Determination of elastic constants of liquid crystal polymer with orthorhombic structure
斜方晶構造を有する液晶ポリマーの弾性率計測

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1. Introduction

Plastics exhibit lightweight, good workability, low stiffness, and low tolerance to heating comparing to metals and ceramics. However, plastics with higher stiffness and resistance to heating are generated in recent years, which are expected to be replaced with metals.

Liquid crystal polymer (LCP) is one of them. The elastic stiffness of LCP is higher than that of other reinforced plastics, and the stiffness per unit mass of LCP is as high as that of aluminum. The distortion temperature under load (DTUL) of LCP exceeds 170 ^{o}C, which is significantly higher than those of conventional crystalline plastics (50–100 ^{o}C). Hence, LCP has been an important material in industry.

LCP shows a liquid crystal structure with some combinations of monomers. In this study, we made LCPs from 6-hydroxy 2-naphthoic acid and p-hydroxyl benzoic acid. We form them by the injection-molding method, leading to high orientation along the injection direction and then high anisotropy. **Figure 1** shows a schematic view of an LCP with the injection-molding method.

The inner structure of LCP is thus aligned along the injection direction. This texture could be different between the outside and the inside. LCP exhibits anisotropy in mechanical characters such as elastic constants and difference of them between the outside and the inside. The injection velocity affects the internal structure and then the mechanical characters. Measuring this relationship is important for material developments and applications. Macroscopically, we regard LCP as the orthorhombic crystal with 9 independent elastic constants; C_{11}, C_{22}, C_{33}, C_{12}, C_{13}, C_{23}, C_{44}, C_{55}, and
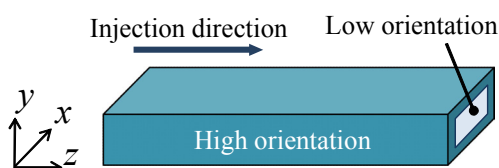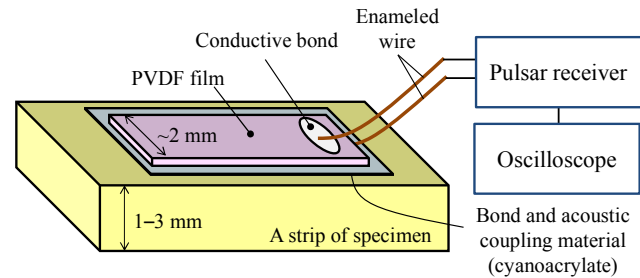

Fig. 1 A schematic view of an LCP.

Fig. 2 The measurement setup of the ultrasonic pulse-echo method using PVDF film sensor.

C_{66}. In this study, we measure C_{11}, C_{22}, and C_{33} of non-strengthened LCP (n-LCP) with different injection velocities and strengthened LCP (s-LCP) and quantitatively investigate the anisotropic change and the relationship between elastic constants and the injection velocity. We strengthened the materials with 30wt% glass fibers, which are denoted as s-LCP.

2. Experiment Procedure

We measure C_{11}, C_{22}, and C_{33} by the ultrasound pulse-echo method using 28-μm poly-vinylidene difluoride (PVDF) films with 0.1-μm NiCu electrode thin films. **Figure 2** illustrates the measurement setup. We cut PVDF films into a rectangular shape of about 2×4 mm^2 and attached enamel wires on both sides of the film using a small amount of conductive bond, and attached this sensor on the specimen surface. We used cyanoacrylate as an acoustic coupling material. We measured the elastic constant of specimen several times by different sensors because the sensors are not reusable. We applied 200-V rectangle pulse voltage with 20-MHz center frequency.

3. Result and Discussion

First, we determine elastic constants C_{11}, C_{22} and C_{33} of n-LCP and s-LCP. **Figure 3** shows determined elastic constants, where shaded and filled bars show n-LCP and s-LCP, respectively. C_{33} is higher than C_{11} and C_{22} for n-LCP by 20–30% and that for s-LCP by 40–50%. Comparing s-LCP with n-LCP, each elastic constant increases by 15%,

28%, and 37%. Therefore, we found that LCP has high elastic anisotropy about the z-axis (the injection direction) and that strengthening enhances not only the stiffness but also the anisotropy. This stems from inner structure: LCP has an orientation along the injection direction, and glass fibers strengthen LCP along the same direction.

