

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

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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, and has an applicability of “thermal diffusivity real-time monitoring system” because of its characteristics. In the present paper, the temporal resolution of continuous measurements was improved to about every second, and sol-gel transition of gellan gum aqueous solution was studied to check the validity of the dynamic measurement of the thermal diffusivity. Through gelation process, dynamical change of the thermal diffusivity was measured, and gelation point can be identified from a series of thermal diffusivity data. The results indicated the capability of the forced Rayleigh scattering method to a real-time thermal diffusivity measurement technique in monitoring even rapidly changing process of a material.

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

1. INTRODUCTION

Due to development and application of new materials and technology, the need for thermophysical properties is increasing and spreading. In the process of internal structure change of a material, its thermophysical properties are expected to change with

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time. In order to strictly control the material changing process, the information of successive data of thermophysical properties are indispensable. Therefore, continual measurement of the transient value of thermophysical property during a changing process can be an effective means to trace and identify the process. Furthermore, real-time thermal diffusivity data enable temperature and quality control in dynamic perspective through 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, not as a function of time. Many of conventional measuring techniques are not suitable to measure dynamically changing thermal diffusivity of a material through a continuous process. In the present study, the validity of the dynamic measurement of thermal diffusivity was discussed, and we measured sol-gel transition in order to trace the process as a function of time near room temperature. The measuring method was the forced Rayleigh scattering method. This is an optical technique of the thermal diffusivity measurement and has possibility of applying to the real-time monitoring of the thermal diffusivity. The element of an experimental system to measure dynamics of the thermal diffusivity was constructed and preliminary measurements were conducted in our previous report [5]. As a test of dynamic detection, the thermal diffusivity through gelation process of gellan gum aqueous solution was measured in the present paper.

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 term was named by analogy with spontaneous Rayleigh scattering based on statistical thermodynamics fluctuation, and 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 were adequately discussed in our earlier publication [9], and here we briefly describe its outline.

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 the corresponding gradient in the refractive index, which produces a transient optical phase grating. Thus, by emitting probing laser beam, diffracted beams can be obtained. After the heating, the excited temperature distribution decays exponentially owing to heat conduction and so does the intensity of diffracted beams. The intensity of the first order diffracted beam I_1 can be expressed as a function of time t as

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

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. The fundamental working equation takes the form

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

in which a represents the thermal diffusivity of a sample, and Λ the grating period determined with the crossing angle and the wavelength of heating laser beams.

2.2. Application to Dynamic Measurement

Considered as one measurement method of the thermophysical properties, the features of the FRSM for the dynamic measurement under transient condition are summarized as follows. (1) Because of contact-free manner in both heating and probing, remote-sensing through a changing process of a sample can be carried out. (2) Since one measurement requires only 1 ms or less, measurement in the course of transition even with subsecond time scale is possible. Here, every measurement is performed once a second. (3) By controlling the probing region, local properties can be measured. Therefore, it is possible to grasp variations of the thermal diffusivity in the order of micrometer. The spatial resolution of the present measurements is around 1 mm^2 , and this can be easily smaller by focusing the probing laser beam. (4) It determines an absolute value. These characteristics indicate the possibility of application to the dynamic measurement of the thermal diffusivity of rapidly changing material by means of repeated pulses at appropriate intervals.

In the theory of the FRSM, the temperature distribution T_x at position x and at time t is

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

T_0 is the mean initial temperature rise, T_1 the temperature distribution by the interference of heating laser beams, and x -axis is the direction perpendicular to the grating. This method can determine the thermal diffusivity by the decay of the temperature distribution of transient thermal grating, namely T_1 . In order to continually measure the thermal diffusivity, the waiting period in which the excited temperature distribution induced by the heating laser, not only T_1 but also T_0 , attenuates is necessary. The temporal resolution of dynamic measurement can be determined by the decay time of T_0 and T_1 . The basic principle of the FRSM mentioned in section 2.1 assume only one-dimensional heat conduction in the heated region, and the

assumption is not enough to estimate an appropriate temporal resolution. To analyze this problem, two-dimensional heat conduction model by the use of Green's function was conducted. Green's function G_z for semi-infinite solid ($0 < z < \infty$) in the case of an adiabatic sample surface is given [10] by

$$G_z = \frac{1}{2\sqrt{\pi at}} \left[\exp\left\{-\frac{(z-z')^2}{4at}\right\} + \exp\left\{-\frac{(z+z')^2}{4at}\right\} \right] \quad (4)$$

Then the temperature distribution T_z at position z and at time t can be expressed as

$$T_z = \int_0^\infty G_z \exp(-\alpha z') dz' \quad (5)$$

where α the absorption coefficient of the wavelength of heating laser. Eq. (4) can be solved as follows.

