A Self-Build Apparatus for Oscillatory Flow Birefringence Measurements in a Co-Cylindrical Geometry

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We developed a high-sensitive apparatus for oscillatory flow birefringence measurement in a co-cylindrical geometry. The apparatus was comprised of a conventional rheometer, an Argon ion laser, and a lock-in amplifier. The laser was irradiated to samples under sinusoidal strains, and transmitted light intensities were analyzed using the lock-in amplifier to evaluate flow birefringence. TTL signals, which were transformed from sinusoidal strains using a comparator, were used as reference signals for lock-on detection at low frequencies. First, phase shifts between the true strain and TTL reference signal generated by the comparator were calibrated. Next, reliability of the apparatus was assessed using a wormlike micellar solution, whose flow birefringence behavior are well known. Finally, sensitivity of the birefringence measurement was checked using a low birefringent cellulose nanofiber (CNF) dispersion. Flow birefringence behavior of the CNF dispersion became measurable thanks to a long optical pass length of the geometry. The apparatus will be a strong tool to reveal dynamics of low birefringent solutions.

Key Words: Flow birefringence / Polymer dynamics / Stress-optical rule

1. INTRODUCTION

Flow birefringence has long been measured to characterize polymers, particularly biomolecular systems. In typical measurements, birefringence of the solution sandwiched between the inner and outer cylinders of the co-cylindrical geometry is measured as a function of shear rates or as decay functions after cessation of steady flow to estimate the rotational diffusion coefficient. Shear flow orients large solute molecules such as proteins while thermal agitation randomizes their orientation through the rotational diffusion. The orientation of solute also gives rise to the entropic stress. There is a close relationship between orientational birefringence and entropic stress, as known as the stress-optical rule. For the case of rod-like polymers, the stress relaxation time after step strain can be represented by the rotational relaxation time. On the other hand, for the case of semiflexible polymers, bending modes and tension modes also originate the stress while these modes do not contribute to the birefringence significantly. This means that the stress-optical rule does not hold valid between the total stress and birefringence for the case of semiflexible polymers. Alternatively, detailed analysis of birefringence and stress relaxation provides us the information on rigidity of semiflexible polymers. Thus, the combined measurements of stress and birefringence are anticipated as an effective method to characterize semiflexible polymers.

For polymeric liquids, we have developed an apparatus for simultaneous measurements of dynamic viscoelasticity and flow birefringence under oscillatory shear deformation (hereafter this apparatus is denoted as “shear FB”). Dynamic measurements using oscillatory shear flow provides us more precious and sensitive measurements of stress and birefringence than steady flow measurements. The dynamics of a variety of polymeric materials such as polymacromonomers, diblock copolymers, polymerized ionic liquids, cellulose/ionic liquid system, and rubber/silica system had been assessed using the shear FB. However, the optical pass of our shear FB is limited to several millimeters and this short optical pass determines lower limits of birefringence measurements. Thus, the shear FB has been applied to polymeric melts or concentrated solutions. In order to evaluate weak flow birefringence of low birefringent materials such as dilute solutions, more sensitive apparatus is required.

In this study, we report a highly-sensitive self-build
apparatus for oscillatory flow birefringence measurements equipped with a co-cylindrical geometry. This geometry with long optical pass length, ~30 mm would be advantageous for measuring low flow birefringence. A conventional rheometer was equipped with an Argon ion laser, optical train, and a lock-in amplifier for birefringence measurements. The laser was irradiated to a sample in the geometry under sinusoidal oscillation. The transmitted light through the sample was detected with a photo detector, and its signal was analyzed using the lock-in amplifier. From the thus determined intensity and phase angle differences, flow birefringence were obtained. In the lock-in amplifier, TTL signals, which were transformed from the strain signal of the rheometer through a comparator, were used as reference signals. The calibration of the apparatus was performed as follows. First, phase shifts due to the comparator for generation of TTL signals were determined as a function of strain amplitude and frequency by using a reference signal originated by an outer cylinder which shaded half of laser light. With this setup, the transmitted light intensity varied with time sinusoidally with oscillatory movements of the outer cylinder. Secondly, reliability of the apparatus was examined with a wormlike micellar aqueous solution [Cetyltrimethylammonium bromide (CTAB)/sodium salicylate (NaSal) solution], whose flow birefringence has already been reported. The complex shear strain-optical coefficients, $K^*(\omega)$, are defined as follows

$$G^*(\omega) = \frac{\sigma^*}{\gamma^*} = \frac{\sigma_0}{\gamma_0} \exp(i\delta) = G' + iG''$$

