Optical Rotatory Power of Biodegradable Polylactic Acid Films

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Summary: Polylactic acid (PLA) is a polymer material on which biodegradability research has been the most advanced. PLA is a chiral polymer in which molecules containing asymmetric carbon atoms have a helical structure. Two optical isomers of PLA exist, PLLA (poly(L-lactic acid)) and PDLA (poly(D-lactic acid)). In this study, using various physical processes, we fabricated various samples such as oriented PLLA film, PLLA fiber, rolled PLLA film and forged PLLA plate. We observed a large optical rotatory power ρ in the cylindrical plate fabricated using a forging process. ρ of forged PLLA plates is 7200°/mm which is approximately 300 times larger than that of α-quartz.

Keywords: biodegradable polymer; chiral polymer; forging process; optical rotatory power; polylactic acid

Introduction

The amount of industrial waste is increasing every year and, as a result, environmental pollution has become more serious than ever. Biodegradable polymers have attracted much attention as they are materials that are expected to alleviate environmental pollution.[1,2] Polylactic acid (PLA) is a polymer material on which biodegradability research has been the most advanced. PLA has been used practically for medical products.[2] For this reason, the research on its mechanical properties and structure, such as its higher-order and crystal structures, has advanced.[3-6] On the other hand, PLA is a chiral polymer in which macromolecules containing asymmetric carbon atoms have a helical structure. Two optical isomers exist in PLA: poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA). For a long time, chiral polymers have been expected to exhibit optical rotary power, ρ, in their solid state, compared with inorganic low-molecular-weight crystals. A typical substance with large

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ρ is α-quartz (α-SiO_2). The definition of ρ is as follows. The vibration plane of the electric field $\boldsymbol{E}$ of linearly polarized light (LP) revolves clockwise or counterclockwise when LP passes through the substance. This is the mechanism of optical activity. In this case, ρ is defined as the ratio of the rotation angle of the vibration plane of $\boldsymbol{E}$ of LP to unit length. ρ of α-quartz is due to the helical structure formed by molecules. Therefore, it is believed that ρ of a chiral polymer is large. Actually, although Kobayashi et al.[7] revealed huge intrinsic ρ of the PLLA crystal, a PLLA film with large ρ in the fiber axis direction has not been prepared for practical use until now. No PLA film with large ρ has been prepared to date, because it was very difficult to control its higher-order structure.

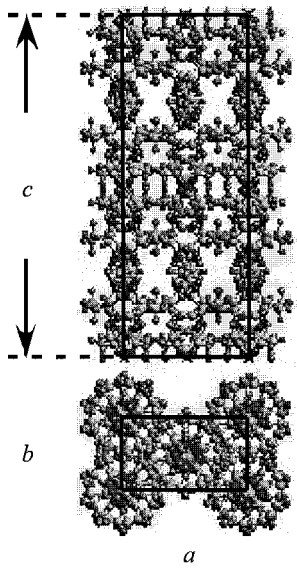

Figure 1. PLLA crystal structure projected onto $(\bar{1}10)$ and (001).

Figure 1 shows the PLLA crystal structure [1-7], based on a base-centered orthorhombic unit cell. It contains two 10/3 helical chains arranged along the c-axis; the point group is D_2. a, b and c are the lengths of the unit cell. Here we emphasize that PLLA is a chiral polymer and, in the crystal, the polymer molecules form the helical structure. The crystal structure of PLLA is characterized by this helical structure, which gives rise to ρ.

Mathematical representation

In order to analyze the optical activity, we derive the mathematical representation.[8,9] The dielectric displacement $\boldsymbol{D}$ in crystals is induced by $\boldsymbol{E}$ of the LP with wavenumber vector $\boldsymbol{k}$ (k_1, k_2, k_3). It is represented as

$$[\boldsymbol{D}]_m = \sum_{l=1}^{3} \varepsilon_{ml} E_l + j[\boldsymbol{G} \times \boldsymbol{E}]_m \quad (m = 1-3) \tag{1}$$

with

$$[\boldsymbol{G}]_m = g_{m1} k_1 + g_{m2} k_2 + g_{m3} k_3 \,. \tag{2}$$

Here, $\boldsymbol{G}$ is the gyration vector. ε_{ml} is the permittivity tensor and g_{ml} is the gyration tensor. As shown by the first term of Eq. (1), $\boldsymbol{E}$ causes $\boldsymbol{D}$ to occur in one direction. On the contrary, according to the second term, under the existence of $\boldsymbol{G}$, $\boldsymbol{D}$ with a phase lag of 1/4 period relative to $\boldsymbol{E}$ exists. Then the direction of $\boldsymbol{D}$ becomes perpendicular to the direction of $\boldsymbol{E}$. This is the reason why the rotation of LP occurs in crystals. In this study, we evaluate g_{ml} of PLLA films.

