Influence of Molecular Weight on the Resistance of Polylactide Fibers by Radiation Sterilization

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SYNOPSIS

The mechanical properties and *in vitro* degradability of poly(L-lactide) fibers with different average molecular weights, prepared by a dry spinning–hot drawing process from $CHCl_3$ solutions, were studied in relation to the γ-irradiation dose. In the range of molecular weight of $1.6–3.6 \times 10^5$, no differences were found in the relative decrease of tensile strength after irradiation of 25 kGy. Changes of the elongation at break are discussed in terms of a network solution theory. *In vitro* degradation of the fibers is also discussed in network solution theory terms. Regardless of the courses of degradation curves, it may be stated that all prepared fibers could be sterilized by γ-rays and the rate of degradation was not affected by the irradiation dose. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Because of its biocompatibility, poly(L-lactide) (PLLA) has been widely studied for biomedical applications such as body-absorbable sutures.[1-7] Sterilization of such materials is very important for their application. γ-Irradiation is believed to be the best method for suture sterilization.

The effect of γ-rays on fiber-forming materials can result in simultaneous chain scission and cross-linking. Which of these will characterize the reaction depends on several factors, including the chemical structure of materials to be irradiated, the amount of dose, the rate of dosage, the environment of the material during irradiation, and the heat of crystallization.[8]

The orientation of long-chain molecules has also been reported to have some influence on the direction of the overall radiation reaction, and this was due to the differences in chain mobility.[9] Also, the scission of polymer chains are more pronounced in the amorphous regions than in the crystalline regions. This might be due to the so-called cage effect.[10]

Parafinic fragments make the polymer chains susceptible to cross-linking, whereas ester groups or heterogeneous atoms enhance the scission. Aromatic structures are able to absorb a great part of the irradiation energy. The fiber's loss of strength depends also on the density of the entanglements of the polymer network, which increases with the molecular weight of the polymer.

Thus, poly(glycolic acid)-based fibers demonstrate the susceptibility of aliphatic ester groups to γ-irradiation degradation.[11] A normal sterilization dose of γ-rays (25 kGy) causes a total loss of strength during the 10 day period after implantation.[12] The radiation resistance of α-hydroxy acid-based degradable polymers may be increased by dilution of these building units with parafinic fragments[13] or inclusion of aromatic units into polymer chains.[14,15]

The scission has also been recognized as the main γ-irradiation degradation mechanism of poly(L-lactide) (PLLA).[16] However, there is little information about radiated PLLA fibers in the literature. Therefore, the presented study was done.

EXPERIMENTAL

Samples

L-Lactide was prepared according to the procedure described by Kulkarni et al.[17] and was five times

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recrystallized from ethyl acetate. Ethyl acetate was dried 48 h over molecular sieves.

PLLA samples with the viscosity-average molecular weight of 1.6, 2.6, and 3.6 $\times 10^5$ was obtained by polymerization of L-lactide at 130°C in the presence of $SnCl_2 \cdot 2H_2O$ as a catalyst for 8, 22, and 35 h, respectively. The $SnCl_2 \cdot 2H_2O$ was used in the amount of 10^{-4} mol per mol L-lactide. The polymers were purified from residual lactide by dissolution in trichloromethane and subsequent precipitation with methanol.

The intrinsic viscosities of the polymers were measured in trichloromethane at 25°C. The viscosity-average molecular weight of PLLA was calculated according to the following formula[18]:

$$[\eta] = 5.45 \times 10^{-4} \bar{M}_V^{0.73}$$

Dry Spinning–Hot Drawing Process

The polymers were dissolved by stirring at 50°C for 16 h. After cooling to 33°C (2 h), the solutions were spun at room temperature through an orifice die of 0.4 × 5 mm with an extrusion speed of 8.3 cm min^{-1}. Filaments were collected on a steel drum at a speed of 5.5 cm min^{-1}. After 48 h, they were hot-drawn (four times) at 90°C with an entrance velocity of 13.8 cm min^{-1} into a 1 × 30 cm tube.

Sterilization and *In Vitro* Degradation

Fibers (in dry argon atmosphere) were subjected to Co^{60} γ-irradiation dose of 25 and 50 kGy, respectively (Bioster s.p., Veverská Bítýška, ČSFR). *In vitro* degradation was performed by submersion of the fibers into McIlvaine buffer (pH 7) for the required time at 37°C.

Characterization of the Fibers

Mechanical properties of PLLA fibers were measured at room temperature using an Instron 1122 tensile tester at a crosshead speed of 4 mm min^{-1}. The length of the specimen was 8 mm.

The diameters of the fibers were measured on a light microscope and represent average values of 15 measurements.

RESULTS AND DISCUSSION

Characterization of the Fibers

Properties of the prepared fibers are shown in Table I.

