12D05

Changes of fine structure of aliphatic polyester fiber by stretching

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Abstract

Hot stretching focused on the improvement of properties of poly(L-lactic acid) fiber. Some aliphatic polyesters are biodegradable under microbial attack and the new unique applications are expected. Generally, these materials have a somewhat low melting temperature and low mechanical properties compared with the aromatic polyesters. In this study, melt-spinning of poly(L-lactic acid) was conducted.

We investigated effects of the stretching and the molecular orientation of aliphatic polyester fibers on the change of fine-structure. Glass transition temperature, molecular orientation and crystallinity increased according to the increase of stretching ratio.

Introduction

An aliphatic polyester, poly(L-lactic acid)(PLLA) produced by fermentation of glucose or sucrose has been used as resorbable materials in medical practice. PLLA has been currently recognized as a suitable material for packaging and consumer goods, due to its several preferable properties, such as mechanical strength, transparency, safety, and degradability in compost. Especially, the biodegradable feature has received much attention from the environmental viewpoint. In the point of view of clothing and textile industry, aliphatic polyester fibers don't occur environmental problems, such poisonous gases after destruction by fire, air-pollution and acid rain as synthetic polyester fibers.

Even as superior properties, melting temperature and mechanical properties of PLLA is lower than aromatic polyesters, such as polyethylene terephthalate and polybutylene terephthalate. In this study, we focused on the improvement of properties of aliphatic polyester fiber by the molecular orientation. At first, melt-spinning of PLLA was conducted and effects of the stretching and the molecular orientation of PLLA fiber on the change of fine-structure were investigated.

Experimental

Materials

Aliphatic polyester, poly(L-lactic acid)(PLLA) offered from Shimazu(Japan) Co. was used. Glass transition and melting temperature of PLLA pellets were 57° and 175 °C, respectively.

Fiber preparation

Melt-spinning of PLLA was done by an single screw extruder and spinneret. Temperature of spinneret was 210 °C and the extruded fibers were cooled with 15°C cooling water and winded.

Stretching

Hot stretching of the unoriented fibers were conducted by a streching machine(Japan, Orientec TOYO). Stretching temperature, speed and torc were 75°C, 50mm/min and 8 ±0.1kgf, respectively.

We used λ as stretching ratio, and was calculated from fibers length before, L_1 and after stretching, L_2, by the following equation.

$$\lambda = L_2 / L_1$$

Analysis of Structure and physical properties

Differential scanning calorimetry(Japan, Rigaku, DSC 8230) was used in measuring thermal property of the stretched PLLA fiber. Wide angle X-ray Scattering(WAXS) test was conducted on processed PLLA fibers to investigate molecular orientation of crystalline regions. Density measurements were done with a density column made of aquous NaBr and IPA as a wetting agent at 25°C.

Dynamic viscoelastic measurement(Rheovibron DDV-II-EA) and Tensilon(Japan, Orientec) were used for measurement of mechanical properties.

Result and Discussion

Stretching behavior of PLLA fiber

From WAXS photographs, the extruded PLLA fibers turned out to be non-oriented. Before stretching, stress-strain curves of PLLA fiber were given from tensile testing in 50-80°C. The yield was seen to the temperature, 70°C. As seen in Fig. 1, yield stress and yield strain changed with increase of stretching temperature. We decided on a stretching temperature of 75°C from results of tensile test. The limit of stretching ratio at 75°C was $\lambda \sim 4.5$.

Orientation and crystallinity of molecular chain

The orientation of crystalline region turned out more and more higher along stretching ratio from X-ray diffractometer photographs of PLLA(Fig. 2). Also in density test, density and orientation degree of PLLA fiber increased along stretching ratio(Fig. 3).

But distinguishable difference of melting temperature was not seen in DSC thermographs(Fig. 4).

