Measurement of Dynamically Changing Thermal Diffusivity by the Forced Rayleigh Scattering Method (Measurement of Gelation Process)[1]

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A measuring method of the thermal diffusivity with high temporal and spatial resolutions has been studied. The forced Rayleigh scattering method is an optical technique to measure the thermal diffusivity of solids and liquids. Based on its characteristics, this method has the applicability to become a "thermal diffusivity real-time monitoring system." The maximum repetition rate of thermal diffusivity measurement is determined by the attenuation of an excited temperature distribution by laser heating, and a mathematical model of three-dimensional heat conduction is constructed. The temporal resolution of continuous measurements was improved to about 1 s, and the sol-gel transition of a gellan gum aqueous solution was studied to check the validity of the dynamic measurement of thermal diffusivity. Through the gelation process, the dynamical change of the thermal diffusivity was measured, and the gelation point of the solution was identified from a series of thermal diffusivity data. The results indicate the capability of the forced Rayleigh scattering method to be a real-time thermal diffusivity measurement technique for monitoring the rapidly changing process of a material.

KEY WORDS: dynamic measurement; forced Rayleigh scattering method; gelation process; gellan gum; thermal diffusivity.

1. INTRODUCTION

The need for thermophysical properties is increasing and spreading as a result of the development and application of new materials and technology.

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During internal structural change in a material, its thermophysical properties are expected to change with time. In order to strictly control the material changing process, real-time information in the form of successive data on thermophysical properties is indispensable. Therefore, continual real-time measurement of the changing values of thermophysical properties during a changing process can be an effective means to identify and potentially control the process. Furthermore, real-time thermal diffusivity data enable temperature and quality control in a dynamic sense throughout material production and chemical reaction processes.

Various methods to measure the thermal diffusivity of solids and liquids have been studied and developed [1–4]. However, in most cases, the measured data can be described as a function of temperature, pressure, density, concentration or composition of a sample, and not as a function of time. Many conventional measuring techniques are not suitable to measure the dynamically changing thermal diffusivity of a material throughout a continuous process. In the present study, the validity of the dynamic measurement of thermal diffusivity is discussed, and we measured a sol-gel transition in order to trace the process as a function of time near room temperature. The measuring method is the forced Rayleigh scattering method, an optical technique that can be applied to the real-time monitoring of thermal diffusivity changes. A basic experimental system to measure the dynamics of the thermal diffusivity was developed, and preliminary measurements were presented in a previous report [5]. The thermal diffusivity through the gelation process of a gellan gum aqueous solution was measured in the present study as a test for the ability of this method to dynamically detect a structural change.

2. THEORETICAL

2.1. Principle of Measurement

Measurements of the thermal diffusivity were carried out by means of the forced Rayleigh scattering method (FRSM). This name was given to reflect spontaneous Rayleigh scattering based on statistical thermodynamics fluctuations. This method has also been called "laser-induced dynamic grating [6]," "laser-induced thermal grating technique [7]," or "transient grating method [8]." Details of the principle and error analysis of this method have been adequately discussed in our earlier publication [9]. Here we briefly describe the method.

First, two pulsed laser beams of equal wavelength and intensity cross in a sample to create an interference pattern. The pattern induces a temperature distribution and a corresponding gradient in the refractive index,

which produces a transient optical phase grating. Emission of a probing laser beam opaque to the sample allows diffracted beams to be obtained. After the heating, the excited temperature distribution decays exponentially by heat conduction, and the intensity of the diffracted beams similarly attenuates. By adopting the diffraction theory, the intensity of the first-order diffracted beam I_1 can be expressed as a function of time t as

$$I_1 \propto \exp\left(-\frac{2t}{\tau}\right), \tag{1}$$

where τ is the relaxation time of heat conduction. Finally, the thermal diffusivity of the sample can be determined by observing the attenuation of the intensity of the first-order diffracted beam, and by measuring the grating period Λ. The fundamental working equation takes the form,

$$a = \frac{1}{\tau}\left(\frac{\Lambda}{2\pi}\right)^2, \tag{2}$$

in which a represents the thermal diffusivity of a sample, and Λ can be determined from the crossing angle and the wavelength of heating laser beams.