$$T_z = \frac{1}{2} \left[\begin{aligned} &\exp(a\alpha^2 t + \alpha z) \operatorname{erfc}\left(\frac{2a\alpha t + z}{2\sqrt{at}}\right) \\ &+ \exp(a\alpha^2 t - \alpha z) \operatorname{erfc}\left(\frac{2a\alpha t - z}{2\sqrt{at}}\right) \end{aligned} \right] \quad (6)$$

Therefore, the temperature distribution in the two-dimensional heat conduction model T_{xz} can be obtained by the multiplication of Eqs. (3) and (6). In addition, the effect of Gaussian intensity distribution was also considered. The intensity distribution of the heating laser is TEM₀₀ mode, and thus heat conduction of x and y directions due to the intensity distribution occurs. Finally, the three-dimensional heat conduction model was used to evaluate the temporal resolution of dynamic measurement of the thermal diffusivity by means of the FRSM. We calculated this mathematical model and evaluated the maximum repetition period. The absorption coefficient (at the wavelength of heating laser) and the thermal diffusivity determine the maximum repetition period, and the results of parametric studies are shown in Fig. 1. In the grey region, it is difficult to measure the thermal diffusivity because the heat conduction of z -axis is faster than that of x -axis. The 2-D conduction limit is determined by the single measurement time which depends on the thermal diffusivity and the grating period, in this calculation the minimum grating period of the present apparatus (20 μm) is used. The absorption coefficient of water used is $8 \times 10^4 \text{ m}^{-1}$ [11]. The Gaussian radius is 2 mm, which is the radius of the heating laser beam of our measurement system, and the effect of three-dimensional heat conduction become conspicuous at the sample of an absorption coefficient lower than 10^3 m^{-1} . In the case of conducting dynamic measurement of every second using the FRSM, all of the samples in this study (water, gellan gum aqueous solution, and its gel) get around this limitation, and the maximum repetition period of water was evaluated to 30 ms.

Comparing to the other measurement techniques of front-heating and rear-sensing as typified by the laser flash method, the FRSM can measure even the sample which temperature rise is so small that the heated area is limited only near

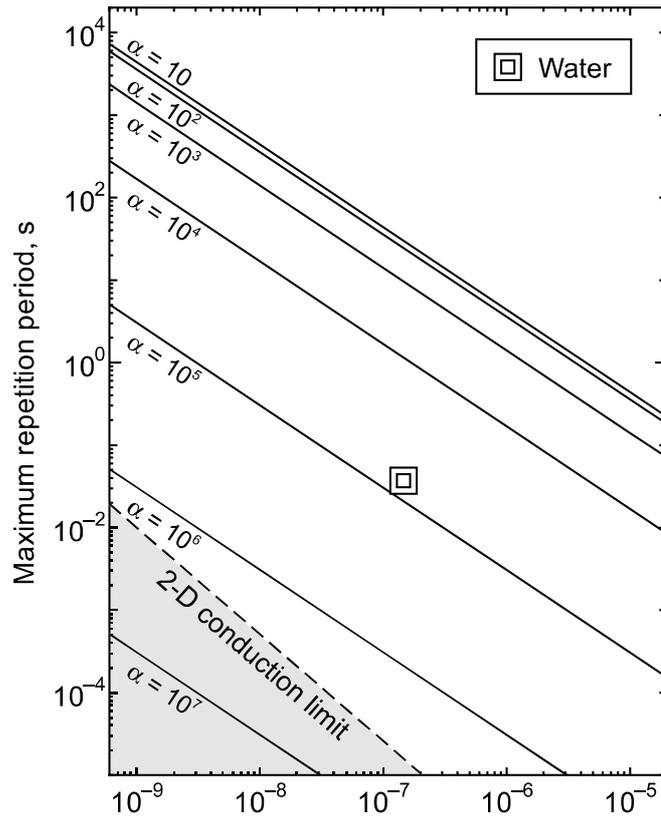


Fig. 1. The maximum repetition period of dynamic measurement of the thermal diffusivity. In grey area, thermal diffusivity measurements have difficulty due to two-dimensional heat conduction.

surface and that the temperature at rear side scarcely rises.

