Effects of Spinning Speed and Heat Treatment on the Mechanical Properties and Biodegradability of Poly(lactic acid) Fibers

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ABSTRACT: We undertook this study to suggest the optimal spinning process conditions that provide a proper range of tenacity and biodegradability in textile fibers. The effect of melt-spinning speed and heat treatment on the mechanical properties and biodegradability of poly(lactic acid) (PLA) fibers were investigated. PLA was spun at a high spinning speed of 2000–4000 m/min, and each specimen was heat-treated. Mechanical properties were estimated by measurement of the breaking stress, and the degree of crystallinity was evaluated with wide-angle X-ray scattering. Biodegradability was estimated from the decreases in breaking stress, weight loss, and degree of crystallinity after soil burial. The results of the experiment reveal that heat treatment of the PLA fibers increased the breaking stress and crystallinity. With increasing spinning speed, breaking stress and crystallinity also increased. An increase in spinning speed was more effective than an increase in heat treatment for enhancing the breaking stress within the range of this study. From the soil burial test, it was revealed that an increase in spinning speed and heat treatment decreased the biodegradability of the fibers. X-ray analysis of the soil-buried fibers showed that fibers with higher crystallinities began to degrade more slowly. J Appl Polym Sci 103: 3099–3104, 2007

Key words: biodegradable; crystal structures; fibers; strength; WAXS

INTRODUCTION

Traditionally, polymeric materials have been developed on the basis of performance, cost effectiveness, and shelf-life. However, resistance to microbial attack is a shortcoming from the viewpoint of environmental protection and solid waste management. Degradable polymers have increasingly become attractive substitutions due to their breakdown in common substances such as water and CO_2 by incineration or landfill disposal.

Polylactides have been studied extensively because of their biodegradability, biocompatiblity, compostability, and nontoxicity. In past decades, the degradation of poly(lactic acid) (PLA) materials has been studied for medical applications, such as drug-delivery systems, sutures, and surgical implants. Currently, several end products are available on the market in the form of sutures, osteosynthetic devices, and drug-delivery systems. Recent advances in the fermentation of dextrose obtained from corn have led to a cost reduction in the manufacture of the lactic acid necessary to make PLA polymers. PLA is usually produced with conventional chemical synthesis. The synthesis is possible through two methods: the polycondensation of lactic acid and the ring-opening polymerization of lactide.[1–3]

The biodegradability of textiles is expected to be influenced by such factors as crystallinity, degree of orientation, degree of polymerization, functional groups, and hydrophilicity of the textile materials. In most studies, polymers with lower molecular weights, lower crystallinities of orientation, and higher hydrophilicities have greater biodegradabilities.[4] The biodegradability of synthesis fibers is thus expected to be influenced by spinning conditions and processing. Previous studies on the properties of polymers have shown greater crystallinity in polymers with higher take-up speeds, higher temperatures, and higher drawing ratios.[5–10]

The degradation of PLA has historically been investigated through chemical hydrolysis. Since Williams found that the hydrolysis behavior of poly(L-lactic acid) is accelerated most in the presence of Proteinase K, among enzymes such as Proteinase K, Bromelain, and Pronase, the hydrolysis of poly(L-lactic acid) has

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TABLE I
Characteristics of the Specimens

Sample	Spinning speed (m/min)	Heat treatment	Yarn number (Denier)
S2000	2000	X	111.5
H2000	2000	O	
S2500	2500	X	111.1
H2500	2500	O	
S3000	3000	X	112.0
H3000	3000	O	
S3500	3500	X	112.1
H3500	3500	O	
S4000	4000	X	111.7
H4000	4000	O	

been studied with Proteinase K. Mostly, the chemical hydrolysis of PLA polymers has been investigated extensively *in vitro*. However, few studies exist on the biodegradation of PLA fibers buried in natural soil conditions, which better reflect true degradation behavior in the environment.[11–18]

This study was done to clarify the effects of spinning speed and heat treatment on the mechanical properties and biodegradability of PLA fibers. In many potential textile technological applications, the fiber-forming process is of general importance. Effective polymer synthesis requires an effective spinning process and the existence of heat treatment. For this purpose, PLA fibers were prepared with different spinning speeds and heat treatments. We monitored the degradation of the PLA fibers by weighing and measuring the change in break stress. The PLA fibers were characterized with regard to the degree of crystallinity by wide-angle X-ray scattering (WAXS).

