Surface Waves and Viscoelastic Properties of Gels

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We studied the properties of surface waves during the gelation process of tungstic acid, gelatin, silica and agar gels by the time resolved surface wave measurements. The distinction of surface mode is clearly shown in the change of the wave number exponent x ($\omega \sim k^x$, the values 1.5 and 1.0 indicate surface tension and elastic wave modes, respectively) from sol state to gel state. The x of the tungstic acid was about 1.4 in the sol state and rapidly decreased to 1.0 at the gelation point. The x of gelatin was about 1.4 (same as tungstic acid) in the sol state and decreased gradually after the gelation point. On the other side, the x of silica gel and agar remained near 1.5 after the gelation point. These differences are possibly due to the differences in the interactions between the networks and solvents and the structures of gels.
Key words: surface wave, viscoelasticity, gel, Tungstic Acid, Gelatin.

1. INTRODUCTION

Since gels have an unique character that is different from those of liquids and solids, those have a potentiality to apply in various fields. Recently, we are interested in the gel of tungstic acid, a kind of transition metal hydroxide gel. It is known to show electrochromism and photochromism [1-4] and expected to be used as display devices or shading devices activated by sunlight or electric current. From the standpoint of manufacturing, tungstic acid is most promising for inexpensive fabrication of large devices by using a sol-gel method. For making a uniform thin film, it is essential to investigate the gel structure and its formation process. However, since the properties of the products have been investigated in these circumstances [5], we studied on the gel structure of tungstic acid and its formation process. [6-12] Since the properties of surface waves reflect the dynamical shear elasticity at high sensitivity [10-14] and the measurements can be performed with both liquid and solid samples, we are using the time-resolved surface wave measuring method.
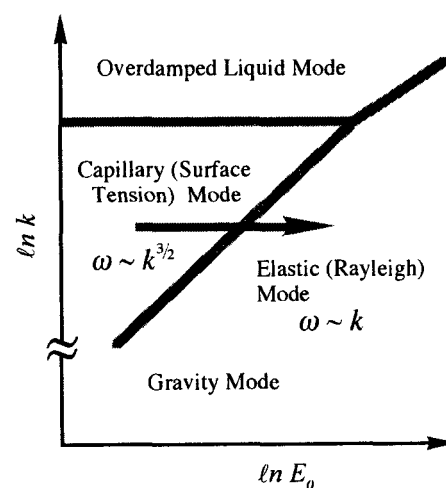

Fig. 1 Surface mode diagram for gels as a function of the wave number k and elastic modulus E_0. The arrow at the center of the figure shows the change of elasticity during the gelation process. [15]

Then, we will discuss what type of surface wave propagates on gels, surface tension waves, surface elastic waves or some other types of wave. There are some theoretical studies of surface waves on gels. [15-17] Figure 1 shows surface mode diagram for gels, [15] which shows the region of capillary (surface tension), Rayleigh (elastic), overdamped and gravity modes as a function of wave number k and elastic modulus E_0. This diagram agreed qualitatively with the experimental results for gelatin gel. [14]

Since the gelation process occurs in a nonequilibrium system, this diagram cannot be applied in the strict sense. However, since this diagram is based only on the simple model depending on viscoelasticity and not on the detailed structure, we may assume that the progress of gelation is the same as the increase of the elastic modulus indicated by the arrow in the center of Fig. 1.

Our experimental results agreed generally with this diagram. [12] In the vicinity of the sol-gel transition point of tungstic acid, we found interesting features in the time variation of the velocities. Namely, the velocities of the surface waves had a maximum near the gelation point, decreased once rapidly, and again increased gradually as the gelation proceeded. The anomaly is clearly shown in the time dependence of the wave number exponent x ($\omega \sim k^x$), too. The x of tungstic acid was about 1.4 (the values 1.5 and 1.0 indicate surface tension and elastic wave, respectively) in the sol state and rapidly decreased to 1.0 at the gelation time. Some researchers [16, 17] have tried to explain this anomalous velocity changes by the detailed calculation with the viscoelastic model.

Therefore, further experimental studies are necessary to clarify the mechanism of this particular property, and we have measured the properties of surface waves and the viscoelasticity of the gelatin samples, [12] which is a well-known gel and has been experimentally investigated. [14] However, gelatin system does not show the anomal behaviors in the vicinity of the sol-gel transition point. In this paper, we have tried to observe the gelation processes of silica gel and agar.