3. EXPERIMENTAL

3.1. Measurement System

Figure 2 shows the schematic diagram of the present apparatus to measure the dynamics of the thermal diffusivity. The heating laser is a CO₂ laser (wavelength = 10.6 μm, 10 W) and the continuous beam is chopped by a rotating mechanical chopper (MC) to generate a pulse of 100 to 2000 μs. The pulsed beam is divided into two beams of equal intensity by a beam splitter (BS), and then 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 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 PMT is sent to a computer and is analyzed to determine the thermal diffusivity. Since the CO₂ laser has an infrared

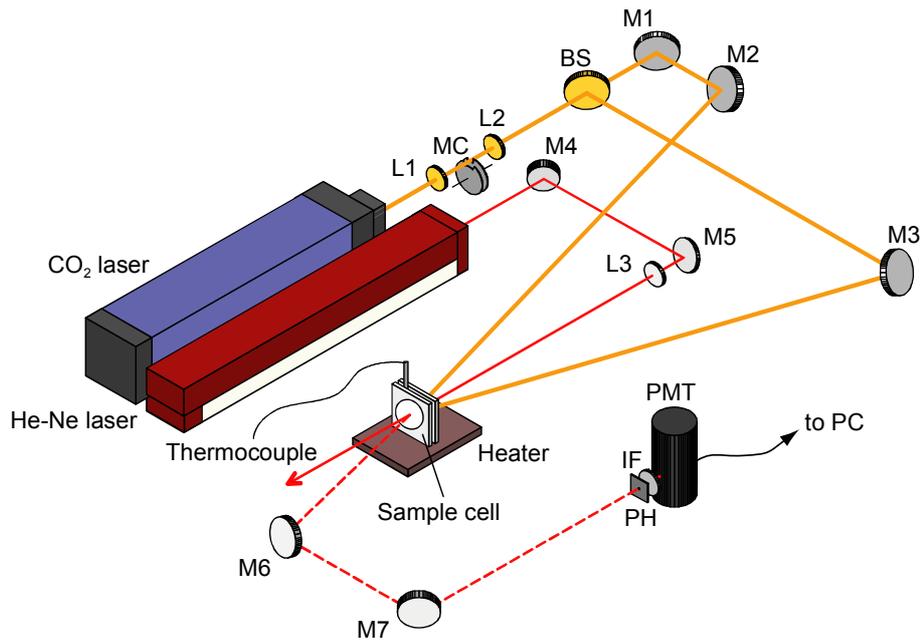


Fig. 2. Schematic diagram of the experimental system.

wavelength of $10.6\ \mu\text{m}$, it is not necessary to add the dye substance in a sample that may affect the process of gelation. The measuring region can be changed by adjusting a lens (L3). The sample is confined in a sample cell made of a ZnSe window, a BK7 window (both windows are anti-reflection coated), aluminum plates, and a rubber spacer that determines the thickness of sample. The selection of windows has considerable effect on S/N ratio of the detected signal. A material of the window of heating laser irradiation side is ZnSe, because of the insolubility in water and the good transmission at both the infrared ($10.6\ \mu\text{m}$) and visible ($632.8\ \text{nm}$) wavelength. On the other hand, a material of the rear window only transmit the beam of probing laser, we employed BK7.

Temperature of the sample is controlled by adjustment of an electric plate heater under the sample cell, and is measured with the aid of a C-A thermocouple (diameter of $0.3\ \text{mm}$) directly immersed in the sample. In the present apparatus, each measurement is carried out around every second, which has been improved from that of our previous report [5] because data acquisition and analysis time were shortened. The sample thickness is fixed to $1.0\ \text{mm}$ and measurement area is about $1\ \text{mm}^2$.

3.2. Sample and Dynamics of Gelation

In order to discuss the validity of the dynamic measurement of thermal diffusivity change, we employed a sol-gel transition process. In sol-gel process, viscoelastic behaviour or the other characteristics change accompanied with development of the polymer network. In the present study, the thermal diffusivity in a course of sol-gel

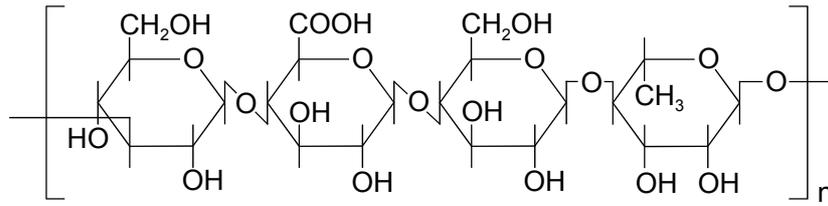


Fig. 3. Molecular structure of gellan gum.

transition of gellan gum aqueous solution was measured. Figure 3 shows the chemical structure of gellan gum used in this study. It is an extracellular polysaccharide produced by a bacterium and it is composed of a tetramer repeat unit consisting of glucose, glucuronic acid and rhamnose at a molar ratio of 2:1:1 [12]. 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 into the cell by a syringe. Then the temperature of the sample was slowly cooled down to room temperature of 298 K. The sample gelled in the cooling process, and the thermal diffusivity of the gellan gum aqueous solution was continually measured.