EXPERIMENTAL

Specimens

The specimens were supplied from Huvis Company (Korea). The number-average molecular weight of the PLA was 80,091, and the weight-average molecular weight of the PLA was 138,411. The characteristics of the specimens are listed in Table I. PLA was spun in a high-speed spinning process with a take-up speed of 2000–4000 m/min. Heat setting was done after a slackwing was placed around the frame, whose width was 49 cm. The frames were put into the oven in 100°C for 30minutes. After that, they were taken out and cooled to room temperature.

S2000 denotes the sample that was spun at a speed of 2000 m/s, and H2000 represents the sample that was spun at a speed of 2000 m/s and then heat-treated.

Methods

Molecular weight measurement

Gel permeation chromatographic analysis was conducted with a M930 solvent delivery system and a RI750F refractive-index detector from Younglin Instrument Co., Ltd. (Korea), with tetrahydrofuran. Styragel HR 5E and styragel HR 6 from Waters were used as gel permeation chromatographic columns. The flow rate was maintained at 1.0 mL/min at 35°C. Polystyrenes were used as standards.

Breaking stress measurement

The breaking stress was measured with an Instron (USA) universal testing instrument (table model 1130, crosshead speed = 10 cm/min; a 500-g load cell was used).

Evaluation of biodegradability

According to AATCC soil burial method 30-1993, natural soil was used to fill a box to a depth of 11 cm. Samples were buried in the soil at depth of 3 cm and allowed to degrade for 25 days.[19] During the degradation period, water was supplied at regular intervals. After degradation, samples were rinsed with distilled water and conditioned at 20 ± 2°C and at a relative humidity of 65 ± 2% over 48 h. Biodegradability was evaluated from the decreasing rate of breaking stress and weight loss. The weight loss ratio was calculated with the weight of specimen before and after biodegradation.

Analysis of internal structure

The changes in crystallinity and internal structure in the specimen were investigated with an X-ray diffractometer (M18XHF-SPA, Mac Science Co., Japan).[20]

RESULTS AND DISCUSSION

Mechanical properties

Effect of spinning speed

Breaking stress is generally known be dependent on the spinning speed. The breaking stress of PLA fibers

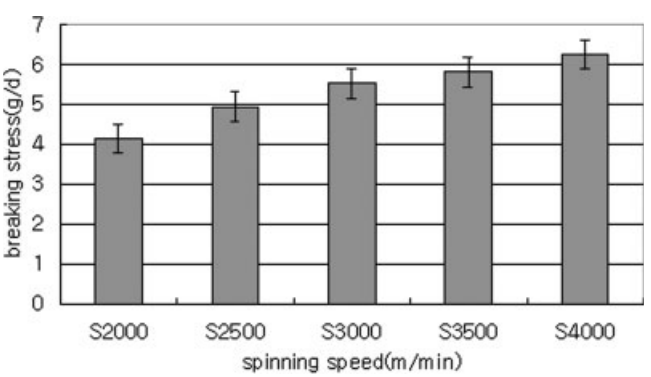

Figure 1 Effect of spinning speed on the breaking stress (untreated).

TABLE II
Crystallinity of the Specimens

	S2000	S2500	S3000	S3500	S4000	H2000	H4000
Crystallinity	*	*	*	8.09	25.36	66.81	69.19

* Cannot be measured from XRD.

according to spinning speed is shown in Figure 1. An increase in spinning speed causes higher molecular orientation and, thus, increases the breaking stress.

In the X-ray diffraction analysis, no crystalline reflections were visible for the fibers spun at lower velocities. The crystalline part in the fiber began to show at an increased spinning speed above 3500 m/min (Table II). This revealed that the stress applied during the process of fiber formation determined the amount of the crystalline part.

The increase in the degree of crystallization observed in the range above 3500 m/min was due to the crystallization initiated by orientation resulting from a higher spinning stress, which is common for usual spinning polymers.

Effect of heat treatment

The increase in the breaking stress after heat treatment is shown in Figure 2. After heat treatment, breaking stress increased by 3–8%, and a greater increase was observed at higher spinning speeds. However, the influence of heat treatment on the breaking stress was lower than the influence of increasing the spinning speed within the range of this study.

Table II shows the effect of heat treatment on the crystallinity of specimens. The crystallinity had a marked increase after heat treatment. H2000 showed higher crystallinity than S2000 but lower crystallinity than H4000. From this, we saw that crystalline part was generated by heating of the specimen. For S4000, as compared to H4000 (Fig. 3), the percentage crystalline part increased but also seemed to have a microstructural rearrangement, which could be expected from the higher height and narrower width of the peak.