Second, we show the injection-velocity dependence of C_{22} and C_{33} of n-LCP in **Fig. 4**; we found that both C_{33} and C_{22} are higher for 5 mm/s than for 25–300 mm/s by 2–5%. Elastic constants are nearly constant between 25–300 mm/s. It is expected that increase of the velocity enhances the orientation, leading to increase of C_{33} and decrease of C_{22}. Another expectation is that increase of the velocity weakens internal bonds, leading to both C_{33} and C_{22} decrease. Therefore, injecting velocity highly affects the internal bonds rather than the orientation between 5–25 mm/s.

Finally, we discuss regional elastic constants in an n-LCP. C_{11} and C_{22} are clearly different between the outside and the inside as shown in **Fig. 5**. Both of the inside elastic constants are higher than outside ones by 6–10%. This stems from higher orientation of the outside due to larger shear stress and highly cooling velocity during the molding. A large velocity gradient makes high shear stress on the outside, which extends molecular chains. The extended molecules solidify without
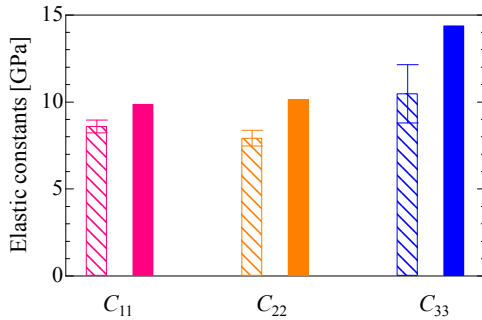
Fig. 5 Regional elastic constants C_{11} and C_{22} of n-LCP, where filled and shaded bars show the outside and the inside, respectively.

structural relaxation due to high cooling velocity. Therefore, the outside has a highly oriented structure. As the orientation along the z-axis increases, C_{33} increases while C_{11} and C_{22} decrease. Our result shows this difference of internal structure between the outside and the inside quantitatively.

4. Conclusion

First, we quantitatively revealed the effect of strengthening that enhances both elastic constants and anisotropy by 15–37% and by ~20%, respectively. Second, we investigated the effect of injecting velocity, and injecting velocity increase makes internal bonds weak between 5 and 25 mm/s. Finally, we measured the regional C_{11} and C_{22}, and both of them are higher those on the inside than those on the outside by 6–10%. This result shows the outside has a highly oriented structure.

Fig. 3 Elastic constants C_{11}, C_{22} and C_{33}. Shaded and filled bars show n-LCP and s-LCP, respectively.
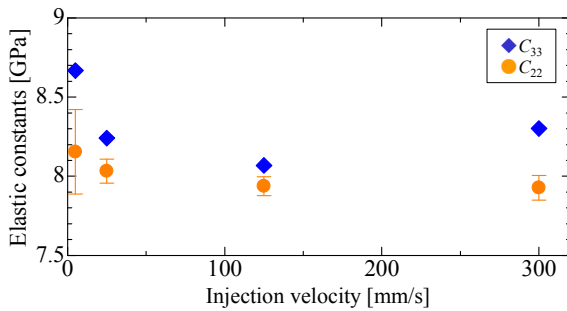
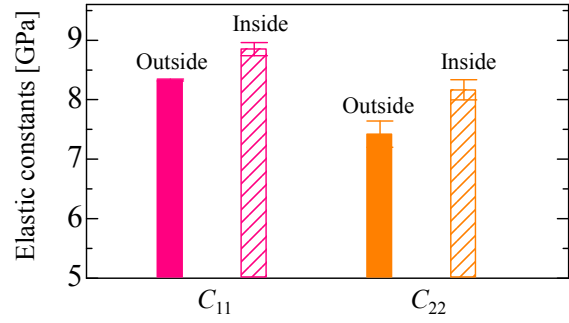Fig. 4 Velocity dependence of C_{22} and C_{33} of n-LCP measured by PVDF film sensor.