4. RESULTS AND DISCUSSION

The thermal diffusivity of distilled water at the temperature range from 298 to 323 K was preliminarily measured, and the results appear in Fig. 4. The reproducibility of the measurements was within $\pm 3\%$, and absolute value was 30% higher than the data calculated from the thermal conductivity [13], the density [14] and the specific heat capacity [14]. 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.*[20]. However it was possible to adopt the analytical model with consideration of the error factor, we did not utilize this model. In order to emphasize on check the validity of dynamic measurement, the relative value of thermal diffusivity normalized by the measured value of the starting point of cooling process was presented in this paper. In the present study, the grating period was chosen from 40.1 to 44.1 μm , and the heating pulse duration time of heating laser was 1 ms. Figure 5 shows the temperature variation of gelation process of 1 wt% gellan gum aqueous solution. The gelation of gellan gum aqueous solution has been reported as an exothermic process, however, heat flux caused by the transition assumed little at low concentration [23]. In fact, as seen in Fig. 5, the temperature of sample dropped exponentially without any steep change all over the cooling process, the influence of exothermic can be negligible. The thermal diffusivity of the sample was slowly decreased corresponding to the temperature variation in the cooling process, and then at 46 min., the thermal diffusivity suddenly dropped down, and this behavior is described in Fig. 6. The decrease of the thermal

diffusivity at this point was around 30 % despite of temperature variation at the same time range was 0.1 K. This thermal diffusivity variation was drawn an inference of contribution of the structural change, gelation. The sample temperature of this change point of the thermal diffusivity was 303 K, and this temperature was recognized as the gelling temperature. Table I shows the previously reported gelling temperature of 1 wt% gellan gum aqueous solution, and these were in good agreement with the gelling temperature extrapolated from the dynamic thermal diffusivity change. We also measured the gelation of 2 wt% gellan gum aqueous solution, and the temperature of a change point of the thermal diffusivity was rather higher than that of 1 wt% solution. Gelation temperature of physical gel is regarded to have positive concentration dependence by both calculation [20] and experimental study [21]. It was demonstrated that the FRSM could detect gelation point through continual and high-speed measurement of the thermal diffusivity. The other technique to identify the gelation point such as differential scanning calorimetry (DSC) was not applied to real-time monitoring. Nuclear magnetic resonance (NMR) observes molecular behavior of hydrogen bonding, thus this method can be limitedly used. Thermal scanning rheology (TSR), which measures the viscoelastic characteristics during gelation, cannot be applied to any nondestructive measurements. The unique features of the FRSM have a great potential to an application of gelation determination technique for widely range of polymer gel. Moreover, it is also expected that real-time monitoring system of the thermal diffusivity by the FRSM can lead to detect the other structural changing process.

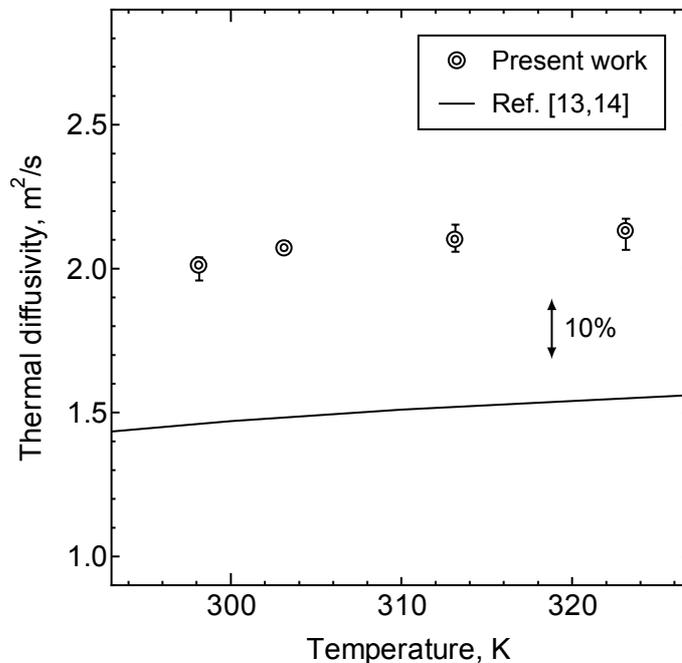


Fig. 4. The results of preliminary measurement of distilled water. Reference data is calculated from the thermal conductivity [13], the density [14], and the specific heat capacity [14].

