Reinforcement of Biodegradable Poly(DL-lactic acid) Material by Equal-Channel Angular Extrusion

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Summary: The purpose of this study was to reinforce biodegradable poly(DL-lactic acid) (PDLLA) material using a new method, equal-channel angular extrusion (ECAE). Different processing parameters, including the number of extrusion passes and the process temperature, were investigated to analyze their effect on the PDLLA properties. Experimental results indicate that the mechanical strength of PDLLA increased with the number of extrusion passes. The extrusion temperature also affected the mechanical strength of the PDLLA. After two ECAE passes, the bending strength of PDLLA increased from 83.3 to 178.7 MPa. The bending fracture mode for PDLLA changed from brittle failure for initial specimens to ductile fracture after ECAE processing. SEM micrographs showed that the longitudinal split surfaces of PDLLA are of a fibrillar structure. Taken together, the results suggest that ECAE might represent a useful approach for the preparation of reinforced PDLLA.

Keywords: equal-channel angular extrusion; PDLLA; Reinforcement

1. Introduction

Biodegradable polymers are among the most popular materials used in biomedical engineering at present. Poly(DL-lactic acid) (PDLLA) has been extensively studied for biomedical applications because of its biocompatibility and suitable degradation rate. However, its initial strength and toughness are insufficient [1–3]. Some studies have reported on PDLLA reinforcement [4–6]. L. Fang and J. Demin et al. used solid state extrusion method to reinforce the strength of PDLLA with molecular weight of 33 kDa. At the optimal conditions, the bending strength and bending modulus of PDLLA arrived 35.1 MPa and 2.41 GPa, respectively [4]. A. Majola et al. have used self-reinforcing (SR) techniques to develop SR-PDLLA/PLLA composites which attained the bending strength of 209 MPa [6]. However, further research is needed to explore effective methods for improving the mechanical properties of PDLLA.

In the present study, biodegradable PDLLA material was processed using a new method, equal-channel angular extrusion (ECAE) [7,8], to reinforce the strength and toughness. The experimental results indicate that the PDLLA bending strength increased from 83.3 to 178.7 MPa. The bending fracture mode for PDLLA was improved from brittle failure to ductile fracture. The reinforcement mechanism and the effect of PDLLA produced by ECAE were analyzed. The influence of the number of extrusion passes and process temperature on the properties of PDLLA is summarized based on the experimental data.

2. Experimental

2.1. Materials

The poly(DL-lactic acid) raw material used was provide by Chengdu Institute of Organic Chemistry, Chinese Academy of

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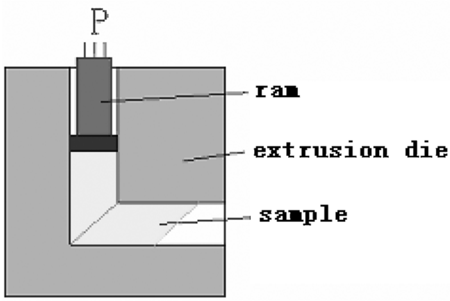


Figure 1.
Schematic diagram of the equal-channel angular extrusion process.

Sciences, China. It has a molecular weight of 600 kDa.

2.2. Specimen Preparation

Specimens used for ECAE were prepared by compression molding at 210 °C. The ECAE process temperature was 65 °C or 75 °C. The angle of the extrusion die was 90° (Figure 1). A specimen was placed in the vertical channel and extruded into the second channel with force *P*. The two channels are of the same cross-section. The specimen undergoes simple shear as it moves from the first channel into the second channel. The great advantage of the technique is that the specimen is approximately the same size and shape of the cross-section after extrusion. Thus, the specimen can potentially be extruded many times, allowing substantial strains to be imparted.

2.3. Mechanical Properties

The mechanical properties were tested according to standard GB/T16419-1996 using an electric tensile test machine (WD-D/E, Testing Instrument Co. Changchun, China).

2.4. Scanning Electron Microscopy (SEM)

The morphology of the deformation of specimen fracture surfaces was investigated using SEM (JSM-6700F instrument).

2.5. Wide-Angle X-Ray Diffraction (WAXD)

WAXD was performed using Cu K_{α} radiation with Rigaku D/max-rA instrument along the extrusion direction of samples.