The complex shear moduli, $G^*(\omega)$, and complex strain-optical coefficients, $K^*(\omega)$, are defined as follows

$$K^*(\omega) = \frac{\Delta n(t)}{\gamma^*} = \frac{n_0}{r_0} \exp(i\delta_0) = K' + iK''$$

Shear birefringence of polymers is measured by applying light to them under oscillatory shear deformation based on the crossed Nicols method. When the shear strains are small, the birefringence $\Delta n$ is calculated from the ratio of the light intensity transmitted through samples under shear deformation, $I(t)$, to the incident-light intensity $I_0$.

$$I(t)/I_0 = |\sin^2(\Delta n(t) l/\lambda)l|$$

where $\lambda$ is the wavelength of light in vacuum and $l$ is the optical path length transmitted through samples. If the birefringence is small, the $I(t)$ values are measured by displacing the quarter wavelength plate between the crossed Nicols and the direction of analyzer is offset with a small angle $\alpha$. For this optical arrangement forming Sénarmont compensator, eq. 6 is modified as follows:

$$I(t)/I_0 = 2\pi\Delta n(t)/\lambda$$

Thus, $\Delta n(t)$ can be measured from $I(t)$.

3. EXPERIMENTAL

3.1 Preparation of CTAB/NaSal solution

Cetyltrimethylammonium bromide (CTAB) and sodium salicylate (NaSal) were purchased from Wako Pure Chemical Industries, Ltd., Japan. CTAB (10 g) was dissolved in 90% v/v acetone/methanol mixture (90 mL) at 70 ºC and then recrystallized at ambient temperature. NaSal was used without further purification. The recrystallized CTAB and NaSal were dissolved in distilled water and stayed at rest at 40 ºC overnight to obtain a homogeneous CTAB/NaSal solution. The concentrations of CTAB and NaSal in the solution were adjusted to 0.03 and 0.23 M, respectively.

3.2 Preparation of dilute CNF/glycerol dispersion

2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), 2 M sodium hypochlorite (NaClO) solution, sodium bromide (NaBr), sodium hydroxide (NaOH), sodium borohydride (NaBH₄), and glycerol were purchased from Wako Pure Chemical Industries, Ltd., Japan and Sigma-Aldrich Co.
U.S.A.. A never-dried softwood bleached kraft pulp (SBKP) with a water content of 80 % was kindly supplied by Nippon Paper Industries Co. Ltd., Japan and used as a starting material for cellulose nanofibers (CNFs). CNFs with a uniform width of ~3 nm were prepared from SBKP by TEMPO-mediated oxidation and subsequent mechanical treatment in water according to a previously reported method\(^8\). The SBKP (1 g) was oxidized in water using a TEMPO/NaBr/NaClO system with 10 mmol NaClO. The pH of the slurry was maintained at 10 by adding 0.5 M NaOH solution. After a designated time (5 h), the oxidation was quenched by adding small amount of ethanol. The oxidized pulp slurry was thereafter reduced with NaBH\(_4\) (0.1 g) for 3 h at pH 10 in order to convert residual aldehydes and ketones to hydroxyl groups\(^9\). After washing thoroughly with distilled water by filtration and centrifugation, the reduction products were sonicated in distilled water for 8 min at the solid concentration of 0.1 % w/w, using a US-300E ultrasonic homogenizer (NIHONSEIKI KAISHA LTD., Japan). Unfibrillated fractions were removed by centrifugation to collect transparent aqueous CNF dispersion. The aqueous CNF dispersion was mixed with equivalent amount of glycerol by weight in order to increase the dispersion medium viscosity. The mixture was evaporated at 50 ºC, and then a CNF/glycerol dispersion was prepared. The solid concentration of the CNF/glycerol dispersion was adjusted to 0.01 % w/w.

### 3.3 Apparatus

Fig. 1a shows an overview diagram of the self-build apparatus. The apparatus was composed of a Rheosol G3000-BFG rheometer equipped with a co-cylindrical geometry (UBM, Japan), an Argon ion laser (\(\lambda = 488\) nm, 163C-1210, Spectra Physics Inc., U.S.A.), and a lock-in-amplifier (SR830, Stanford Research Inc., U.S.A.). Optical arrangement for birefringence measurement is schematically illustrated in Fig. 1b and 1c. The CTAB/NaSal solution or CNF/glycerol dispersion were put into an outer cylinder of the geometry, in which BK7 glasses were mounted at the top and bottom. Sinusoidal shear strains were directly applied to the outer cylinder by a vibrator. The Argon ion laser was irradiated to the samples under the strains, and the transmitted laser lights through the samples were detected by a photo detector (C6386-01, Hamamatsu Photonics K. K., Japan). The polarization state of light is generally modified by reflection of mirrors due to the difference in reflectance of s and p polarization state. In our apparatus, the two mirrors were aligned so that only p polarization is reflected. Strain and frequency dependencies of the amplitudes \(R\) and phase angle differences \(\delta_b\) for the transmitted laser lights were analyzed using the lock-in-amplifier. In order to measure the \(R\) and \(\delta_b\) values at low frequencies (< 1 Hz), TTL signals were generated from the sinusoidal strain signals using a comparator and used as reference signals in the lock-in-amplifier. Since the \(R\) values are generally displayed in Volts RMS, the actual amplitude (\(\sqrt{2} \times R\)) were used for the calculation of birefringence \(\Delta n\).