Concentration of the spinning dopes was 20.9, 13.7, and 8.2 w/w % for the spinning of fibers 202, 203, and 119, respectively. Because of the rising amount of inhomogeneities, it was impossible to spin fibers from solutions with the same polymer concentration. However, the relation between the concentrations of polymer dope and the fineness of the spun fibers is linear, as shown in Figure 1. This means that it is possible to consider the mechanical properties of the fibers as a function of $\bar{M}_v$.

The relation between the viscosity-average molecular weight and the mechanical properties of the fibers is shown in Figure 2. The shape of both curves

Table I Characterization of the Fibers

Fiber No.	Type[a]	Fineness (tex)	d (μm)	$\Delta n \cdot 10^2$	σ (GPa)	ϵ (%)	$[\eta]$ (dL g^{-1})
202	A	—	190	0.07	—	—	3.43
	NS	14.7	126	2.57	0.26	44	3.43
	25	14.7	126	—	0.22	43	1.25
	50	14.7	126	—	0.19	44	1.01
203	A	—	176	0.34	—	—	4.89
	NS	11.2	88	2.82	0.32	33	4.89
	25	11.2	88	—	0.27	40	1.55
	50	11.2	88	—	0.22	42	1.25
119	A	—	147	0.34	—	—	6.13
	NS	8.5	86	2.75	0.47	28	6.13
	25	8.5	86	—	0.40	35	2.16
	50	8.5	86	—	0.31	41	1.79

[a] A, as-spun; NS, nonsterilized; 25 and 50, radiated with dose of 25 and 50 kGy, respectively.

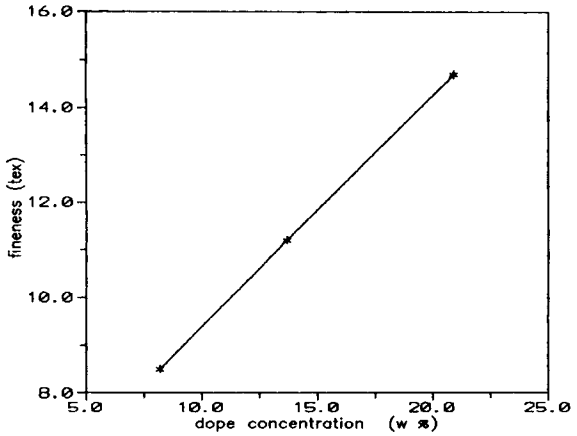

Figure 1 Relation between a dope concentration and the fineness of the final fibers.

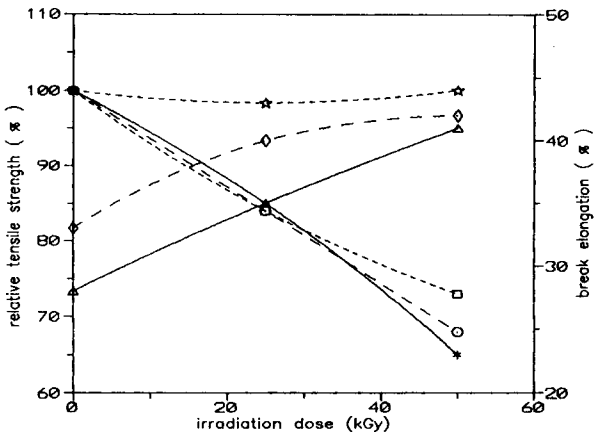

Figure 3 Dependence of mechanical properties of the fibers on the irradiation dose. Tensile strength: (*) 119; (○) 203; (□) 202. Break elongation: (△) 119; (◇) 203; (☆) 202.

is expected, especially that of the strength curve.[3] The drop of elongation may be explained in terms of the network solution theory. The density of entanglements in polymer solutions increases both with the polymer molecular weight and its concentration. This network is also fixed in the dry fiber and causes decreasing of the elongation. The break elongation values of fibers 202 and 203 indicate that these fibers are not drawn to the maximum draw ratio (λ_{max}), whereas the 119 fiber elongation approaches λ_{max}. The influence of $\bar{M}_v$ on the strength values seems to be more pronounced due to the lesser number of chain ends and better orientation.

The changes of mechanical properties of the fibers after irradiation are shown in Figure 3. The normal sterilization dose of irradiation decreases the strengths of all the fibers to about 85% of their initial values. The double sterilization dose causes a decrease in strength of 75–65%. The actual fiber strength does not depend only on the actual molecular weight, but also on the "history of the polymer." A dense entanglement network in the amorphous regions of a high molecular weight polymer together with orientation causes retention of a high fiber strength after irradiation. This entanglement reduces an influence of chain ends on the tensile strength. It acts like a cross-linking.