$$\rho = \frac{\pi G}{\lambda n_0} \tag{3}$$

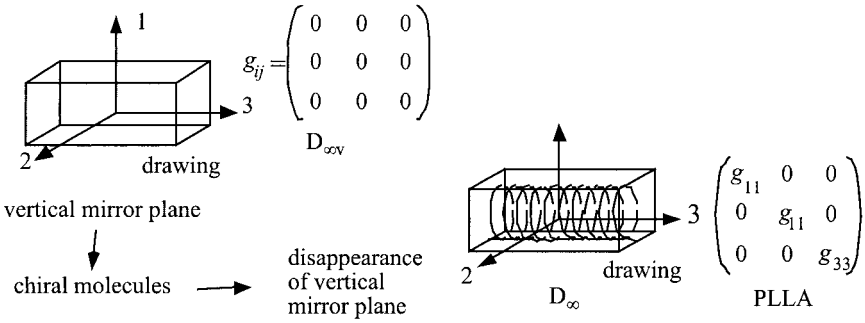

Figure 2. Macrosymmetry change due to physical processing, such as stretching, of polymer samples.

with

$$G = \boldsymbol{G} \cdot \boldsymbol{k} \,. \tag{4}$$

Equation (3) shows a simple relationship between ρ and G, which was used for evaluation of ρ in this report. This discussion concerns single crystals; next we consider the optical acitivity of a PLLA film.

Optical rotatory power of polymer film

Polymer films of 100% crystallinity cannot be obtained by conventional methods. Amorphous components are always present in complex higher-order structures. Furthermore, no one-to-one correspondence is found between the macrooptical properties and crystal characteristics. For crystalline polymer film, we must consider macroscopic symmetry based on the point group theory, as shown in Fig. 2.[9,10] ρ of an isotropic film
does not exist, even though g_{ml} is present in the crystal state. Also, the point group of a drawn polymer film is $D_{\infty v}$. Although optical activity does not arise, a PLLA molecule has chirality. The mirror plane disappears and the point group becomes D_{∞}. In the case of PLLA, the crystal symmetry differs from the macroscopic symmetry. ρ of the oriented PLLA film used here is based on g_{11} and g_{33}.

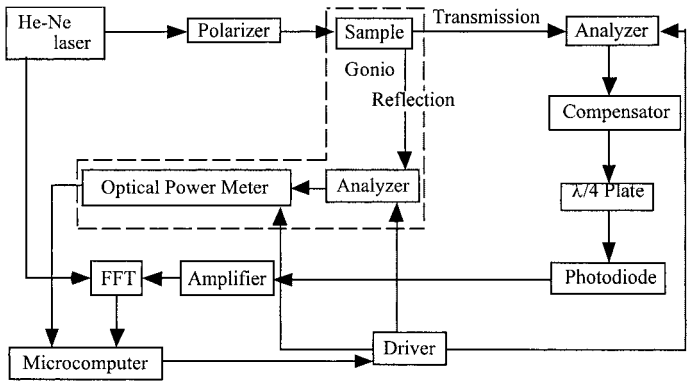

Figure 3. Schematic diagram of the experimental setup for measuring the optical activity.

Measurement System

We developed a new experimental system for measuring the optical activity of polymer film, as shown in Fig. 3.[11] LP is incident on the film and then becomes elliptically polarized due to the dichroism of the polymer film. The elliptic axis rotates around the optical axis (fiber axis) due to ρ. The vector operation of the Stokes parameters with the optical arrangement can be represented as [11-13]

$$S' = P_{\phi} \cdot R_{\delta,x} \cdot T_{\theta} \cdot P_0 \cdot S \quad . \tag{5}$$

Here, S is the Stokes parameter of LP from the He-Ne laser. The terms $P_{\delta,\chi}$ and T_{θ} are

Mueller matrixes of a linear phase shifter and the azimuth rotator equivalent to that of a polymer film, respectively. The rotation angle θ of the elliptic axis is caused by ρ. The apparent retardation δ of the linear birefringence is due to the dichroism of the polymer film. In practice, we obtain θ and δ using the least-squares method. From these θ and δ, we calculate the gyration tensor g_{ij}.

Sample preparation

We prepared PLLA with a molecular weight of 100,000 ~ 600,000 and D-isomer content of 0.001 ~ 1.000 %. Then, using physical processes, we fabricated various samples such as stretched film, fiber, rolled film and a forged cylindrical plate.[10] To enable measurement, we cut each sample perpendicular to its length using a microtome and polished it. The forging process for metals, in which metal is struck into a die with a hammer, is well known. It is difficult to apply a forging process to polymers, because polymers have poor ductility characteristics. As a result of many considerations of issues such as how to apply pressure, the temperature and the die shape, we were able to fabricate a PLLA forged sample.[14]

Optical rotatory power of PLLA and PDLA samples

Using our measurement system, we obtained ρ of PLLA and PDLA samples. We summarize typical experimental results in Table 1.

Rolled PLLA film (hot rolling) and stretched PLLA film

A heated PLLA sheet was repeatedly passed through a pair of counter-rotating rollers and rolled to a fixed size and shape. The PLLA films obtained here were rolled to thicknesses of 100 μm to 1 mm.