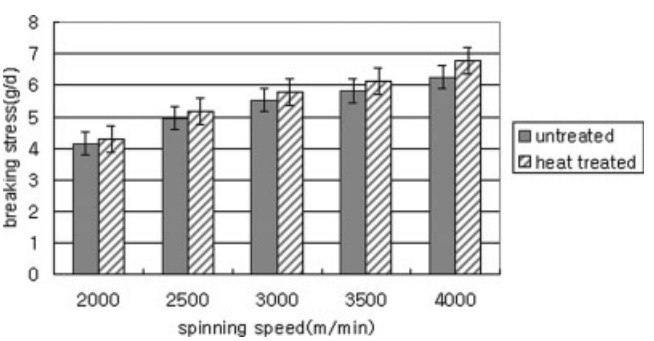

Figure 2 Breaking stress of the heat-treated specimens.

Biodegradability

A soil burial test was performed to investigate the biodegradability of the PLA fibers. The rate of biodegradation was estimated from the decreasing ratios in the breaking stress and weight loss. The degraded PLA fibers were characterized with regard to the degree of crystallinity by WAXS.

Breaking stress

Figure 4 show the decreasing ratio (%) in breaking stress of the degraded samples by the soil burial test. As degradation progressed, breaking stress decreased gradually. Heat-treated samples showed a lower decreasing ratio in breaking stress than untreated samples did. Fibers that had lower crystallinity showed higher biodegradability, as amorphous regions were more prone to be attacked from microorganisms. Heat-treated samples exhibited a lower decreasing ratio of breaking stress compared to the untreated ones because the crystalline region was rearranged in a regular compact pattern.

Weight loss

Figure 5 shows that the weight loss increased as the degradation processed. Heat-treated samples showed a lower weight loss than untreated samples with the same behavior as the decreasing ratio in breaking stress. The weight loss of untreated samples was between 0.6 and 1.2%; that of the heat-treated samples (except H2000) was lower than 0.5%. Interestingly,

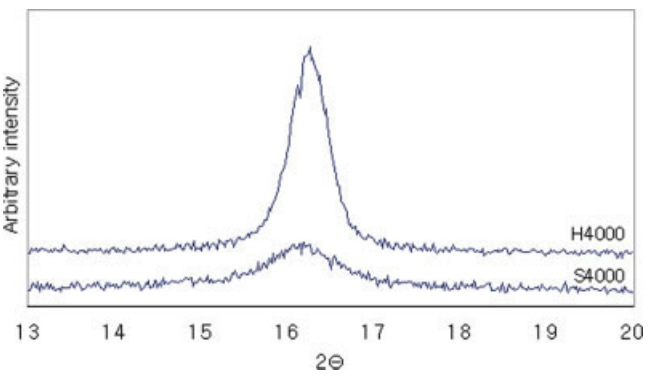

Figure 3 X-ray diffraction patterns. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

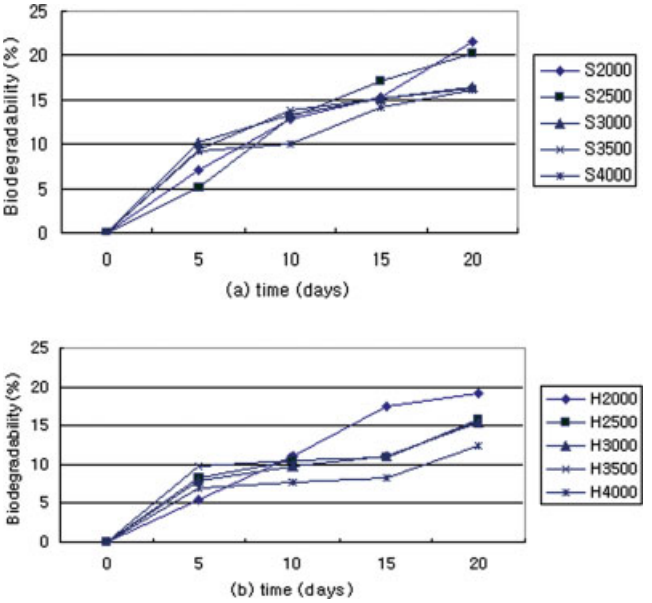

Figure 4 Biodegradability estimated from the decrease of breaking stress. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

this difference was greater in the fibers spun at a high spinning speed.

