Polymer Degradation and Stability 96 (2011) 1522–1529

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Influence of hydrolytic degradation on the surface properties of poly-5D/95L-lactide resorbable bone plates

Hsin-Tai Hu [a], Tsai-Chin Shin [a], Sheng-Yang Lee [a], Chien-Chung Chen [b], Jen-Chang Yang [c,*]

[a] School of Dentistry, College of Oral Medicine, Taipei Medical University, Taipei 110-52, Taiwan, ROC
[b] Graduate Institute of Biomedical Materials & Engineering, College of Oral Medicine, Taipei Medical University, Taipei 110-52, Taiwan, ROC
[c] School of Dental Technology, College of Oral Medicine, Taipei Medical University, No. 250 Wu-Hsing Street, Taipei 110-52, Taiwan, ROC

ARTICLE INFO

Article history:
Received 24 January 2011
Received in revised form
15 April 2011
Accepted 25 April 2011
Available online 11 May 2011

Keywords:
PLA95 (poly-5D/95L-lactide)
Resorbable bone plates
In vitro degradation
ATR-FTIR
MDSC
Surface morphology

ABSTRACT

This study explores in vitro aging effects on the surface properties of resorbable PLA95 (poly-5D/95L-lactide) bone plates. The in vitro degradation of injection molded PLA95 bone plates was undertaken by soaking them in a PBS solution. Specimens were harvested at 0, 4, 6, 8, 12, 20, and 26 weeks. After each in vitro aging period, the surface morphology, viscosity, chemical structure, wettability, and thermal properties of the PLA95 bone plates were examined by scanning electron microscopy (SEM), capillary viscometers, attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR), contact angle, and modulated differential scanning calorimetry (MDSC), respectively. The surface morphology of aged PLA95 bone plates exhibited bulk erosion. As hydrolysis progressed, the inherent viscosity (I.V.) of the PLA95 plates gradually decreased from 0.83 ± 0.01 dL/g at week 0–0.46 ± 0.03 dL/g at week 26. However, the absorbance peak intensity ratio between $\delta_{as\ CH3}$ ($A_{1452\ cm^{-1}}$) and $\nu_{C=O}$ ($A_{1750\ cm^{-1}}$) and the contact angle reveal different tendencies than that of molecular weight, which decreases. The contact angle of the PLA95 plates decreased until week 4, increased until week 8, and subsequently decreased again. Peak separation analysis reveals that the equilibrium part of the modulated DSC overlapped curves exhibit triple endothermic peaks. Over time, in vitro degradation changes the position and area of the individual peaks. After different time periods of degradation, the variation of wettability shows a tendency similar to the change of PLA95 plates crystallinity; the intensity ratio of $A_{1452\ cm^{-1}}$ and $A_{1750\ cm^{-1}}$ ($\delta_{as\ CH3}/\nu_{C=O}$) absorbance peaks varied like the ratio of β/α-crystal heat of fusion. Results also show a similarity in the degradation time dependence in MDSC, contact angle, and ATR-FTIR measurements. During the in vitro aging process, the breakdown and subsequent recrystallization of PLA95 molecular chains might be attributed to a progressive change in wettability and the molecular conformation between $\delta_{as\ CH3}$ and $\nu_{C=O}$.

1. Introduction

Resorbable devices for fracture fixation have attracted a lot of attention due to their advantages over metallic implants. For example, resorbable devices avoid potential drawbacks such as the stress shielding effect, interference with diagnostic or therapeutic radiation, growth disturbance in children, and the need for secondary operations [1–7]. Lactide-based aliphatic polyesters are some of the most promising resorbable materials in the field of medical devices. Due to the adverse reactions associated with pure poly-L-lactide (PLLA), polyglycolide acid (PGA), and their poly (glycolide co-lactide) acid (PLGA) copolymer, typical bioresorbable bone plates/screws are fabricated by copolymers consisting of PLLA, poly-DL-lactide (PDLA) or PGA.

The parameters affecting the degradation of PLA implants include backbone chemical stability, wettability, initial molecular weight, polydispersity, crystallinity, manufacturing procedure, and geometry (surface/volume ratio) and site of implantation [8,9]. The hydrolysis behaviors of PLA implants can be realized in terms of molecular and phenomenological aspects. The in vivo degradation of the PLA molecular backbone is believed to be governed by chemical hydrolysis rather than enzymatic cleavage. As body fluid contacts the implant surface, it begins the process of hydrolytic de-esterification. This chemical reaction of hydrolytic degradation breaks the ester linkages and forms PLA oligomers [10]. The low molecular weight PLA continues to breakdown to single lactic acid molecules metabolized by lactate dehydrogenase through the pyruvatic cycle into CO_2 and H_2O. Driven by a concentration

* Corresponding author. Tel.: +886 2 27361661x5124; fax: +886 2 27362295.
E-mail address: yang820065@tmu.edu.tw (J.-C. Yang).

0141-3910/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2011.04.020

gradient, the diffusion of soluble oligomers from the implant into the external medium decreases acidity around the surface layer. Autocatalysis due to the trapped carboxylic end-groups enhances the degradation rate inside the internal part of the implant [11–17]. Thus, thick PLA implants usually reveal heterogeneous degradation: faster degradation inside than at the surface [18].

In term of phenomenological aspect, the degradation mechanism for resorbable implants includes surface erosion and bulk erosion, depending on the relative backbone degradation rate and oligomer diffusion rate [19]. Size stability and surface morphology are two major factors distinguishing surface eroding and bulk eroding. Unlike surface eroding, the high hydrolysis rate of an aged polymer compared to its diffusion rate leads to size reduction. Bulk eroding turns the polymer into a rough, beehive-like surface, but produces little or minor dimensional change.