2.2. Application to Dynamic Measurement

FRSM, considered as one measurement method of thermophysical properties, has the following features for dynamic measurements under transient conditions: (1) Due to the noncontact manner in both heating and probing, remote-sensing throughout the changing process of a sample can be carried out. (2) Since one measurement requires only 1 ms or less, measurements in the course of a transition, even on a subsecond time scale, are possible. In the present experimental system, every measurement is performed once per second. (3) By controlling the probing region, local properties can be measured. Therefore, it is possible to detect variations in the thermal diffusivity over a microscopic area. The spatial resolution of the present measurements is around 1 mm, and this can be easily made smaller by focusing the probing laser beam. (4) The thermal diffusivity perpendicular to the transient thermal grating can be measured. Therefore, it is possible to measure the anisotropic behavior of the thermal diffusivity by rotating the optical setup or the sample. These characteristics indicate the possibility of application to the dynamic measurement of the thermal diffusivity of a rapidly changing material by means of repeated pulses at appropriate intervals.

In order to conduct high-speed measurements of the thermal diffusivity, it is necessary to know the time over which the excited temperature rise by heating laser beams adequately attenuates. According to the basic theory of the FRSM, the temperature distribution T_x at position x and at time t is

$$T_x = T_0 + T_1 \exp\left(-\frac{t}{\tau}\right)\cos\left(\frac{2\pi x}{\Lambda}\right), \tag{3}$$

where T_0 is the mean initial temperature rise, T_1 is the temperature distribution from the interference of heating laser beams, and the x-axis is the direction perpendicular to the thermal grating. In this method, the thermal diffusivity can be determined by the decay of the temperature distribution of a transient thermal grating; namely, by the second term of Eq. (3). However, in this theory, the heating laser beam is assumed to be a plane wave, and the temperature rise T_0 remains in the sample. In fact, the heating laser beam has the intensity distribution of TEM_{00} mode, and laser absorption in the depth direction occurs; thus, the exact temperature rise in the sample is more complicated. The temporal resolution of the dynamic measurements can be determined by considering this decay. To analyze this, we took a three-dimensional heat conduction model into account by the use of Green's function. Under the assumptions of a semi-infinite solid ($-\infty < x < \infty$, $-\infty < y < \infty$, $0 < z < \infty$) and of an adiabatic sample surface, the Green's function G_{xyz} in a sample is given [10] by

$$G_{xyz} = \frac{1}{2\sqrt{\pi at}} \exp\left\{-\frac{1}{4at}\left[(x-x')^2 + (y-y')^2\right]\right\}$$
$$\times \left\{\exp\left[-\frac{1}{4at}(z-z')^2\right] + \exp\left[-\frac{1}{4at}(z+z')^2\right]\right\}, \tag{4}$$

where (x', y', z') are the coordinates of heating source. The temperature distribution in the x direction is represented by the combination of the temperature rise of the thermal grating induced by interference of the heating laser and that of the Gaussian intensity distribution of the beam. The temperature distribution on the x-axis is described as

$$T_{xt} = \frac{w}{\sqrt{w^2 + 8at}} \exp\left(-\frac{2x^2}{w^2 + 8at}\right)$$
$$\times \left[T_0 + T_1 \exp\left(-\frac{w^2}{w^2 + 8at}\frac{t}{\tau}\right)\cos\left(\frac{w^2}{w^2 + 8at}\frac{2\pi x}{\Lambda}\right)\right], \tag{5}$$

where w is the Gaussian radius of the heating laser. The y direction temperature distribution is caused by the Gaussian intensity distribution of the heating laser. The temperature distribution in the y direction can be written as follows:

$$T_{yt} = T_0 \frac{w}{\sqrt{w^2 + 8at}} \exp\left(-\frac{2y^2}{w^2 + 8at}\right). \tag{6}$$