Thus, for example, although the 119, 25 kGy fiber should have, according to its [η] (Table I), the tensile breaking strength of 0.20 GPa, its real value is 0.40 GPa. In addition, the highest density of an entanglement network may be the reason for the greatest decrease of the 119 fiber's relative strength

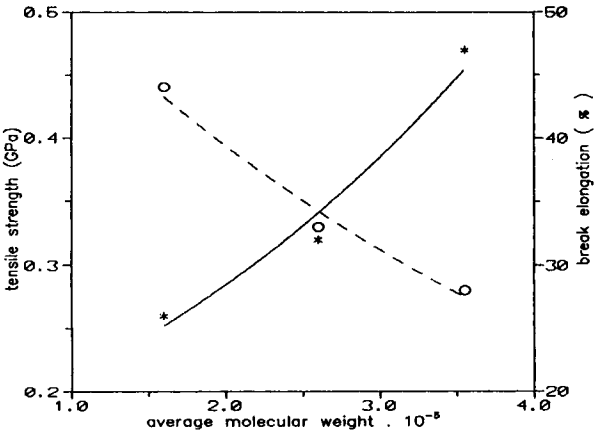

Figure 2 Dependence of mechanical properties of the fibers on average molecular weights of starting materials: (*) tensile strength; (○) break elongation.

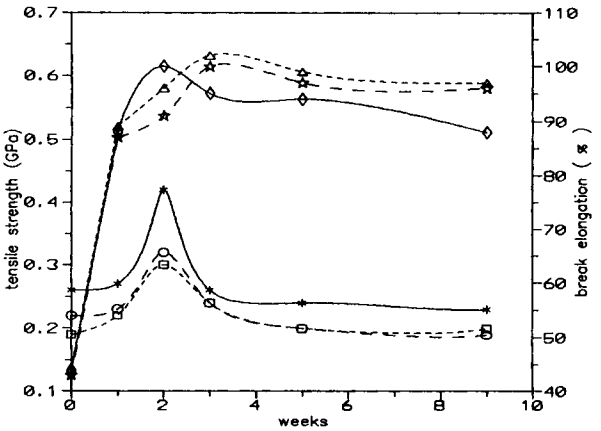

Figure 4 *In vitro* degradation of fiber 202. Strength: (*) NS; (○) 25 kGy; (□) 50 kGy. Break elongation: (◇) NS; (☆) 25 kGy; (△) 50 kGy.

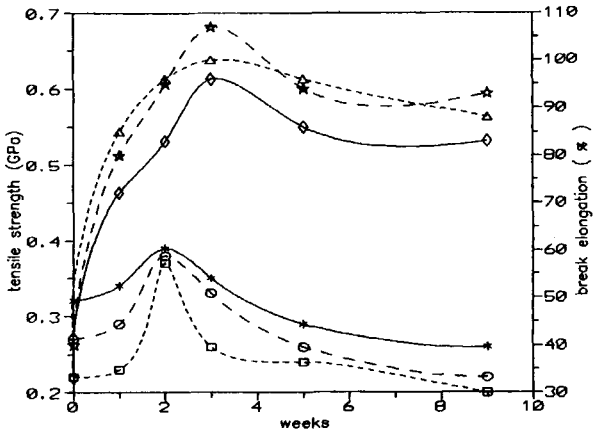

Figure 5 *In vitro* degradation of fiber 203. Strength: (*) NS; (○) 25 kGy; (□) 50 kGy. Break elongation: (◇) NS; (☆) 25 kGy; (△) 50 kGy.

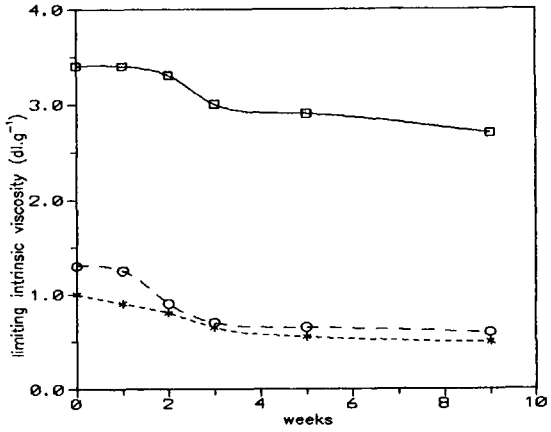

Figure 7 Changes of limiting intrinsic viscosities during *in vitro* degradation at 37°C of fiber 202: (□) NS; (○) 25 kGy; (*) 50 kGy.

after irradiation of 50 kGy (perhaps the highly stretched chains are more sensitive to γ-ray action).

The irradiation of the fibers also increases their break elongation. The reason is the same as that for the breaking strength. This increase is evidence for scission as the main degradation mechanism. The scission of macromolecules frees some points of the network and, therefore, the structure's deformability increases. This effect takes place more dramatically in polymers with higher molecular weight (higher density of entanglements) than in those with lower $\bar{M}_v$.