The gap in the percentage biodegradation values between the heat-treated and untreated samples as expressed by breaking stress loss was smaller than that measured by weight loss. Generally, numerical

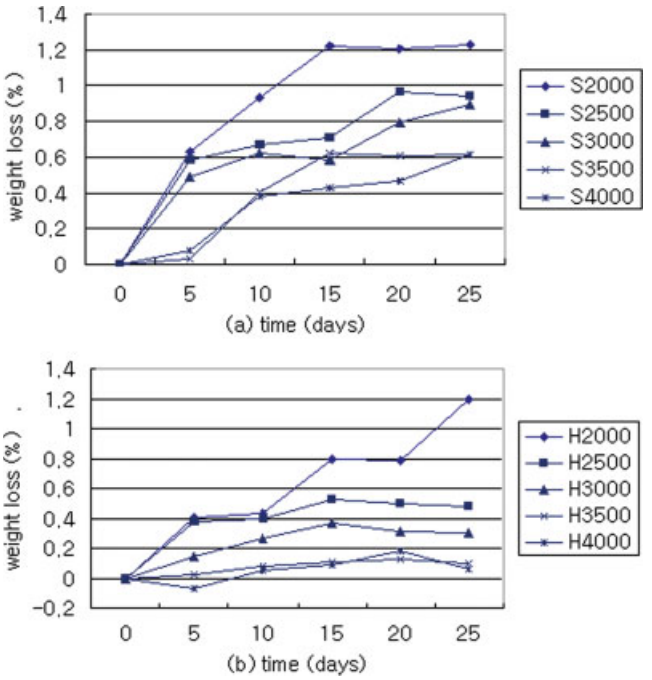

Figure 5 Biodegradability estimated from the weight loss according to soil burial time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

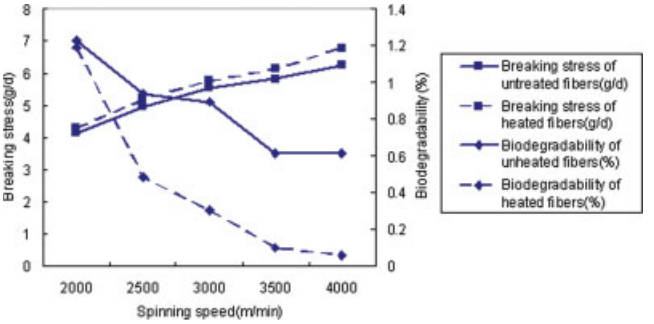

Figure 6 Breaking stress and biodegradability calculated by weight loss. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

values calculated from weight loss measurements are smaller those from breaking stress. This is because weight loss reflects a whole change in the fibers, whereas breaking stress represents the breaking of a weak point. The beginning of polymer degradation takes place in the amorphous region first where the weak point occurs; therefore, breaking stress is easier to detect than weight loss. Therefore, it can be said that breaking stress reflects the degradation in the amorphous region more than weight loss does.

Figure 6 shows the breaking stress and biodegradability of PLA fibers buried in soil for 25 days. As shown in this figure, an increase in the spinning speed was more effective in an enhancement in the breaking stress. Biodegradability, however, was more influenced by heat treatment than by the spinning speed increase in most cases. This tendency was the same when the biodegradability was expressed by the breaking stress loss after soil burial.

Crystallinity

Table III shows the crystallinity of specimens buried in soil, and Figure 7 shows the X-ray diffraction patterns of specimens according to burial time.

Figure 7(A) shows the X-ray diffraction pattern of S2000 and shows the seldom crystalline part. As the degradation proceeded, there was no visible change in crystallinity. Figure 7(B) shows the X-ray diffraction pattern of S4000, where crystallinity increased for the first 15 days and then began to decrease. As biodegra-

TABLE III
Crystallinity of the Specimens Buried in Soil

		Burial time				
Sample	Control	5 days	10 days	15 days	20 days	25 days
S2000	—	—	—	—	—	—
S4000	25.36	41.14	50.61	40.34	28.87	26.42
H2000	66.81	72.60	73.62	74.16	74.71	59.57
H4000	69.19	76.70	79.23	79.47	81.21	83.55