Considering a laser absorption in the z direction, the temperature distribution at position z and at time t can be expressed as

$$T_{zt} = \frac{T_0}{2} \exp(a\alpha^2 t)\left[\exp(\alpha z)\,\mathrm{erfc}\left(\frac{2a\alpha t + z}{2\sqrt{at}}\right) + \exp(-\alpha z)\,\mathrm{erfc}\left(\frac{2a\alpha t - z}{2\sqrt{at}}\right)\right], \tag{7}$$

where α is the absorption coefficient of the sample at the wavelength of the heating laser. Finally, the temperature rise in the three-dimensional model can be obtained by the multiplication of Eqs. (5)–(7);

$$T_{xyzt} = T_{xt}T_{yt}T_{zt}. \tag{8}$$

In the present study, the attenuation of the temperature rise was considered using Eq. (8). We used this mathematical model to evaluate the maximum repetition rate (MRR). The temporal resolution of dynamic measurements of the thermal diffusivity by the FRSM can be determined from MRR. In all the calculations, the Gaussian radius of the heating laser was fixed at 2 mm, which value is used in our experimental system. Figure 1 shows the results of this analysis. The absorption coefficient (at the wavelength of the heating laser) and the thermal diffusivity determine the MRR. It is difficult to measure the thermal diffusivity in the grey region in Fig. 1 because the repetition rate is faster than one measurement time. This single measurement limit can be determined by the thermal diffusivity of the sample and the grating period; in this calculation, the minimum grating period of the present apparatus (20 μm) is used.

Water (at 300 K) and Na_2CO_3 (at 1000 K) are illustrated as examples. The MRR of water and Na_2CO_3 are estimated to be 30 and 500 ms, respectively. In this calculation, the absorption coefficient of water used is $8 \times 10^4\,\mathrm{m}^{-1}$ [11], and that of Na_2CO_3 is $1 \times 10^4\,\mathrm{m}^{-1}$ [12]. MRR of many other aqueous solutions are close to that of water. The effect of heat flow by the Gaussian intensity distribution becomes conspicuous when a sample with an absorption coefficient less than $10^3\,\mathrm{m}^{-1}$ is used. In the case of conducting dynamic measurements at every second using the FRSM, all of
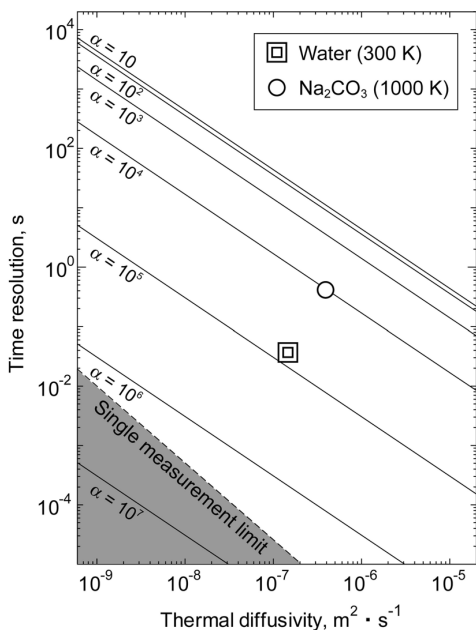
Fig. 1. Maximum repetition rate (MMR) of dynamic measurement of the thermal diffusivity. In the grey area, it is difficult to measure because the repetition rate is faster than the time for a single measurement.

the samples in this study (water, gellan gum aqueous solution and its gel) avoid this limitation. By using this model, the relation between temporal resolution of the continual measurements of the thermal diffusivity by FRSM and properties of the sample is quantitatively clarified.

3. EXPERIMENTAL

3.1. Measurement System

Figure 2 shows a schematic diagram of the present apparatus to measure the dynamics of the thermal diffusivity. The heating laser is a CO_2 laser (wavelength $= 10.6\,\mu m$, $10\,W$), and the continuous beam is chopped by a rotating mechanical chopper (MC) to generate a pulse of 100 to $2000\,\mu s$. The pulsed beam is divided into two beams of equal intensity by

