(Received 6 February, 2001; Accepted 10 March, 2001)

In Vitro Hydrolysis of Blends from Enantiomeric Poly(lactide)s.

2. Well-Stereocomplexed Fiber and Film

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Abstract: Well-stereocomplexed 1:1 fiber and film were prepared from poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) by the melt-spinning and hot-drawing and the solution-casting methods, respectively, and their hydrolysis in phosphate-buffered solution (pH 7.4) at 37°C was investigated. The decrease rates of weight remaining, tensile strength, elongation-at-break, and melting temperature (T_m) during hydrolysis were higher for the fiber than for the film. The accelerated hydrolysis of the fiber was ascribed to the high concentrations of the catalytic oligomers and monomers during hydrolysis, resulting from their high initial concentration caused by thermal degradation during melt-spinning and hot-drawing and from their retarded elution from the fiber due to the bulky microscopic shape. The changes in T_m , crystallinity, and weight remaining suggest that the hydrolysis of the fiber proceeds mainly via bulk erosion mechanism, that the chain cleavage of the fiber occurred in the crystalline region and at the folding surface as well as in the other amorphous region, and that lamella thickening of the film took place without significant chain cleavage in the crystalline region and at folding surface.

1. Introduction

Blending biodegradable polymers is commercially advantageous to prepare biodegradable materials having a wide variety of physical properties and hydrolysis rates [1-9]. Since the study by Cha and Pitt [10] on the hydrolysis of blends from aliphatic polyesters, poly(L-lactide) (PLLA), poly(L-lactide-co-glycolide), and poly(ϵ -caprolactone), a great amount of investigations have been performed for polylactides (PLAs) and their copolymers based polymer blends in order to vary their physical properties and biodegradability [1-9].

Blends from enantiomeric PLLA and poly(D-lactide) (PDLA) are different from the other PLAs and their copolymers based blends because

stereocomplexation or racemic crystallization occurs in the former blends owing to a strong interaction between L- and D-lactide unit sequences [7-9]. In previous studies, it became evident that the mechanical properties [11] and hydrolysis-resistance [12,13] of PLA films can be increased by stereocomplexation between PLLA and PDLA. The increased mechanical properties of the well-stereocomplexed blend films are ascribed to stereocomplexation or formation of stereocomplex microcrystallites composed of L- and D-lactide unit sequences, which caused three-dimensional (3D) gelation in the course of solvent evaporation [10]. The 3D gelation will increase tie chain density and suppress the formation of a large size spherulites in the well-stereocomplexed blend films, resulting in their increased mechanical properties compared

with those of the non-blended films [11]. The hydrolysis-resistance of the well-stereocomplexed film is ascribed to the peculiar strong interaction between L- and D-lactide unit sequences in the amorphous region and/or its 3D micro-network structure, which will decrease the diffusion rate of water molecules into the amorphous region and/or the concentration of catalytic oligomers formed by hydrolysis due to their rapid elution [13]. On the other hand, we reported that the well-stereocomplexed fibers can be prepared by dry- and wet-spinning from mixed solution of PLLA and PDLA and that the tensile strength of the dry-spun complex fiber can be increased up to 94 kg/mm² by hot-drawing [14].

The information available on the hydrolysis of the well-stereocomplexed blends from PLLA and PDLA is solely for the specimens prepared by solution-casting without any thermal processes. The purpose of the present work was to investigate and compare in vitro hydrolysis of well-stereocomplexed fiber and film prepared by the methods of melt-spinning and hot-drawing and of solution-casting, respectively.

2. Experimental

2.1 Materials

PLLA and PDLA were synthesized by ring-opening polymerization of L- and D-lactides, respectively, in bulk at 140°C using stannous octoate (0.03 wt%) and lauryl alcohol as catalyst and initiator, respectively [7-9,11,13]. The synthesized polymers were used after purification by precipitation using methylene chloride and methanol as solvent and non-solvent, respectively. A stereocomplex fiber with a diameter ca. 20 μm was prepared by melt spinning from the equimolar mixture (242°C) of PLLA ($M_v=3.13 \times 10^5$) and PDLA ($M_v=2.64 \times 10^5$). Two stage hot-drawing of the fiber was carried out at 130°C to the ratio of 2.3 and at 170°C to the ratio of 1.2. A stereocomplex film was prepared by solution-casting of the 1:1 mixed solution from PLLA ($M_w=1.56 \times 10^5$, $M_w/M_n=1.8$) and PDLA ($M_w=1.52 \times 10^5$, $M_w/M_n=1.6$) using methylene chloride as a solvent [7-9,11,13].