\[
\Delta n(t) = \sqrt{2} R \lambda / 2 \pi n l\phi
\]

where \(l\) is substituted with 35 mm (Fig. 1b). The incident-light intensity \(I_0\) of the laser was measured each time a measurement using a digital multimeter (34401A, HP Inc., U.S.A.). The small angle \(\alpha\) was calculated from the \(I_0\) and the light intensity \(I_{\alpha}\) at which the quarter wavelength plate was displaced by \(\alpha\).

\[
\alpha = \sin^{-1}(\sqrt{I_{\alpha}/I_0})
\]
The real part $K'$ and imaginary part $K''$ of the complex shear strain-optical coefficients $K^*$ for the samples are calculated from the $\Delta n$ and $\delta_B$ values as follows\(^6\);

$$K' = \frac{\Delta n}{2\pi} \cos \delta_B \quad (10)$$

$$K'' = \frac{\Delta n}{2\pi} \sin \delta_B \quad (11)$$

The birefringence measurements were conducted at 25 ºC and 5–25 ºC for the CTAB/NaSal solution and the CNF/glycerol dispersion, respectively. The measurement temperature was controlled using a gas chiller and a heater gun.

In the above argument, we consider only the phase retardation due to the compensator. The correction factor may be written more generally in the complex form.

### 3.4 Other analyses

Dynamic viscoelastic measurements were conducted on the CTAB/NaSal solution using a HAAKE MARS rheometer (Thermo Fisher Scientific Inc., U.S.A.) with a cone-plate geometry (plate diameter: 60 mm, angle: 1°). Frequency dependences of the complex shear moduli $G^* (= G' + iG'')$ were evaluated within the linear viscoelastic region.

Flow birefringence of the CTAB/NaSal solution and CNF/glycerol dispersion was also investigated at 10–25 ºC using the shear FB based on an oblique laser beam method\(^1\). The obtained $K'$ and $K''$ were used as reference data (hereafter denoted as $K_{OB}'$ and $K_{OB}''$, respectively) and compared with those evaluated using the self-build apparatus.

### 4. RESULTS AND DISCUSSION

#### 4.1 Calibration of phase angle shift

As described in the experimental section, our system is based on a conventional rheometer. Dynamic birefringence detection is performed with the lock-in amplifier which require TTL reference signals for lock-on detection at low frequencies. Therefore, the rheometer was modified to transform strain signal to TTL signal using a comparator. Firstly, we checked the phase difference between this TTL signal and actual movement of the outer cylinder of coaxial fixture. This phase difference should be zero irrespective of strain amplitude and frequencies. This calibration was performed as follows. A slip of paper was attached at the bottom of the outer cylinder as the half of the laser was shaded, and the outer cylinder was oscillated by the vibrator (Fig. 2a). The intensity of transmitted laser light oscillates sinusoidal with the same phase as the sinusoidal strains (i.e. true strains). The phase of this true strain was compared with that of the TTL signals (i.e. nominal strains), and the phase angle difference between the true and nominal strains, $\Delta \delta_B$ was analyzed (Fig. 2b). Fig. 3 shows frequency dependencies of the $\Delta \delta_B$ values thus determined. The amplitude of the strains varied from 0.3 to 5 %. The $\Delta \delta_B$ values showed a similar tendency at high frequencies (> ~10 s\(^{-1}\)) regardless of the amplitude of the strains and then increased moderately with decreasing the frequencies. As the strain amplitude became smaller, the $\Delta \delta_B$ values at low frequencies (< ~1 s\(^{-1}\)) became more deviated. Thus, the $\Delta \delta_B$ values depended on not only frequencies but also amplitude of strains. This can be attributed to a time lag of the comparator for transforming the TTL signals from the sinusoidal signals. Generally speaking, comparators originate the square wave when the reference signal exceeds a certain level of voltage, $V_C$. If $V_C = 0$, no phase shift occurs. In our system, the strain may be written as follows

$$v_{\text{strain}}(t) = G \exp(i\omega t) \quad (12)$$
Here, $C$ is a proportionality coefficient. The time lag can be written

$$\omega t_{lag} = \sin^{-1}(\frac{\delta y}{C y})$$

If we consider the response time of the comparator, $t_{res}$, $\Delta \delta_B$ may be written

$$\Delta \delta_B = \frac{t_{lag} + t_{res}}{T} = \frac{1}{2\pi} \sin^{-1}(\frac{\delta y}{C y}) + \omega t_{res}$$