EXPERIMENTAL

The samples used were silica gel and agar. The reference samples of tungstic acid and gelatin were pre-
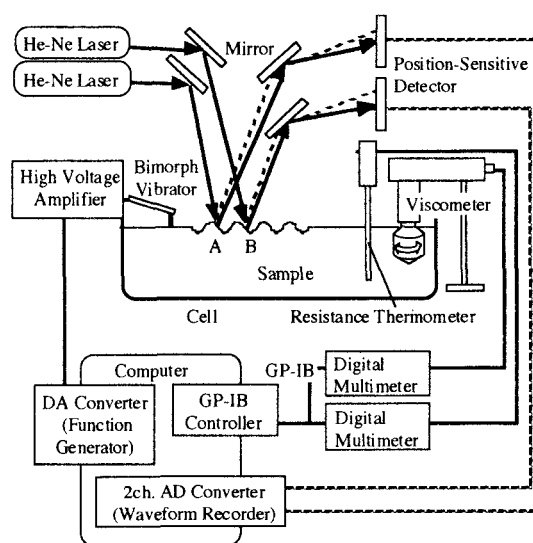

Fig. 2 Schematic diagram of surface wave and viscoelasticity measuring system.

pared in the manners as described in a previous paper. [12] The sample of silica gel was prepared from tetramethyl orthosilicate (tetramethoxysilane, Si $(OCH_3)_4$; Kishida Chemical) and water (with concentration 10 vol.% 20ml/200ml). The gelation was initiated by the mixing of tetramethyl orthosilicate and distilled water. [18] Agar sample was prepared from agar powder (Kishida Chemical) and distilled water (with concentration 0.5 wt.% 1g/200ml). The sample in the sol state was kept at 110°C for 2 hours, and cooled from 110°C to 40°C. Since, the gelation of agar occurs near the temperature of 30°C, the measurement was performed during the cooling process to room temperature as same as gelatin.

Figure 2 shows the surface-wave-measurement system using the optical deflection method. [10-13] In the measurement, the samples prepared in the manner described above were poured into a cell. The surface wave excited by the bimorph vibrator consists of six cycles of sine waves (50,100, 150, 200Hz). The distance between the two laser-beam spots was 2mm~5.5mm (distance from the vibrating tip to the first detection point was 7.5mm, and 9.5mm~13mm to the second point). Furthermore, the absolute value of complex viscosity $|\eta|$ was measured simultaneously by means of a torsion type viscometer (Yamaichi denki Co., Ltd. VM1A-L: to be exact, the rotational resistivity measuring apparatus

with the cylindrical probe).

3. RESULTS AND DISCUSSION

We define an attenuation as a ratio of amplitude between points A and B as shown in Fig. 2. Figure 3 shows an absolute value of complex viscosity $|\eta|$ dependence of the attenuation at the frequency of 100Hz. As shown in Fig. 3, all samples showed the maximum attenuation at the $|\eta|$ range between 10^{-2} and 10^{-1}Pa.s. The arrows indicate the points of the maximum attenuation. Due to the correspondence to the titling test (the gelation point is defined at the time when the sample tilts with its vessel by the disappearance of its fluidity), we treated the points of maximum attenuation as the gelation points in the following description. [11] The attenuation of agar showed most gentle change in four samples, and that of the tungstic acid gel showed most steep change. The agar results were probably affected by considerable change of temperature.

Figure 4 shows the changes of surface wave velocities at a frequency of 100Hz. The anomalous discontinuous velocity curve of the tungstic acid attracts attention. The velocity curves of gelatin and silica gel didn't show such discontinuity, and the velocities just decreased slightly near the gelation points. On the other hand, the velocity change of agar shows linear dependence. However, it is noticed that the velocity values of gelatin, silica gel and agar around the gelation points are between the values in the sol and the gel of tungstic acid. This fact probably suggests that the network in tungstic acid grows more uniformly than that of other gels, and the gelation occurs more drastically. At the gelation points, the value of $|\eta|$ of tungstic acid is largest and this property may be due to the larger elasticity of tungstic acid. For more precise comparison between experimental results and viscoelastic theory, we should measure the shear modulus instead of the absolute value of the complex viscosity (The reason for measuring the absolute value of the complex viscosity instead of the shear modulus was the restriction of our experimental apparatus).