2.2 Hydrolysis

Hydrolysis of the fibers (100 mm x φ ca. 20 μm) and films (18 mm x 30 mm x 50 μm) was performed in 0.15 M phosphate-buffered solution (pH=7.4±0.1) at 37°C for predetermined periods of time exchanging the buffered solution once a month. After hydrolysis, the fibers and films were washed thoroughly with distilled water at room temperature, followed by drying under a reduced pressure for at least 2 weeks.

2.3 Measurements

The intrinsic solution viscosity ($[\eta]_{\text{HFIP}}$) values of the fiber and film before hydrolysis were determined in 1,1,1,3,3,3-hexafluoro-2-propanol at 25°C. The weight- and number-average molecular weights (M_w and M_n , respectively) of the film were evaluated in chloroform at 40 °C after dissolving at 90 °C [13] using a Tosoh GPC system with TSK gel columns (GMH_{XL} x 2) and polystyrene as a standard. The melting temperature (T_m) and the enthalpy of melting (ΔH_m) of the fibers and films were determined by a Shimadzu DT-50 differential scanning calorimeter. The specimens were heated at a rate of 10 °C/min under a nitrogen gas flow of 50 ml/min. T_m and ΔH_m were calibrated using tin, indium, and benzophenone as standards. The crystallinities ascribed to homo- and stereocomplex crystallites in the specimens ($x_{c,H}$ and $x_{c,S}$, respectively) were evaluated according to the following equations [11,13,15]:

$$x_{c,H} (\%) = 100 \cdot \Delta H_{m,H} / 93 \quad (1)$$

$$x_{c,S} (\%) = 100 \cdot \Delta H_{m,S} / 142 \quad (2)$$

where 93 and 142 (J / g of polymer) are $\Delta H_{m,S}$ of the PLLA (or PDLA) and the stereocomplex crystals having the infinite crystal thickness reported by Fischer et al [16] and Loomis et al. [17] and $\Delta H_{m,H}$ and $\Delta H_{m,S}$ are $\Delta H_{m,S}$ of homo- and stereocomplex crystallites, respectively. The melting peaks of the homo- and stereocomplex crystallites appear in DSC thermograms at the temperature ranges 140-180 and 200-240°C, respectively. Tensile properties of the films were measured at 25°C and 50 % relative humidity using

Table 1 Characteristics of Well-Stereocomplexed Fiber and Film before Hydrolysis.

Sample	$[\eta]_{\text{HFIP}}^{\text{a)}}$	$M_w/10^5$ (g/mol)	M_w/M_n	$T_{m,H}$ (°C)	$T_{m,S}$ (°C)	$x_{c,H}$ (%)	$x_{c,S}$ (%)	$\sigma_B^{\text{b)}}$ (kg/mm ²)	$\epsilon_B^{\text{c)}}$ (%)
Fiber	0.93	-	-	-	221	0	54	45.7	7.8
Film	1.13	1.50	1.6	177	225	10	35	2.1	13.9

^{a)} Intrinsic viscosity in 1,1,1,3,3,3-hexafluoro-2-propanol.

^{b)} Tensile strength.

^{c)} Elongation-at-break.

a tensile tester at a crosshead speed of 100 %/min. The initial gauge lengths were always kept at 50 and 20 mm for the fibers and films, respectively. Table 1 tabulates observed values of $[\eta]_{\text{HFIP}}$, M_w , M_w/M_n , $T_{m,H}$, $T_{m,S}$, $x_{c,H}$, $x_{c,S}$, tensile strength (σ_B), and elongation-at-break (ϵ_B) of the fiber and film before hydrolysis. As seen, the initial $[\eta]_{\text{HFIP}}$ and total x_c ($x_{c,H}+x_{c,S}$) of the fiber and film are very similar and the stereocomplex crystallites are dominant crystalline species in both the fiber and film.

3. Results

3.1 Weight remaining

Figure 1 shows the changes in weight remaining of the well-stereocomplexed fiber and film during

Fig. 1 Weight remaining of well-stereocomplexed fiber and film as a function of hydrolysis time.

hydrolysis. The weight loss is an index for the content of water-soluble oligomers formed by hydrolysis and then released from the mother specimens into the surrounding media. Without any induction periods, the weight remaining of the fiber decreased monotonously to 69 % at 24 weeks, while no significant weight loss was recognized for the film at the same period. The weight remaining of the film started to decrease at 24 months (104.3 weeks) and the final weight loss was 2 % even at 30 months (130.4 weeks).