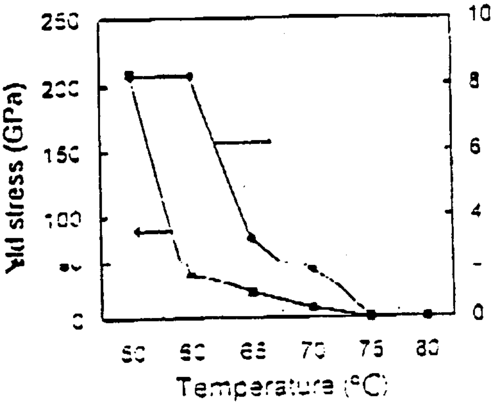

Fig. 1. Yield stress and yield strain of non-stretched PLLA fiber

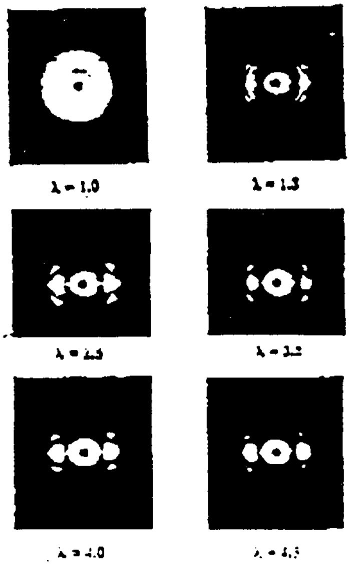

Fig. 2. WAXS photographs of stretched PLLA fibers

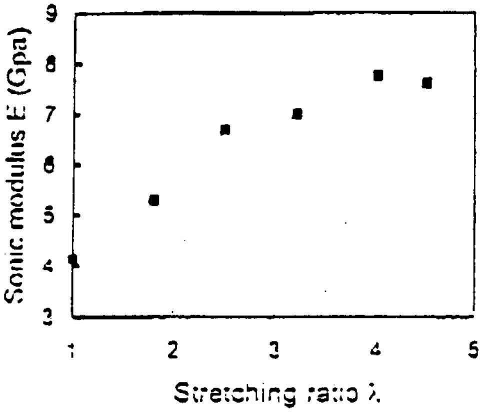

Fig 3. Relationship between sonic modulus and stretching ratio

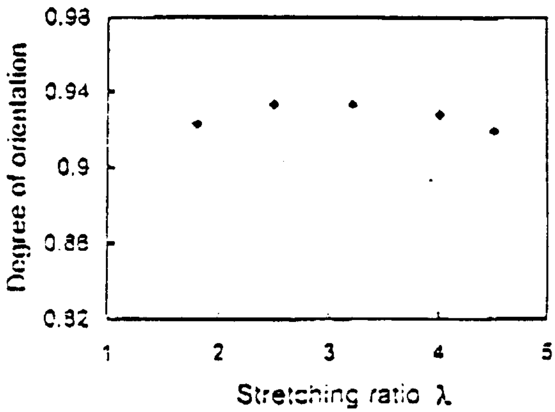

Fig. 4. Degree of orientation of stretched PLLA fibers

Mechanical properties

Stress-strain curve of the stretched PLLA was shown in Fig. 6 and 7. Yield phenomenon seen at lower stretched ratio disappeared above λ=3.2. Tensile strength(both break and yield) shown distinguishable increase along stretching ratio. It was considered that randomly oriented crystals transformed into crystals oriented along the stretching direction.

