A BRILLOUIN SCATTERING STUDY
ON THE OPTO-ACOUSTIC ANISOTROPY OF POLYMER FILMS

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Abstract
The elastic and opto-acoustic anisotropy of polymer films have been investigated non-destructively using Brillouin scattering techniques. The elastic and optical properties of polyvinylidene fluoride (PVDF) films were first investigated. A strong directivity of hypersonic wave properties in the plane was estimated.

During the ultra-drawing process of polypropylene (PP) film, an interesting profile of longitudinal wave velocity was observed. The optical anisotropy was also observed as the appearance of birefringence. The refractive index of the extraordinary ray kept almost constant during the ultra-drawing process, while the index of the ordinary ray gradually decreased.

The appearance of anisotropy was also observed in the epoxy adhesive layers of the single lap joint. In the glassy state layer, the effect of tensile stress was observed as a velocity decrease of longitudinal wave in the stress direction, whereas the velocity in the rubbery layer increased.

Introduction
Recently, Brillouin scattering is one of the strong tools for measuring transparent materials and opaque surface layers. This technique enables the non-destructive and non-contact measurement of the hypersonic wave velocity in a minute part of the sample using a focused laser beam.

In the previous Brillouin studies, we have investigated the elastic properties of epoxy curing layers and SiC nano layers [1,2]. In particular, we have succeeded in the precise and continuous measurements. At several geometries of Brillouin scattering, it should be noted that the selected phonon wave vector $q$ is dependent on the refractive index $n$ of the sample. This often becomes a problem for the material characterization by Brillouin scattering, because we should know the actual value of the refractive index to obtain hypersonic wave velocities.

From a different point of view, however, this problem implies that we can estimate the refractive index by measuring the Brillouin shift frequencies. Because the elastic properties are mostly beyond the high frequency limit of relaxation in the GHz range, there seems to be no frequency dispersion in velocity. One can then deduce the information of refractive index by comparing the hypersonic wave velocities obtained from two different Brillouin scattering geometries. Making use of this idea, we focus on the refractive index in this paper. In addition to the elastic

Ki : Wave vector of the incident light.
Ks : Wave vector of the scattered light.

Figure 1: Directions of incident, scattered and reflected laser lights in thin samples. 90° A geometry (a) and R10 A geometries ((b) and (c)).
and optical properties of some isotropic polymer films, the gradual appearance of birefringence in the films layers is discussed.

**Methods**

Brillouin scattering measurements were carried out using a high-performance six pass tandem Fabry-Perot spectrometer (TFPI), with an argon-ion laser at the vacuum wavelength $\lambda_0=514.5$ nm. The laser power at the sample was approximately 10 mW. The effect of continuous laser irradiation was carefully checked before measurements. The experimental system and the characteristics of this spectrometer have been discussed elsewhere [3].

In this study, we have used $90^0$ A, $180^0$ Reflection Induced $\theta A$ (RI$\theta$A) and “two pass” scattering geometries. [4-6] The longitudinal and shear wave velocities at the $90^0$ A scattering geometry (Fig.1 (a)) are independent of the refractive index of the sample and obtained by the equation, $v = f_{90A} \lambda_0 / \sqrt{2} \cdot$, using observed Brillouin shift frequency $f_{90A}$. At the $180^0$ scattering (back scattering) geometry, they are calculated by, $v = f_{180} \lambda_0 / 2n \cdot$ Assuming no frequency dispersion of wave velocity in the GHz range, we can obtain the refractive index $n$ by comparing the observed two shift frequencies, $f_{90A}$ and $f_{180}$. The “two pass” scattering geometry, which is a simple combination of $90^0$ A and $180^0$ geometries, enables the simultaneous measurements of both components.

The RI$\theta$A scattering measurement enables to measure RI$\theta$A and $180^0$ Brillouin components in one frequency spectrum. The scattering geometry is schematically shown in Figs. 1(b) and (c). Because wave velocities of RI$\theta$A components can be obtained by the equation $v = f_{\theta A} \lambda_0 / \left(2\sin(\theta/2)\right)$, they are also independent of the refractive index. By comparing the $f_{\theta A}$ and $f_{180}$ in one spectrum, we can obtain the refractive index.

It should be noted here that the optical anisotropy of uniaxial films could be easily obtained from the above Brillouin measurements. By selecting the isotropic plane as the scattering plane, the refractive indices of ordinary and extraordinary rays can be obtained using $s$ and $p$ polarized laser beams.