3.2 Changes in Mechanical properties

Figure 2(a) and (b) demonstrates the changes of residual tensile strength and elongation-at-break of the well-stereocomplexed fiber and film during hydrolysis. The tensile properties are indexes for the density of the remaining tie chains in the amorphous region. The residual tensile strength and elongation-at-break of the fiber started to decrease without any induction periods and finally reached 0 % at 8 weeks. On the other hand, a 14 % increase and a 39 % decrease were observed for the tensile strength and elongation-at-break of the film, respectively, at 17.4 weeks. The tensile strength of the film almost retained the initial value (104 %) but its elongation-at-break decreased to 5 % at 30 months.

3.3 Change in the crystalline region

Figure 3 (a) and (b) shows the changes in $x_{c,S}$ and $T_{m,S}$ of the well-stereocomplexed fiber and film during hydrolysis. The $x_{c,S}$ of the fiber gradually increased from 54 % and reached plateau around 60 % at 8 weeks, while that of the film increased gradually over 30 months from 35 % to 46 %. The $T_{m,S}$ of the fiber decreased continuously from 221 to 207°C at 24 weeks whereas that of the film increased slowly from 225 to 227°C at 30 months.

Fig. 2 Residual tensile strength (a) and elongation-at-break (b) of well-stereocomplexed fiber and film as a function of hydrolysis time.

On the other hand, the $x_{c,H}$ and $T_{m,H}$ of the film increased gradually from 10 to 14 % and decreased slowly from 177 to 175°C. respectively, at 30 months.

4. Discussion

The results obtained by gravimetry, tensile testing, and differential scanning calorimetry indicate that the hydrolysis rate of the well-

Fig. 3 $x_{c,S}$ (a) and $T_{m,S}$ (b) of well-stereocomplexed fiber and film as a function of hydrolysis time.

stereocomplexed fiber was higher than that of the well-stereocomplexed film. The complex fiber was prepared by the melt-spinning and hot-drawing, which will cause the thermal degradation or the formation of the catalytic oligomers and monomers in the fiber, and therefore will increase their initial concentration before hydrolysis. On the other hand, the film was reported to have 3D micro-network structure composed of the fibers with diameter ca. 1 μm [11], which was one order of

magnitude lower than that of the complex fiber (diameter ca. 20 μm). The 3D micro-network structure will reduce mean distance for the catalytic oligomers and monomers, which are formed by hydrolysis, to diffuse out from the film, resulting in their reduced concentration in the film compared with those in the fiber during hydrolysis. The increased initial concentration of the catalytic oligomers and monomers in the fiber and their retarded elution may have accelerated the hydrolysis of the fiber compared with that of the film.

The decreases in $T_{m,S}$ and weight remaining without any induction periods strongly suggests that the hydrolysis of the fiber proceeds mainly via bulk erosion mechanism. If the hydrolysis takes place mainly via surface erosion, no significant decrease in $T_{m,S}$ will be recognized even when a large weight loss occurs [18]. The rapid saturation of $x_{c,S}$ of the fiber at 8 weeks is attributed to the high initial $x_{c,S}$ or low crystallizability of the fiber. The unchanged $x_{c,S}$ for the hydrolysis period of 8-24 weeks in spite of the continuous decreases in weight remaining and $T_{m,S}$ is probably due to the hydrolysis of the chains in the stereocomplex crystalline region and/or at the folding surface in addition to that of the chains with free ends and the tie chains in the amorphous region. On the other hand, the increased $T_{m,S}$ and $x_{c,S}$ of the film at 30 months reflect the thickening of lamellae and no significant chain cleavage in the stereocomplex crystalline region and at the folding surface. Moreover, the decreased $T_{m,H}$ and increased $x_{c,S}$ suggest that the chain cleavage occurred in the crystalline region and/or at the folding surface of the original homo-crystallites and that the new homo-crystallites were formed during hydrolysis.

5. Acknowledgements

The encouragement and support of Prof Yoshito Ikada, Suzuka University of Medical Science, are greatly appreciated. This research was supported by a Grant-in-Aid for Scientific Research on Priority Area, "Sustainable Biodegradable Plastics", No.11217209 from the

Ministry of Education, Culture, Sports, Science and Technology (Japan).

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