y. Tabata, S. Ito, and S. Tagawa, "CRC Hand-book of Radiation Chemistry", CRC, Boston (1991), Vol. XIV. B., pp. 739–69.

[4] W.-M. Kulicke, A. H. Kull, W. Kull, and H. Thielking, *Polymer*, **37**, 2723–31 (1996).

[5] G. Sitaramaiah and D. A. I. Goring, *J. Polym. Sci.*, **58**, 1107–31 (1962).

[6] M. G. Wirick, *J. Polym. Sci. A.*, **6**, 1965–74 (1968).

[7] For example, S. Kondo, T. Igarashi, T. Nakamura, and T. Okuizumi, *Colloid. Polym. Sci.*, **261**, 819–24 (1983).

[8] K. Ooi, S. Kouchi, T. Dobashi, S. Kondo, H. Ichikawa, *Trans. Mater. Res. Soc. Japan*, **26**, 605–08 (2001).

[9] T. Isojima, S. Fujii, K. Kubota, and K. Hamano, *J. Chem. Phys.*, **111**, 9839–46 (1999).

[10] S. Yagihara, N. Miura, Y. Hayashi, H. Miyairi, M. Asano, G. Yamada, N. Shinyashiki, S. Mashimo, T. Umehara, M. Tokita, S. Naito, T. Nagahama, and M. Shiotsubo, *Subsurface Sensing Technologies and Applications*, **2**, 15-29 (2001).

[11] N. Miura, T. Hashimoto, M. Goto, Y. Hayashi, N. Shinyashiki, S. Yagihara, T. Shigematsu, S. Shioya, H. Nishida, T. Dobashi, and F. Yoshii, submitted to *Trans. Mater. Res. Soc. Japan*.

[12] For example, M. Kakiuchi, Y. Aoki, H. Watanabe, and K. Osaki, *Macromolecules*, **34**, 2987–91 (2001).

[13] G. Yamada, T. Hashimoto, T. Morita, N. Shinyashiki, S. Yagihara, and M. Tokita, *Trans. Mater. Res. Soc. Japan*, **26**, 701-04 (2001).

[14] J. P. Runt and J. J. Fitzgerald eds. "Dielectric Spectroscopy of Polymeric Materials", American Chemical Society, Washington, DC (1997).

[15] H. Fujita and T. Homma, *J. Polym. Sci.*, **15**, 277-95 (1955).