Table 1. Optical rotatory power of various materials (wavenumber: 632.8 nm).

Material	Optical rotatory power (∞/mm)
Stretched PLLA sample	9.5
Rolled PLLA sample	4.5
Fiber PLLA sample	20.2
Forged PLLA sample	7200
Forged PDLA sample	-7110
α-Quartz (α-SiO_2)[7]	25
$AgGaS_2$[7]	720
α–HgS[7]	-300

The value of ρ was less than 10°/mm. ρ of the rolled PLLA film increases with increasing temperature of the heating gate and rollers. We performed uni- and biaxial stretching of PLLA films, but the value of ρ was less than 10°/mm even though the conditions during drawing, such as drawing ratio from 4 to 7 and drawing temperature from 70 to 120 °C, were controlled. The value of ρ of less than 10°/mm was almost the same as that of rolled PLLA film.

PLLA fiber

We tried, while spinning PLLA into fibers, to control the conditions of spinning. The value of ρ reached over 20°/mm. These are highly significant results. We also found that ρ increased with increasing drawing ratio. The maximum ρ value of rolled and stretched film was less than 20°/mm, while that of fiber reached 20°/mm. Here, we emphasize that ρ of 20°/mm is almost the same as that for α-quartz which is known to exhibit high ρ. There is a high probability that ρ of a fiber sample fabricated under optimum conditions will increase.

Giant optical rotatory power of forged PLLA and PDLA samples

ρ of the forged PLLA sample was 300 times that of α-quartz. This is an outstanding value.

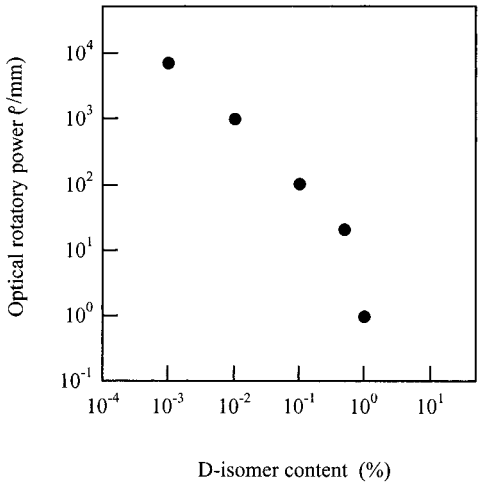

Figure 4. The D-isomer content dependence of optical rotatory power of forged PLLA sample.

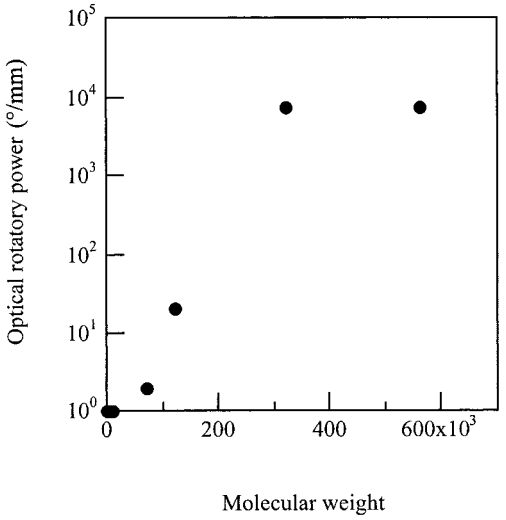

Figure 5. The molecular weight dependence of optical rotatory power of forged PLLA sample.

On the other hand, PDLA films possess dextrorotatory power. This is consistent with the right-handed rotation of helical chain molecules of PDLA. Other important findings are as follows. The factors affecting the value of ρ are the D-isomer content and molecular weight. Figures 4 and 5 show the plots of ρ against D-isomer content and molecular weight. ρ of PLLA increases with increasing molecular weight and decreasing D-isomer content. The higher-order structure of PLLA films is greatly influenced by the D-isomer content and molecular weight. Thus, the unprecedented giant ρ of the PLLA sample is due to its higher-order structure.

Conclusion

We fabricated various PLLA film and fiber samples and developed a new experimental system for measuring the optical activity of polymer films. Using the new system, we measured ρ of PLLA samples. As a result, in the film fabricated using the new physical process, we observed giant ρ. The findings from this study are summarized as follows.

(1) PLLA and PDLA films possess levorotatory power and dextrorotatory power, respectively. ρ of PLLA increases with increasing molecular weight and decreasing D-isomer content. The

higher-order structure of PLLA films is greatly influenced by the D-isomer content and molecular weight. Thus, the unprecedented giant ρ of the PLLA sample is due to its higher-order structure.

(2) The maximum ρ value of a rolled and stretched of PLLA film is less than 20°/mm, while that of a PLLA fiber reaches 20°/mm which is almost the same as that for α-quartz. We believe that there is a strong probability that ρ of a PLLA fiber sample fabricated under optimum conditions will increase.

(3) ρ of forged PLLA film is 7200°/mm which is approximately 300 times larger than that of α-quartz. This is an outstanding value.

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