Shear moduli of liquid crystalline polymers and relaxation process in poly methyl methacrylate studied by resonant ultrasound spectroscopy

Kazushi Fujita‡, Akira Nagakubo*, and Hirotsugu Ogi (Grad. School Eng., Osaka Univ.)

1. Introduction

Polymer materials are applied in a wide range of fields in our daily lives, for example, rubber, plastics, and so on. Recently, the development of polymer materials with excellent performance, such as liquid crystalline polymer (LCP), is in progress. These materials are very attractive because their mass densities are much smaller than those of metals and it is easier to machine them. In applying these materials to products, the evaluation of their elastic properties is very important for designing and manufacturing applications because deformation behavior determines its function and performance as a material.

In addition, polymer materials have attracted scientific interest because they have a disordered structure in which molecular chains interact with each other in a disorderly manner. Therefore, their microscopic behavior and properties have been keenly studied. A typical example is the relaxation phenomenon. For example, it has been reported that 40% of the force applied to polymer material is relaxed within 30 minutes[1], therefore, it is important to consider the elastic constants and the relaxation process to design a machine incorporating polymer material. Such relaxation phenomena are also very important in determining the macroscopic properties of polymer materials.

In this study, we use the three-point supported Resonant Ultrasound Spectroscopy (RUS) method to measure the elastic properties and relaxation phenomenon of LCPs and poly methyl methacrylate (PMMA). It is difficult to measure shear moduli and elastic anisotropy by conventional measurement methods such as the pulse-echo method. Relaxation phenomena are also difficult to measure in the high-frequency band due to large attenuation. On the other hand, the three-point supported RUS method can accurately measure acoustic attenuation because it does not require an acoustic coupling agent and can detect ideal eigen resonances under no external force. In addition, all independent elastic constants can be determined from a single specimen. Therefore, we measure the shear elastic constants and relaxation phenomenon of polymer materials using the RUS method.

2. Method

The RUS method can determine all independent elastic constants and acoustic attenuation from the resonant spectrum[2]. We show the experimental setup in **Fig. 1**, which composes the three-point supported RUS measurement system with a heater and a Laser Doppler Interferometer (LDI) system[3]. Here, we fabricate the needle-type pinducers using piezoelectric, a glass rod, and an aluminum pipe.

The three-point supported type RUS constructs three supporting needles, where we use two pinducers for excitations and detection of ultrasonic signals and one thermocouple to measure the specimen temperature. We applied continuous sinusoidal wave to a pinducer and detect the specimen's vibration from the other pinducer. By sweeping the frequency of the applied wave, we can determine the resonance frequencies of the specimen, which depend on its dimensions, mass density, sample shape, crystal axis orientation, and elastic constants. Accordingly, the elastic constants can be determined from the inverse calculation by comparing the measured resonant frequency, obtained from the experiment resonant spectrum, with the calculated resonant frequency using the estimated value of the elastic constants. It is important to note that when comparing the calculated

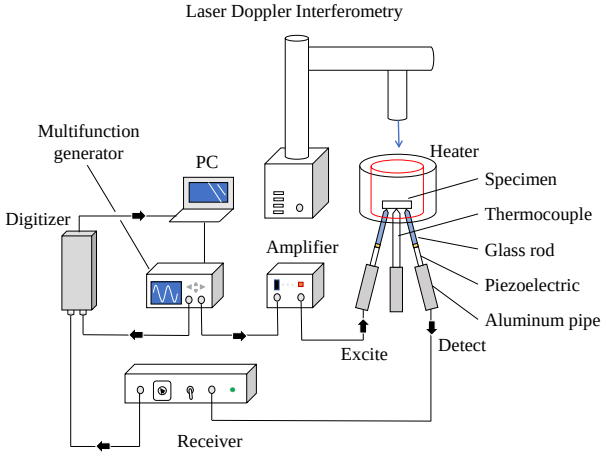

Fig. 1 Schematic of the three-point supported type RUS measurement system.

and measured resonant frequencies, we must choose the same vibration modes[4]. Therefore, we use the LDI method to obtain the vibration distribution of the sample surface in a vibrating condition, and the vibration modes were identified by comparing the measured vibration distribution image with the calculated one. LDI measurement also enables us to precisely detect resonance vibration of soft and light materials without noise from the detection-pinducer resonance.