a beam splitter (BS), and the beams cross in the sample to produce an interference pattern. The probing laser is a He–Ne laser (wavelength = 632.8 nm, 15 mW), and this beam is vertically impinged on the center of the heating area. The first-order diffracted beam is detected by a photo-multiplier tube (PMT) through a pinhole (PH) and an interference filter (IF). Signal data taken from the PMT is sent to a computer and is analyzed to determine the thermal diffusivity. Since the CO_2 laser has an infrared wavelength of 10.6 μm, it is not necessary to add a dye substance to a sample; addition of dye may affect the process of gelation. The measuring region can be changed by adjusting the lens (L3). The sample is confined in a sample cell comprised of a ZnSe window, a BK7 window (both windows are anti-reflection coated), aluminum plates, and a rubber spacer that determines the sample thickness. The selection of windows has a considerable effect on the S/N ratio of the detected signal. The material of the window of the heating laser irradiation side is ZnSe, selected because of its insolubility in water and its good transmission at both infrared (10.6 μm) and visible (632.8 nm) wavelengths. All samples used in this study absorb the heating laser well (the absorption depths are at most
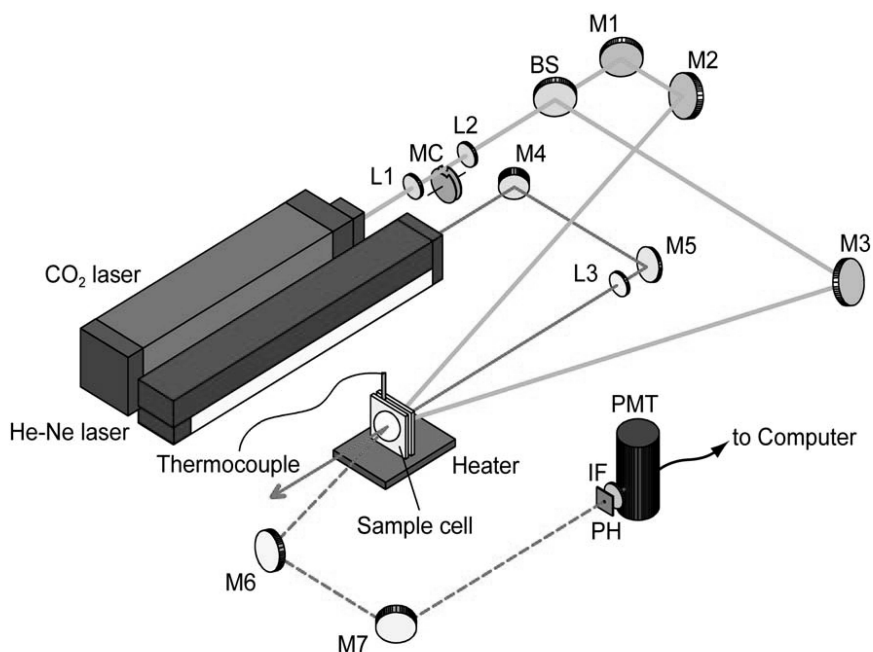

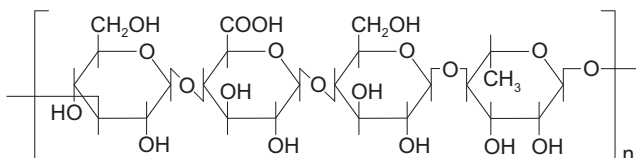Fig. 2.   Schematic diagram of the experimental system.

Fig. 3.   Molecular structure of gellan gum.

100 μm), and it is necessary to transmit only the probing beam. BK7 is employed for the material of the rear window because of its high transmittance at the wavelength of the probing laser. In the present study, the thickness of the sample was 1.0 mm.

The temperature of the sample is controlled by adjusting an electric plate heater under the sample cell, and is measured with the aid of a sheathed C-A thermocouple (diameter of 0.3 mm) directly immersed in the sample. In the present apparatus, a series of measurements is performed at intervals of 1 s; this system has been improved from that of our previous report [5] by shortening the data acquisition and analysis time. In the present study, the measurement area is fixed at about 1 mm^2.

