牙用/骨用聚乳酸的結晶與熱裂解行爲之探討

Crystallinity and thermal degradation behavior of poly-L-lactide for dental/orthopedic use

中文摘要

本研究之目的在於探討具生物分解性的聚左乳酸(poly-L-lactide，簡稱 PLLA)加工過程中，溫度及環境對分子量改變和結晶行爲的影響，以期在製備新型生物可吸收性材料時，能控制其機械強度與降解速率，以應用於牙科或骨科硬組織之修復。實驗採熱熔熱壓成型法，製備聚乳酸試塊，探討：(1)PLLA 複合材之基本性質，以 MTS 測試其彎曲強度，用 DSC 來檢測熔點，再以測定毛細管黏度分析分子量的變化；(2)量測 PLLA 在溶解、再沈、乾燥、熔融和熱壓等加工過程中，其分子量的降解程度。另外，利用濕式成膜的方式，製備聚乳酸薄膜對聚乳酸的結晶性進行探討。實驗發現 220 C 爲所測試聚乳酸熱熔加工的適當溫度；在不同的加溫氣氛中，聚乳酸到達融熔所需的時間有所不同，空氣下熱熔較有效率，但過程之熱性質變化較爲激烈，而真空下加溫所得聚乳酸彎曲強度明顯大於在空氣中加溫。不同降溫系統亦造成不同聚乳酸彎曲強度，在氮氣下降溫的彎曲強度較空氣中的值高。亦即，於真空中熱熔並在氮氣下冷卻的聚乳酸所得之彎曲強度(115.9 + 1.3 MPa)最高，而於空氣中加溫並冷卻的聚乳酸之彎曲強度(76.9 + 1.8 MPa)最低。結晶熱焓、熔點波峰和繞射角隨著時間而變化，其影響因素包含了再結晶效應與熱裂解效應。所得聚乳酸的成型物經由適當的熱處理，可以改變聚乳酸的結晶度和晶型，藉此進一步的掌握降解速率。但對於 PLLA，以射出成型之試樣經過熱處理後，彎曲強度會下降(由 113.5 下降至 87.6 MPa)，物性較脆；而藉由 PDLLA 的改質，經過熱處理後，彎曲強度增加(由 116.8 增加至 146.5 MPa)和伸長率都會增加，且有適當的結晶度。本實驗對於寡乳酸聚合物的基本性質和加工條件已有初步瞭解，以射出成型所製備之聚乳酸試樣經由熱處理後的彎曲強度亦高達 146 MPa，聚乳酸的機械強度和降解速率與其分子量、結晶度息息相關，因此對於升溫環境的保護，以及適當時間的再結晶處理，都是聚乳酸加工條件最佳化的重要因素。

英文摘要

Poly-L-Lactide (PLLA) was used to prepare objects as useful dental/orthopedic biomaterial in this investigation. Samples were prepared by compression molding in the study. PLLA was heated at 220 C in air atmosphere and nitrogen atmosphere, respectively, to achieve a molten phase for molding. The PLLA was then molded immediately by with hot press, followed by cooling in nitrogen atmosphere or in air atmosphere. PLLA film used for the annealing experiment was obtained through the solvent-casting method. Annealing of PLLA films was performed under different

annealing time. The basic characterization of the prepared PLLA samples were performed by differential scanning calorimeter and X-ray diffraction pattern for thermal properties and crystallinity, and by material testing system for mechanical strength. The bending strength of samples prepared under nitrogen atmosphere (115.9 + 1.3 MPa) (or under vacuum) was better than that of samples prepared under air atmosphere (76.9 + 1.8 MPa). The thermal property of the sample prepared under nitrogen atmosphere (or under vacuum) was more stable than that of samples prepared under air atmosphere. The crystallinity and melting temperatures of PLLA film increased with annealing time. The enthalpy of crystallization, melting peak and X-ray diffraction angle were change depended on the annealing time, the effect factors included recrystallization and thermal degradation effect. The bending strength of PLLA/PDLLA specimen that prepared by injection molding and via thermal treatment was reached 146 MPa . These results suggest that better PLLA objects can be obtained under optimal conditions, as described above.