Where, $T = 2\pi/\omega$ is the period of strain. This equation explains frequency and strain dependence of $\Delta \delta_B$. Thus, $\Delta \delta_B$ is determined by $V_c$ and $t_{res}$, and therefore the actual values of $\Delta \delta_B$ change with the performance of comparator. In actual analysis, weak frequency dependence of $V_c$ and $t_{res}$ were further considered phenomenologically. The compensation of the $\Delta \delta_B$ was conducted as a function of frequency and strain with reference to Fig. 3.

### 4.2 Reliability assessment of the apparatus using the CTAB/NaSal solution

Flow birefringence of the CTAB/NaSal solution was evaluated using the self-build apparatus after the calibration of the phase shifts. Frequency dependencies of the $G^*$ and $K_{OB^*}$ for the CTAB/NaSal solution were preliminarily measured at 25 ºC using the HAAKE MARS rheometer and shear FB, respectively. The result is shown in Fig. 4. As reported in a literature, the stress-optical rules ($K' = CG'$) held well in the almost entire ranges of $\omega$ with $C = -4.0 \times 10^{-7}$ Pa$^{-1}$. The $G^*$ and $K_{OB^*}$ were described by a single Maxwell model (shown as dotted lines) at low frequencies, when the relaxation time and plateau modulus were determined as 3 s and 6.5 Pa, respectively.

The $K'$ data taken with the self-build apparatus was compared with $K_{OB'}$ in Fig. 5. The $K'$ and $K''$ values were in good agreement with the $K_{OB'}$ and $K_{OB''}$ values, respectively. Therefore, flow birefringence of the CTAB/NaSal solution were evaluated accurately from the $\Delta n$ and $\delta_B$ values using the self-build apparatus.

### 4.3 Flow birefringence of the dilute CNF/glycerol dispersion

The measurement sensitivity of the self-build apparatus to flow birefringence was investigated using the dilute CNF/glycerol dispersion (0.01 % w/w), whose birefringence was...
much lower than the CTAB/NaSal solution. The $K^*$ values of the CNF/glycerol dispersion were evaluated according to the aforementioned calibration, and compared with the $K_{OB}^*$ values. The $K^*$ and $K_{OB}^*$ values after applying the time-temperature superposition principle are shown in Fig. 6. The $K_{OB}^*$ at 10 ºC and 25 ºC were not completely overlapped each other, and their deviations were pronounced at low ($< 1$ s$^{-1}$) and high (> 100 s$^{-1}$) frequencies. The relaxation behavior of the $K_{OB}^*$ values was unclear in the entire ranges of frequencies. Meanwhile, the $K^*$ values at 5 ºC were overlapped on those at 25 ºC, and clear relaxation behavior was observed. This is because the optical pass length $l$ (35 mm) of the self-build apparatus was one order of magnitude longer than that of the shear FB (~2 mm). As shown in eq. 7, the light intensity $I(t)$ values are proportional to the optical pass length. The $I(t)$ values increase as the optical pass length become longer. Consequently, flow birefringence can be analyzed using the self-build apparatus even for weak-birefringence samples, which was difficult using the shear FB.

5. CONCLUSIONS

A highly-sensitive apparatus for oscillatory flow birefringence measurements in a co-cylindrical geometry was developed. The laser was irradiated to sinusoidally oscillating samples in an outer cylinder of the geometry, and amplitudes and phase angle differences of the transmitted light through samples were analyzed using the lock-in amplifier. For measuring birefringence at low frequencies, calibration of phase shift between the sinusoidal and TTL reference signals was quite important. The phase shift $\Delta \delta_h$ between the TTL (nominal strains) and sinusoidal signals (true strains) was calibrated with a half shaded glassy fixture. The measured $\Delta \delta_h$ values depended on strains as well as frequencies. The reliability of the apparatus is further examined with the CTAB/NaSal solution. Finally, $K^*$ values of a dilute CNF dispersion with low birefringence were evaluated. The $K^*$ values measured by the shear FB were scattered, and their relaxation behavior was unclear. In contrast, those measured by the highly-sensitive apparatus showed clear relaxation behavior. It is expected that the flow birefringence measurement using the high-sensitive apparatus can provide new insights on dynamics of low birefringent polymeric materials which used to be difficult.

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