3.2. Sample and Dynamics of Gelation

In order to evaluate the validity of the dynamic measurement of thermal diffusivity change, we employed the observation of a sol-gel transition process. In the sol-gel process, the viscoelastic behavior or other characteristics change with the development of the polymer network. In the present study, the thermal diffusivity during the sol-gel transition of a gellan gum aqueous solution was measured. Figure 3 shows the chemical structure of the gellan gum used in the present study. It is an extracellular polysaccharide produced by a bacterium, and is composed of a tetramer repeat unit consisting of glucose, glucuronic acid, and rhamnose at a molar ratio of 2:1:1 [13]. The samples of gellan gum were obtained from Wako Pure Chemicals Industries, Ltd. An aqueous solution of gellan gum was prepared at 363 K with constant stirring, and was injected by a syringe into the cell. Then the temperature of the sample was slowly cooled to 298 K. The sample gelled in the cooling process, during which the thermal diffusivity of the gellan gum aqueous solution was continually measured.

4. RESULTS AND DISCUSSION

The thermal diffusivity of distilled water in the temperature range from 298 to 323 K was preliminarily measured, and the results appear in

Fig. 4. The experimental standard deviation of the measurements was within $\pm 3\%$, and the absolute value was 30% higher than the values calculated from thermal conductivity [14], density [15], and specific heat capacity [15]. This difference was caused by two-dimensional heat conduction due to surface heating (Section 2.2), and this error factor was analyzed by Otsubo et al. [16]. Because the analytical procedure considering this factor and correcting measured data takes so much time that the continual measurements cannot be conducted, we did not utilize this procedure. In order to emphasize the validity of dynamic detection of the thermal diffusivity change, the relative value of thermal diffusivity normalized by the measured value of the starting point of the cooling process is presented in this paper. In the present study, the grating period from 40.1 to 44.1 μm was chosen, and the heating pulse duration time of the heating laser was 1 ms. Figure 5 shows the temperature variation in the gelation process of a 1 mass% gellan gum aqueous solution. The gelation of the gellan gum aqueous solution has been reported as an exothermal process [17], although the heat flux caused by the transition is negligibly small compared to the heat gradient by the laser heating. In fact, as seen in Fig. 5, the temperature of the sample dropped exponentially without any
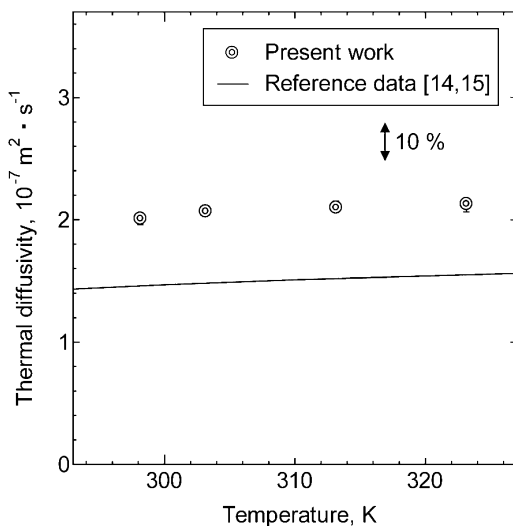

Fig. 4. Results of preliminary measurements of distilled water. Reference values are calculated from thermal conductivity [14], density [15], and specific heat capacity [15].
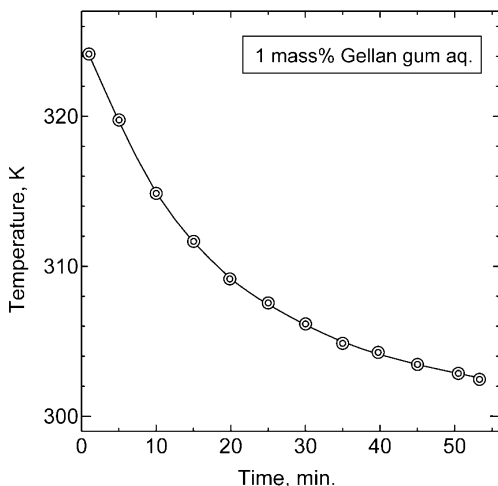
Fig. 5. Temperature variation through the gelation process of 1 mass% gellan gum aqueous solution.

steep change throughout the cooling process. The thermal diffusivity of the sample decreased slowly corresponding to the temperature variation in the cooling process from 0 to 45 min. Then, at 46 min., the thermal diffusivity suddenly dropped. This behavior is described in Fig. 6; the decrease in the thermal diffusivity at this point was around 30% despite the temperature variation of 0.1 K over the same time range. This large thermal diffusivity variation implies a contribution from the structural change, i.e., from gelation. The sample temperature for this change in the thermal diffusivity was 303 K, and this temperature was recognized as the gelling temperature.