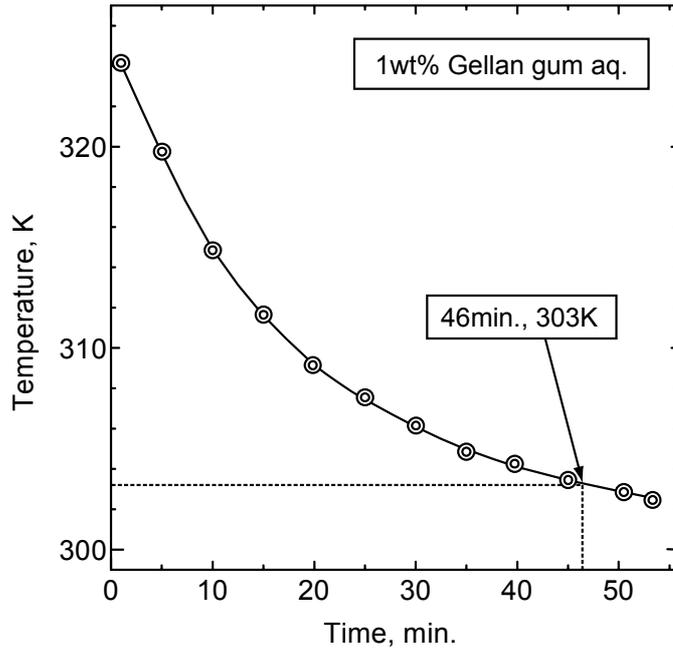


Fig. 5. The temperature variation through the gelation process of 1wt% gellan gum aqueous solution.

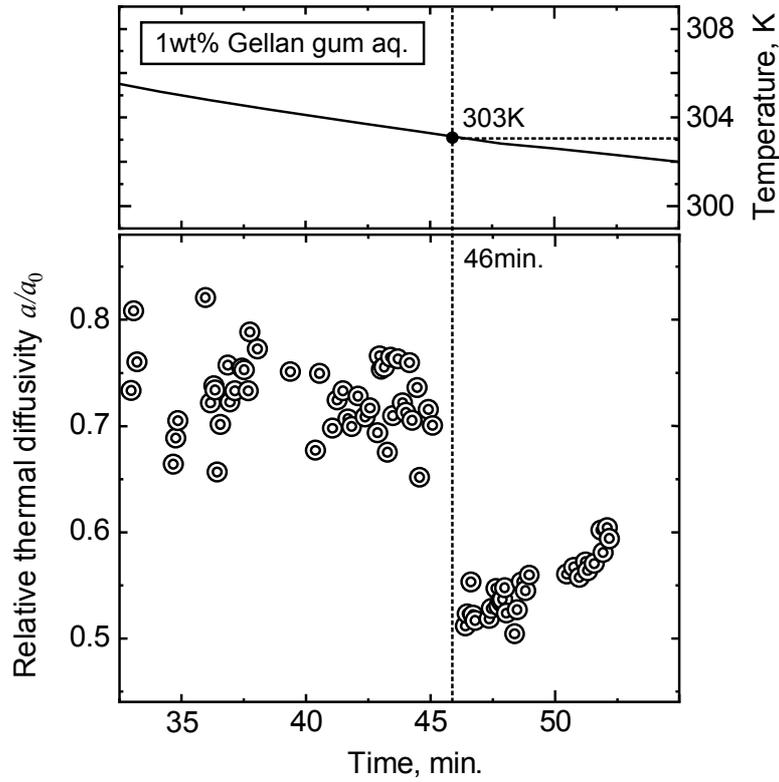


Fig. 6. The changing point of the thermal diffusivity through sol-gel process of 1 wt% gellan gum aqueous solution.

Table I. Gelation temperature of 1wt% gellan gum aqueous solution

Author	Method	Gelation temperature (K)
Akutu <i>et al.</i> [18]	TSR	298
Matsukawa <i>et al.</i> [19]	¹ H NMR	303
Miyoshi <i>et al.</i> [16]	DSC	302
Nishinari [17]	DSC	302
Present work	FRSM	303

5. CONCLUDING REMARKS

An apparatus to measure the dynamics of the thermal diffusivity of changing materials was developed, and continual measurement through the gelation process of gellan gum aqueous solution was carried out. The thermal diffusivity of the solution reduced promptly at the supposed sol-gel transition temperature. In the next stage of this study, it is planned to improve the method to follow more rapid change of the sample properly with high precision. According to the results of the experimental measurements, the capability of the forced Rayleigh scattering method to the dynamic measurement of thermal diffusivity is demonstrated.

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