For bulk eroding polymers, such as poly(D,L-lactic acid) (PDLLA), things are more complicated because they have no constant erosion velocity [20]. These polymers usually do not erode for long periods of time, after which erosion sets in spontaneously. During the hydrolytic degradation, the plate causes reduction of the molecular weight, and finally loss of implant strength. Despite the importance of mechanical stability for resorbable implants, the mechanism of erosion is still relatively unclear, hindering us from taking full advantage of these materials [20]. Since the processing, chemical composition and physical state (i.e., crystallinity and orientation) of poly lactic acid (PLA) can easily affect its mechanical and erosion properties, this study explores the crystalline structures of bio-resorbable implants through thermal analysis of PLA95 bone plates after various in vitro aging periods.

2. Materials and methods

2.1. Materials

The resorbable 6-hole straight bone plates (Bonamates®, REF No. 122,002, BioTech One Inc., New Taipei, Taiwan) used in this study were prepared by injection-molding the PLA95 (poly-5D/95L-lactide, $M_w = 120$ kDa) copolymer. The 6-hole straight bone plates had dimensions of 23.5 × 6.7 × 1.2 mm^3, with a hole diameter of 2.6 mm.

2.2. In vitro degradation of poly-5D/95L-lactide resorbable bone plates

In this degradation study, the 6-hole straight bone plates ($n = 3$) were placed into a flask and soaked in a phosphate-buffered saline (PBS) solution. The pH was maintained at 7.4 ± 0.2 and the specimen mass/PBS solution ratio was 1:20. The flasks were placed in a horizontal shaking bath at a water temperature of 37 °C following ASTM F1635. The inherent viscosity, wettability, functional group, surface morphology, thermal property of the PLA95 were evaluated at degradation times of 0, 4, 6, 8, 12, 20, and 26 wks.

2.3. Inherent viscosity of PLA95 bone plate

The inherent viscosity (IV) of PLA95 was measured by a Cannon-Ubbelohde viscometer at a polymer concentration of 25 mg/25 ml in $CHCl_3$ at 250C and determined from the relative viscosity (η_r) using the following equation: $IV = \ln(\eta_r)/c$.

2.4. Scanning electron microscopy of PLA95 bone plate at various time periods

In vitro degradation specimens were collected and cleaned after various time periods. The PLA95 bone plate specimens were mounted on aluminum stubs and sputter-coated (Ion coater, IC, IB-2, Hitachi, Japan) with gold by vacuum evaporator at a voltage of 15 kV for 60 s. The surface morphology of the PLA95 bone plate was investigated by scanning electron microscopy (SEM) (S-2400, Hitachi, Japan).

2.5. Attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR)

Infrared spectroscopy is based on the absorption of IR radiation, whose intensity and frequency provides information regarding the structure and bonding of a molecule. ATR-FTIR analyses were performed using a Perkin–Elmer spectrophotometer (model Spectrum 2000). The peaks at wave-numbers 4000 cm^{-1} and 550 cm^{-1} were selected as the most suitable ones for PLA95 analysis. Each sample was scanned 12 times, and the scanned area was 2 × 2 cm. The scan interval was 1 cm^{-1}, and the articulation was 4 cm^{-1}. The CH symmetric and asymmetric stretch region of 3200–2800 cm^{-1}, CH, CH_3 bending, and C–O–C stretching band region of 1500–1000 cm^{-1}, and the backbone stretching and CH_3 rocking band region of 960–830 cm^{-1}.

2.6. Contact angle of the PLA95 bone plate

The wettability of the PLA95 bone plate was examined with a contact angle meter (Dynamic Contact Angle Meter, DigiDrop-PROD, GBX, France). Using a micro-syringe (Gilmont, Barrington, IL, USA), 4 μl distilled water was dropped on the surface of the tablet from a distance of less than 1 mm from the bone plate surface. The droplet image was observed using a light microscope to determine the contact angle. The image of the droplet shape was recorded by a CCD video camera and analyzed to determine the contact angle evolution.

2.7. Modulated differential scanning calorimetry (MDSC)

The advantages of MDSC include increasing sensitivity for detecting weak (glass) transitions, eliminating baseline curvature and drift, increasing resolution without loss of sensitivity, separating complex thermal events and transitions into their heat capacity and kinetic components, and measuring heat capacity (structure) changes during reactions and under isothermal conditions. This method can also determine heat capacity and separate heat flow into that due to reversible and non-reversible events. Heat flow in DSC experiments consists of two parts, but DSC can only measure the sum of them.

$$dH/dt = C_p(dT/dt) + f(T,t)$$

Total = Heat capacity + Kinetic heat flow component (DSC)
= Reversing heat flow + Non-reversing flow (MDSC)

The thermal properties of the PLA95 bone plates were examined with a temperature modulated differential scanning calorimeter (MDSC) (TA Instruments, Q100, Newcastle, DE) in a N_2 atmosphere. About 5 mg of sample was placed in an aluminum pan with a perforated lid. The MDSC analysis was undertaken at a ramp rate of 5.00 °C/min, 4 modulations per minute, and an amplitude of 1 °C from temperatures of 25 °C–200 °C. Temperature and heat flow calibration was performed with indium. The degree of crystallinity of the PLA95 bone plate was calculated using the following formula [21].

$$\text{Degree of Crystallinity } (\%) = \Delta H_M/93.7 \times 100 \quad (2)$$

Where ΔH_M is the melting enthalpy (in J/g) calculated from the fusion peak of MDSC. To elucidate the relative change of crystallinity