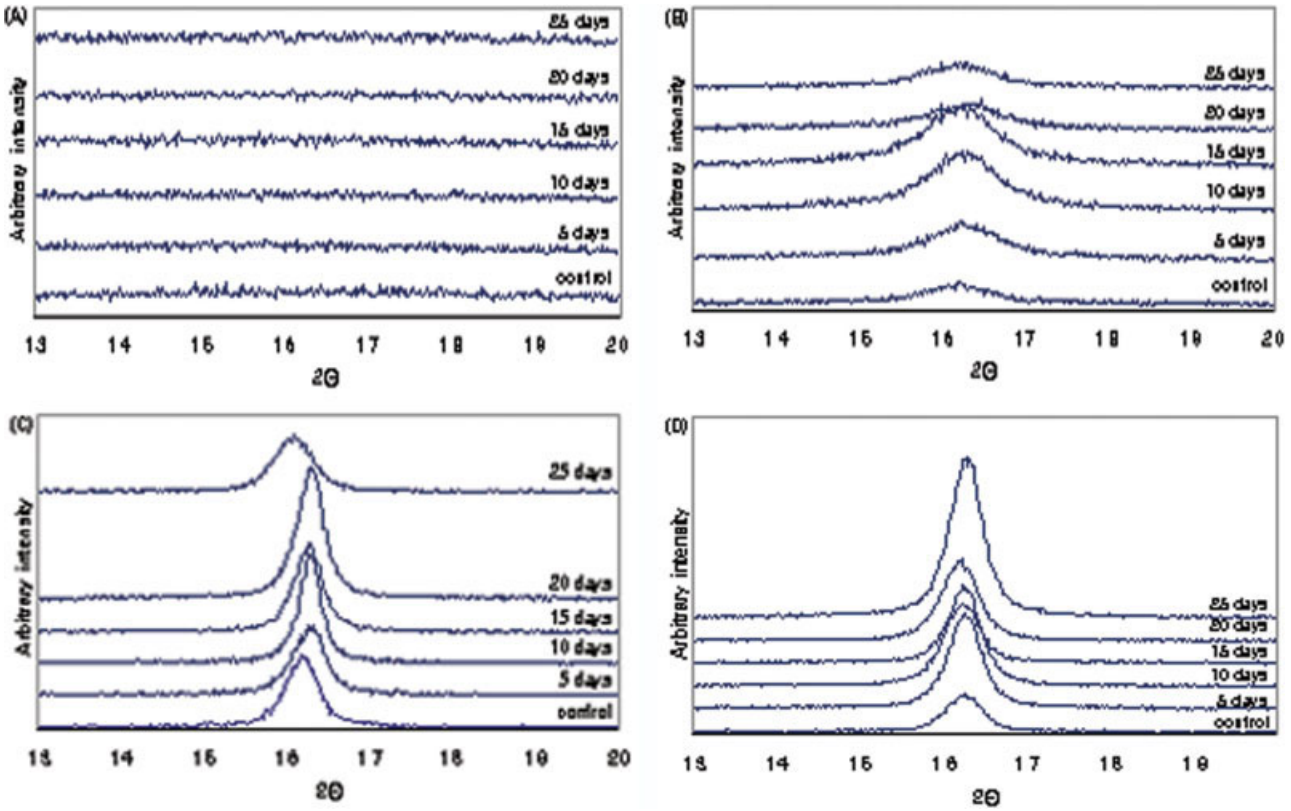

Figure 7 X-ray diffraction pattern of the specimens: (A) S2000, (B) S4000, (C) H2000, and (D) H4000. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

dation proceeds, the amorphous region in the internal structure are the first target for soil microorganisms; this decreases the amorphous region and increases the crystallinity. Microorganisms then attack the crystalline part after the amorphous region has decomposed. That explains why the crystallinity increased relatively at first and then decreased as degradation progressed.[20] Figure 7(C) shows the X-ray diffraction pattern of H2000. The peak was broader at 25 days; we interpreted this to mean the degradation of crystalline part had started. Figure 7(D) shows the X-ray diffraction pattern of H4000; for this sample, crystallinity continuously increased for 25 days. Heat treatment and spinning speed affected internal structure in their own ways and, thus, resulted in different biodegradabilities or crystallinity changes.

CONCLUSIONS

The effects of spinning speed and heat treatment on the mechanical properties and biodegradability of PLA were investigated. The mechanical properties were evaluated by breaking stress, and the degree of crystallinity was evaluated by WAXS. Biodegradability was measured by a soil burial test and evaluated from the decreasing rates of breaking stress, weight loss, and degree of crystallinity:

1. With increasing spinning speed, the breaking stress and crystallinity of the fibers increased. X-ray analysis showed that in the range above 3500 m/min, a crystalline region was generated within the fiber.
2. Heat treatment also increased the breaking stress and crystallinity. In the range between 2000 and 4000 m/min, the sample spun at higher spinning speed revealed a greater crystallinity increase than that generated by heat treatment.
3. In this study, an increase in the spinning speed was more effective than heat treatment for enhancing the breaking stress.
4. As shown by the soil burial test, an increase of spinning speed and heat treatment decreased the biodegradability of the fibers.
5. X-ray analysis of the soil-buried specimens showed that fibers with higher crystallinities began to degrade more slowly.
6. The degradation rate was influenced more by spinning speed than by heat treatment within the range of this study.

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