An exponent x of the wave number ($\omega \sim k^x$) reflects the properties of surface waves. [11] The values of exponent x of the surface tension wave and Rayleigh wave are 1.5 and 1.0, respectively. Figure 5 shows $|\eta|$ depen-

dence of x that was calculated by using the dispersion from 50Hz to 200Hz. In lower range of $|\eta|$, the values of x of all samples were about 1.4. The frequency dispersion of tungstic acid above the gelation point disappeared suddenly, and the surface wave changed drastically from the surface tension wave to the Rayleigh wave at the gelation point. On the other hand, the frequency dispersion of gelatin, silica gel and agar remained above the gelation points. The value of x of
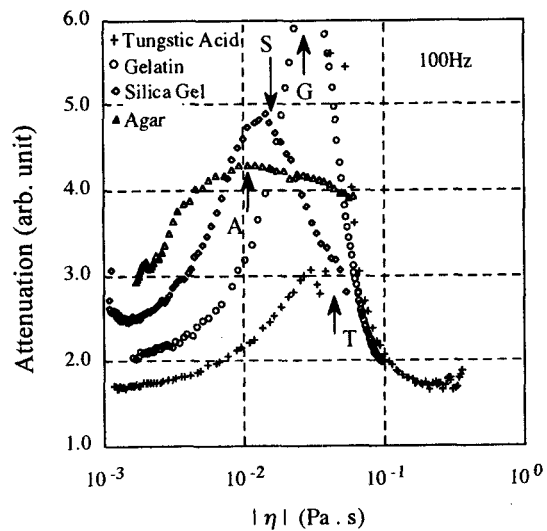

Fig. 3 Attenuation (ratio of amplitude between points A and B in Fig. 2) vs. absolute value of complex viscosity $|\eta|$. The arrows indicate the gelation points
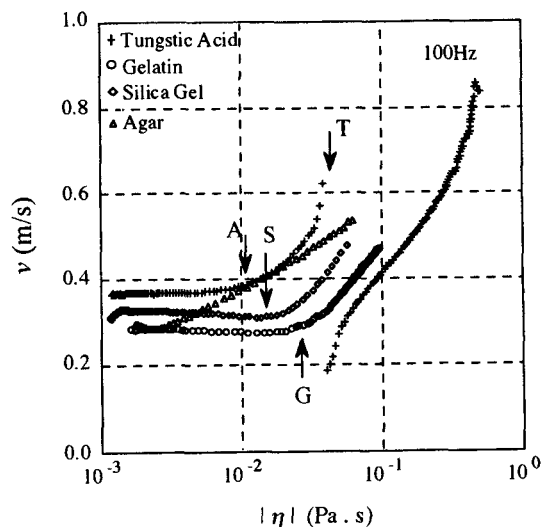

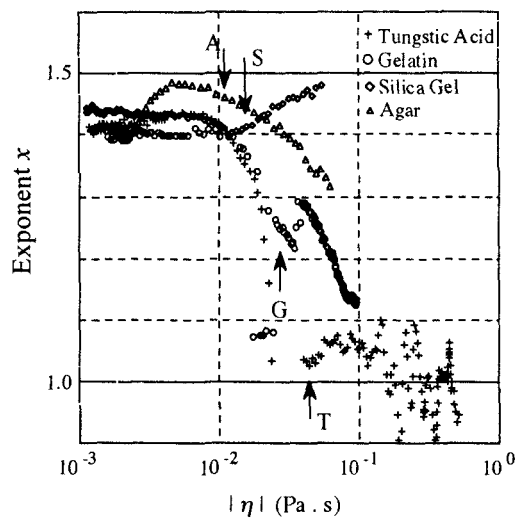Fig. 4 Velocity vs. absolute value of complex viscosity $|\eta|$.

Fig. 5 Wave number exponent x in the dispersion relation $\omega \sim k^x$ (ω is angular frequency) vs. absolute value of complex viscosity $|\eta|$.

gelatin and agar decreased gradually above the gelation point. As gelation progressed and $|\eta|$ increased, those approached values of about $1.1{\sim}1.3$ at the gelation points. On the other hand, the value of x of silica gel remained near 1.5 above the gelation point, and the surface wave on silica gel was just a surface tension wave. This may be due to the weak coupling between the network of silica gel and the solvent. The viscoelastic theories assume the "infinite coupling limit", but the silica gel is possibly an exception. The interaction between the network and solvent of agar gel is probably weaker than that of the tungstic acid and gelatin, too.

As described above, surface mode diagram under gelation process changes sample to sample. The quick change of the velocity or the exponent near the gelation point of tungstic acid is only one example in many complex behaviors. Therefore, further investigations are necessary to clarify the mechanism to decide surface mode. So, we will try to measure the change in the real elastic modulus near the gelation point by means of improved viscometer. If we have achieved the measurement, we can compare the results with the theories qualitatively. And we plan to measure the properties of the other gels. For example, the vanadic acid, a kind of transition metal hydroxide may be up for the first

sample.

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