**Results and discussion**

*Elastic properties of PVDF films*

Figure 2 shows a typical observed spectrum of a PVDF film (Kureha chemical Industry, thickness 40 $\mu$m) by RI$\theta$A scattering geometry. Here, the angle of the incident laser beam is $\pi/2$. The strong central Rayleigh component was mechanically excluded to avoid the damage to the optical detection system. As
can be seen, both RIθA and 180° scattering components are clearly observed in the spectrum. Because PVDF is a uniaxial oriented film, the anisotropy in the plane was also observed by rotating the sample. In Fig.3, longitudinal wave velocity becomes higher in the direction of stretching, showing strong orthotropic anisotropy.

**Elastic and optical properties of ultra-drawing PP films**

A typical Brillouin spectrum from a PP film (Hanazono Co., thickness 30 µm) is shown in Fig. 4. This spectrum was obtained from two-pass geometry. At this geometry, we can obtain both of 90°A and 180° scattering components in one spectrum.

It is known that the isotropic PP film gradually shows strong anisotropy due to the uniaxial stretching. This phenomenon is called as ultra-drawing, which results from the oriented re-crystallization due to the tensile stress. In order to investigate the appearance of anisotropy in this process, we have then continuously measured the changes in the Brillouin scattering components during tensile test (Ez-test, Shimadzu Co., crosshead speed 0.5 mm/min, maximum load 500 N). Here we have used a dumbbell shape (JIS K7113-1995) PP film sample and measured the wave velocity in the direction of stress or the direction perpendicular to the stress. As shown in Fig.5, the stress-strain curve indicates the typical process of crystalline polymer films, showing the phenomenon of ultra-drawing at the strain higher than 200%. The longitudinal wave velocities in Fig.5 are all obtained from 90°A scattering components of the spectra. The longitudinal wave velocity in the stress direction showed a small peak in the initial state and gradually increased as a function of strain. Longitudinal wave velocities in the direction perpendicular to the stress decreased in the initial state and became constant. This implies the appearance of elastic anisotropy by the stress, which is clearly observed in the polar plots of velocities at the strain of 400% (Fig.6).

The appearance of anisotropy is also observed as the birefringence. Here, we have selected a scattering plane which is normal to the stress direction, in order to avoid the quasi elastic wave effects to the frequency spectra [4]. In addition, we used two different polarizations of the incident light beam for birefringence measurement. The results are shown in Fig. 7. The p and s polarizations indicate the parallel or perpendicular electrical fields of the incident light beams to the scattering plane. The appearance of elastic anisotropy is observed here is the increasing difference between the two refractive indices, which results in the birefringence.
Elastic properties of the epoxy adhesive layer

The stress effect of the epoxy adhesive layers was next investigated using single lap joint samples. The epoxy prepolymer used was DGEBA (diglycidyl ether of bisphenol A, Epon 828) supplied by Shell petroleum. The curing agent used was isophorone diamine (IPDA), supplied by Wako Chemicals. The mixing ratio of the curing agent was 60%, where 100% indicates a 1:1 ratio of curing agent to the prepolymer. After mixing, the sample was degassed for 5 minutes and was set between two glass plates with a spacer of 0.1 mm thick. The size of adherend was 25x10 mm. The mixtures were then cured at room temperature for one day. After curing, the glass transition temperature (Tg) of the cured layer was measured by Differential Scanning Calorimetry (Shimadzu Co.). The hypersonic wave velocities of the stress direction were continuously observed under the tensile test using 90° A scattering geometry.

Figure 8 shows the longitudinal wave velocities of the stress direction at room temperature. Because Tg of the adhesive layers is higher than the temperature, the adhesive layer is in the glassy state. Longitudinal wave velocities decreased monotonously with the increase of strain until the fracture around the strain of 7%. From the ultrasonic wave measurements in the MHz range, Matsushige has reported a similar decrease of longitudinal wave velocities in the bulk PMMA sample and pointed out the effect of softening phenomenon due to the micro cracks [7]. Actually, we could find several crazing due to necking from the initial state, which implies the generation of micro voids and cracks in the layer. On the other hand, the velocities of the layers in the glass transition region increased with the strain until the fracture. Figure 9 shows the longitudinal wave velocities in the direction of stress at temperatures higher than Tg. Considering the small strain in the sample, we cannot expect the hardening effect due to the crystallization like highly stretched rubbers. The increase of longitudinal wave velocity, however, possibly indicates that the linear main chains of epoxy layer were stretched and aligned to the stress direction, which causes the elastic anisotropy.

Conclusion

Brillouin scattering techniques have been applied to investigate the anisotropy of polymer thin films and layers. Making use of several scattering geometries, non-destructive, non-contact, continuous and simultaneous measurements of elastic and optical anisotropy were performed.

References