Table I shows the previously reported gelling temperature of a 1 mass% gellan gum aqueous solution, and these data were in good agreement with the gelling temperature extrapolated from the dynamic thermal diffusivity change. We also measured the gelation of a 2 mass% gellan gum aqueous solution, and the temperature corresponding to an abrupt change in the thermal diffusivity was 305 K; this value is rather high relative to that of the 1 mass% solution, and it also agreed with other experimental results. The gelation temperature of a physical gel has been reported to have a positive concentration dependence based on both calculation [22] and experimental studies [17]. From the results, it is demonstrated that the FRSM can detect a gelation point through continual and high-speed measurements of the thermal diffusivity. A technique to identify the gelation point such as differential scanning calorimetry (DSC) cannot be applied to real-time monitoring because of its low temporal resolution.
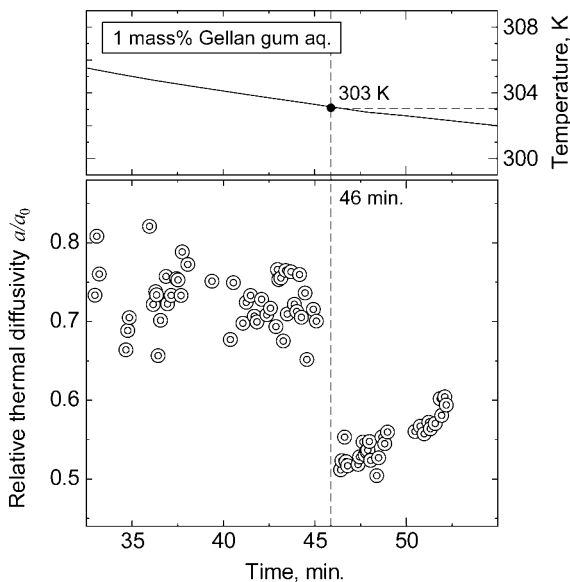
Fig. 6. Changing point of the thermal diffusivity throughout the sol-gel process of 1 mass% gellan gum aqueous solution. Relative data normalized by the measured value of the starting point of the cooling process are shown.

Nuclear magnetic resonance (NMR) can be used to observe the molecular behavior of hydrogen bonding; that is, this method is limited in application. Thermal scanning rheology (TSR), which measures the viscoelastic characteristics during gelation from the frequency response of the probe, cannot be applied to any nondestructive measurements. The unique

Table I. Gelation Temperature of 1 mass% Gellan Gum Aqueous Solution

First author	Ref.	Method	Gelation temperature (K)
Miyoshi	[18]	DSC[a]	302
Nishinari	[19]	DSC	302
Akutu	[20]	TSR[b]	298
Matsukawa	[21]	NMR[c]	303
Present work		FRSM	303

[a] DSC: differential scanning calorimetry.
[b] TSR: thermal scanning rheology.
[c] NMR: nuclear magnetic resonance.

features of the FRSM confirm it to have a great potential as a gelation determination method for a wide range of polymer gels. Moreover, it is also expected that the real-time monitoring system of the thermal diffusivity by the FRSM can lead to the detection of other structural changing processes.

5. CONCLUDING REMARKS

An apparatus to measure the dynamics of the thermal diffusivity for materials undergoing structural changes was developed, and continual measurements throughout the gelation process of a gellan gum aqueous solution were carried out. The thermal diffusivity of the solution decreased promptly and significantly at the supposed sol-gel transition temperature. In the next stage of this study, improvements to the method to allow more rapid changes in the sample with higher precision are planned. According to the results of the experimental measurements, the capability of the forced Rayleigh scattering method to carry out dynamic measurements of thermal diffusivity has been demonstrated.

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