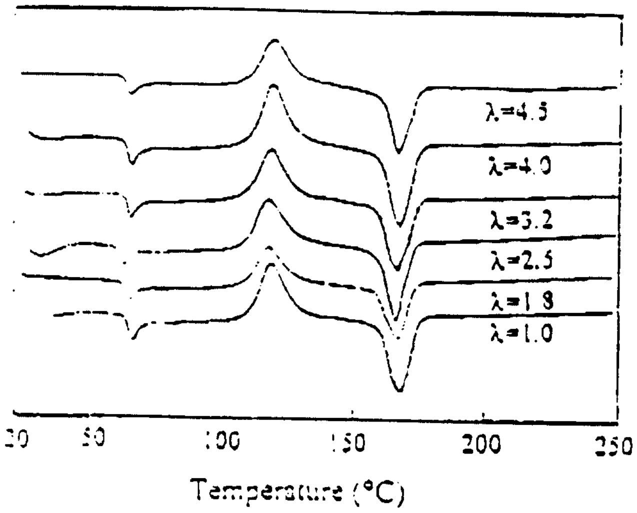

Fig. 5. DSC thermographs of stretched PLLA fibers

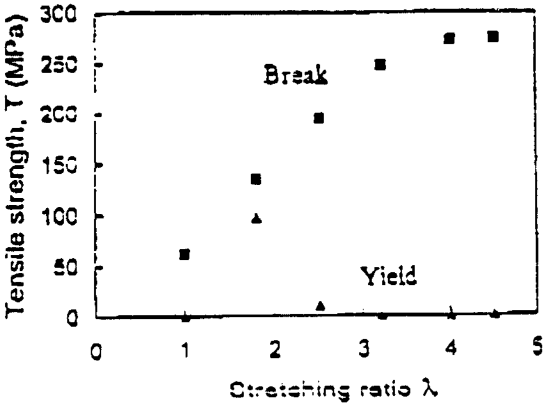

Fig. 6. Relationship between tensile strength and stretching ratio

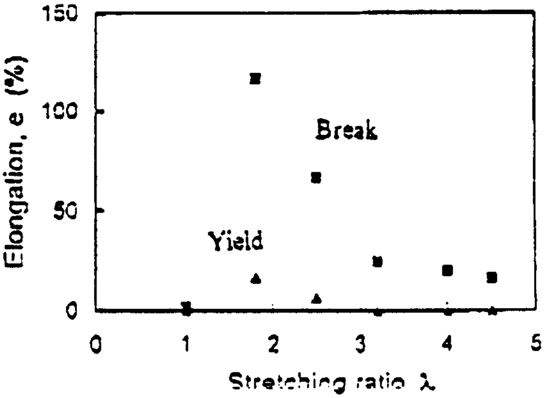

Fig. 7. Relationship between elongation break and stretching ratio

Dynamic viscoelastic measurement

Time dependence of dynamic viscoelastic measurement by Rheovibron on stretched fiber was investigated. α-disperse peak temperature based on glass transition increased with stretching ratio, and tension of amorphous region of molecular chain by stretching was founded. In dynamic storage modulus, distinguishable difference was shown in Fig. 8.

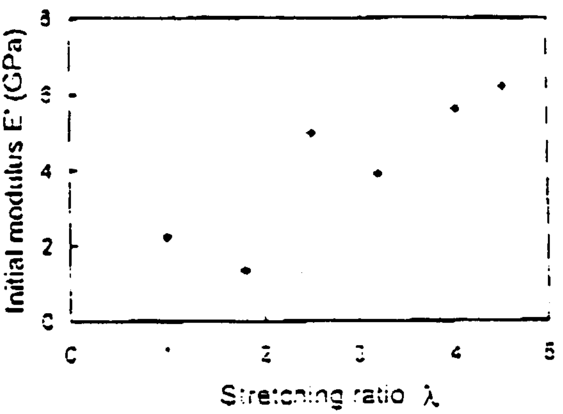

Fig. 8. Relationship between modulus of elasticity and stretching ratio

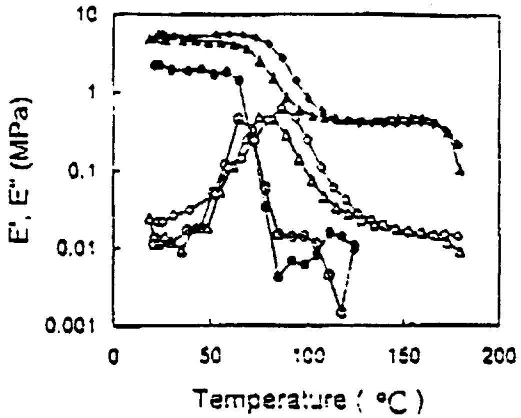

Fig. 9. Dynamic viscoelastic properties of stretched PLLA fibers at 110Hz
: ---○--- , λ=1.0 ; ---Δ--- , λ=2.5 ; ---◇--- , λ=4.0
; E', closed state ; E'', open state

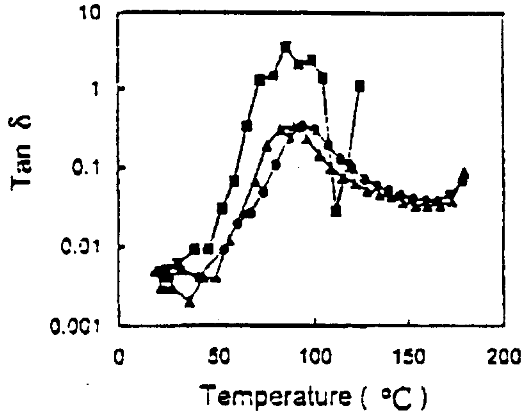

Fig. 10. Tan δ of stretched PLLA fibers
: ---□--- , λ=1.0 ; ---Δ--- , λ=2.5 ; ---◆--- , λ=4.0

Conclusion

Effects of the stretching and the molecular orientation of aliphatic polyester fibers on the change of fine-structure are as follow ;

(1) Stretching temperature, 75°C was effective to change fine-structure of PLLA fibers.

(2) With increase of stretching ratio, crystalline degree almost decreased more and more.

(3) From X-ray photographs, higher orientation of crystalline region was shown with stretching ratio.

(4) Stretched fibers shown improvement of tensile strength compared with unstretched fiber.

(5) It was considered that stretched fibers had considerable storage modulus until melting temperature from dynamic viscoelastic measurement of temperature change.