In Vitro Degradation

The influence of an *in vitro* degradation at 37°C on the fibers' mechanical properties is shown in Figures 4–6, and on $[\eta]$, in Figures 7–9. The mechanism of changes by hydrolytic degradation is probably the same as that by irradiation. Scission of the amorphous polymer chains again takes place, and the density of the entanglement decreases. The break elongation increases and so does the breaking strength, which may be caused by heterogeneous drawing during the breaking test.

The break elongation increases during the next degradation, but the number of the elements that are responsible for the breaking tensile strength decreases during that time. Therefore, the breaking strength also starts to decrease. The elongation does not increase during the next period. It decreases, and the fibers become slowly brittle. This is accompanied by a further decrease of strength.

The decreasing height of the tensile breaking peak

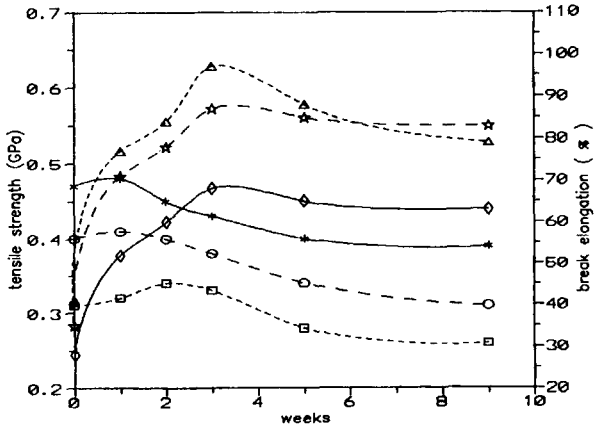

Figure 6 *In vitro* degradation of fiber 119. Strength: (*) NS; (○) 25 kGy; (□) 50 kGy. Break elongation: (◇) NS; (☆) 25 kGy; (△) 50 kGy.

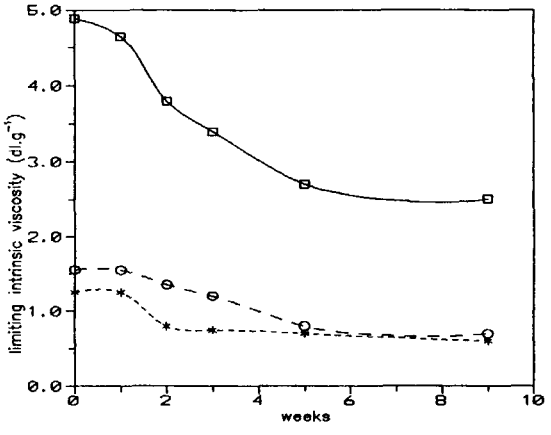

Figure 8 Changes of limiting intrinsic viscosities during *in vitro* degradation at 37°C of fiber 203: (□) NS; (○) 25 kGy; (*) 50 kGy.

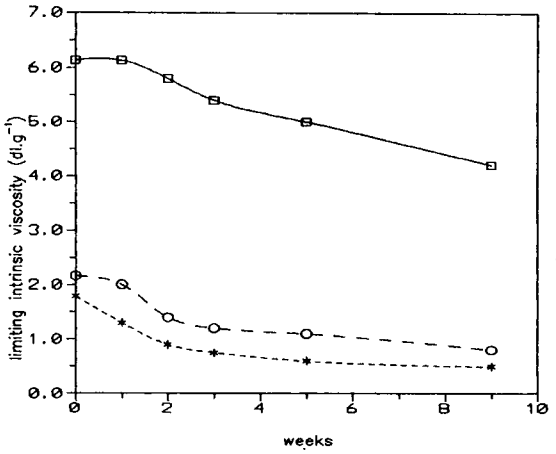

Figure 9 Changes of limiting intrinsic viscosities during *in vitro* degradation at 37°C of fiber 119: (□) NS; (○) 25 kGy; (*) 50 kGy.

in Figures 4–6 is a function of the drawing ratio and the entanglement network density. It may be seen, by comparing Figures 7–9, that the strength peak appears in the area of the highest rate of $[\eta]$ fall. This is in agreement with the indicated mechanism.

CONCLUSIONS

It is obvious that when both the starting and final state of tensile breaking strength were compared the *in vitro* degradation rate did not change by the radiation sterilization. All the prepared fibers were able to be sterilized by γ-irradiation (25 kGy) without significant loss in breaking strength.

The data obtained in this study may not be interpreted generally. As mentioned in the Introduction, the resistance to γ-irradiation depends also on other factors, such as the crystallinity degree. Therefore, the changes of the mechanical properties of PLLA fibers upon irradiation can be regulated by the parameters of the spinning process.

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