The width of the resonant spectrum corresponds to the acoustic loss at the resonance mode. Therefore, the Q^{-1} can be calculated from the width of the resonant spectrum, and the relaxation phenomenon can be observed by measuring the Q^{-1} at various temperatures.

3. Result and Discussion

Figure 2 shows the resonant spectra of PMMA measured by pinducer and LDI at room temperature. The dashed lines indicate calculated resonant frequencies. In the case of using LDI, we irradiated a continuous wave laser beam at each point on the sample surface. In Fig. 2, we show spectra obtained at the center and the edge points. The spectrum obtained by the LDI is clearer than the that obtained by the pinducer. Moreover, the intensity of LDI spectra changes with measurement point, insisting on selectivity for eigen resonance modes. Then we calculate elastic constants C_{11} and C_{44} using measured resonant frequency. The calculated elastic constants were consistent with reported values measured by the pulse-echo method and SAW method[5] within 3%. This result confirms the reliability of the determined elastic constants of polymer materials calculated using RUS. Therefore, we will determine and discuss the elastic constants C_{11}, C_{44}, C_{66}, C_{33}, and C_{13} of LCP.

For PMMA, we also measured the dependence of the resonant spectra on temperature and calculated the internal friction Q^{-1} for each vibration mode. We assume that internal friction at our frequency range follows Debye's equation;

$$Q^{-1} = \Delta_M \frac{\omega\tau}{1+(\omega\tau)^2} \qquad (1)$$

where Δ_M, ω, and τ are the relaxation strength, angular frequency, and the relaxation time, respectively. Because internal friction takes the maximum at $\omega\tau = 1$, the relaxation time can be calculated from the relation. In this case, the relaxation time for the Au-1 mode at 49 kHz was determined to be as ~20 μs. This value is consistent with previous dielectric relaxation measurements, indicating that the relaxation phenomenon measured in this study is β-relaxation[6].

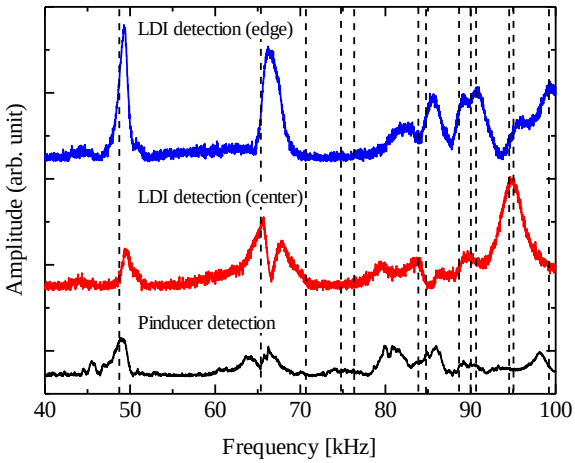

Fig. 2 Resonant spectra of PMMA measured by each method; blue and red lines are detected by LDI irradiated to the edge and center respectively, black line is detected by pinducer. black dashed lines are calculated resonant frequencies.

4. Conclusion

In this study, we measured the elastic property and relaxation phenomenon of PMMA and LCP using the three-point support type RUS. We succeeded in accurately identifying the vibration modes of PMMA by comparing the measured vibration distribution with the calculation. Then. we determined the elastic constants, which are consistent with previously reported values.

We also studied the relaxation phenomenon of PMMA. The relaxation time we obtained is consistent with reported values for the β-relaxation. Our method makes it possible to measure the mechanical relaxation of polymer materials in the kHz band.

References

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