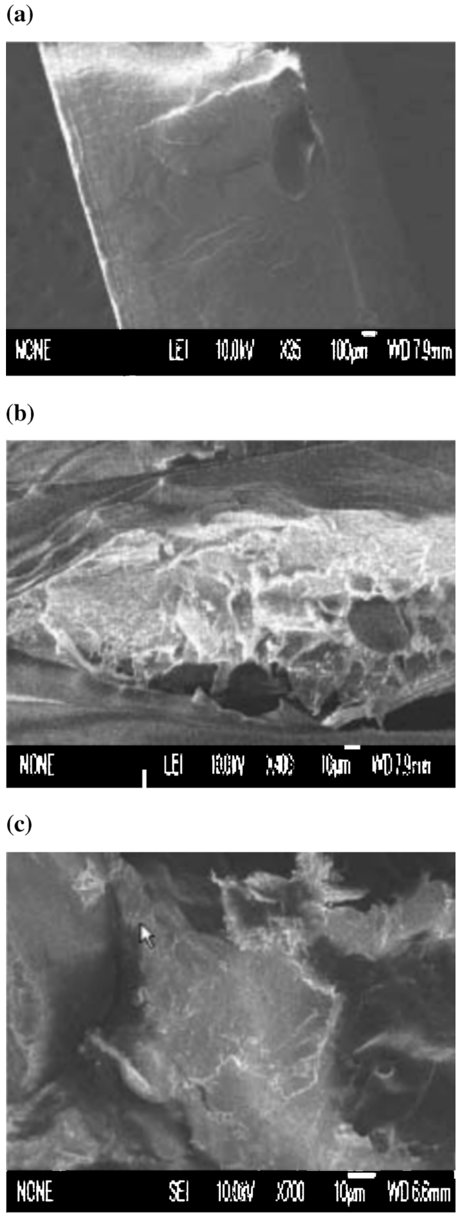


Figure 2.
SEM micrographs of the bending fracture surfaces of PDLLA: (a) compression molding specimen; (b) one-pass ECEA specimen; and (c) one-pass ECEA extension fracture specimen.

2.6. Differential Scanning Calorimetry (DSC)

To examine the thermal properties of extruded specimens, DSC scans were recorded using a NETZSCH DSC 204 instrument in the range 25–160 °C at a heating rate of 10 °C/min in an N_2 atmosphere.

3. Results and Discussion

Figure 2a shows a micrograph of the bending fracture surface of a compression-molded PDLLA specimen. It can be observed that the surface comprises regular grains without a fibril structure. In fracture experiments it was easy to bend the specimen, which broke in the form of a brittle fracture. Figure 2b is a micrograph of extruded PDLLA. The fracture surface shows numerous fibril ends. In bending strength tests, one-pass ECEA specimens curved without breaking. These specimens could only be broken via tension using external force, as shown in Figure 2c. This is because the PDLLA interior is shear-orientated at temperatures above T_g.

WAXD spectra of specimens processed at 75 °C are shown in Figure 3. Comparison of the one-pass and two-pass curves shows that the diffraction intensity after two passes is greater than after one-pass extrusion. Figure 4 shows DSC heating curves for PDLLA after extrusion at 75 °C. Two different endothermic and two exothermic peaks can be distinguished for the different extrusion regimes, which are quite narrow. Comparison of the peaks clearly shows that T_g increased by more than 2 °C after two-pass compared to one-pass extrusion. With an increase in the number of extrusion passes, the shear strength builds up. The hot resistance of two-pass specimens was better than for one-pass samples. This may improve the strength attenuation of PDLLA in the body and broaden the possible applications for bone fixation.

Results for the bending strength of PDLLA under different process conditions are shown in Figure 5, indicating that ECAE can improve the toughness of PDLLA. The bending strength and bending modulus were increased from 83.3 to 124.6 MPa and 2.3 to 3.9 GPa respectively after one-pass extrusion. For two-pass extrusion at 65 °C the bending strength and bending modulus were increased to 155.8 MPa and 5.1 GPa respectively. Extrusion at 75 °C led to a greater increase in bending strength and ending modulus than for extrusion at 65 °C. After two-pass extrusion the bending strength and bending modulus were increased from 83.3 to 178.7

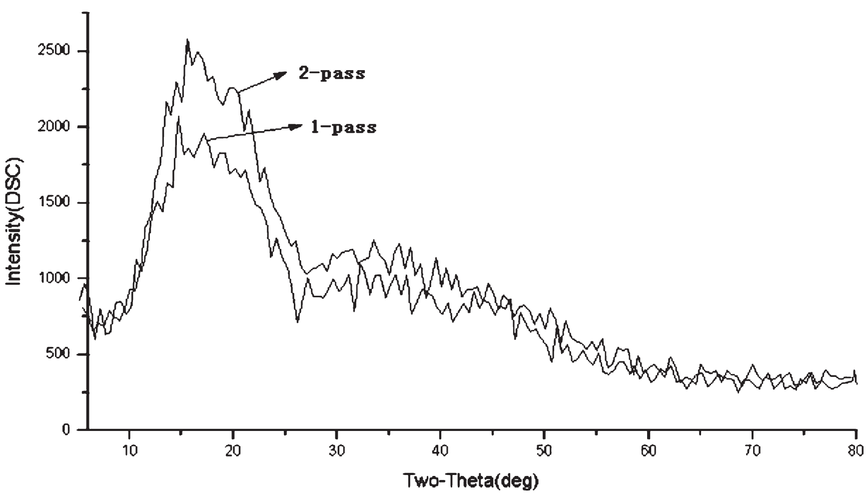


Figure 3.
Wide-angle X-ray diffraction spectra of extruded specimens.

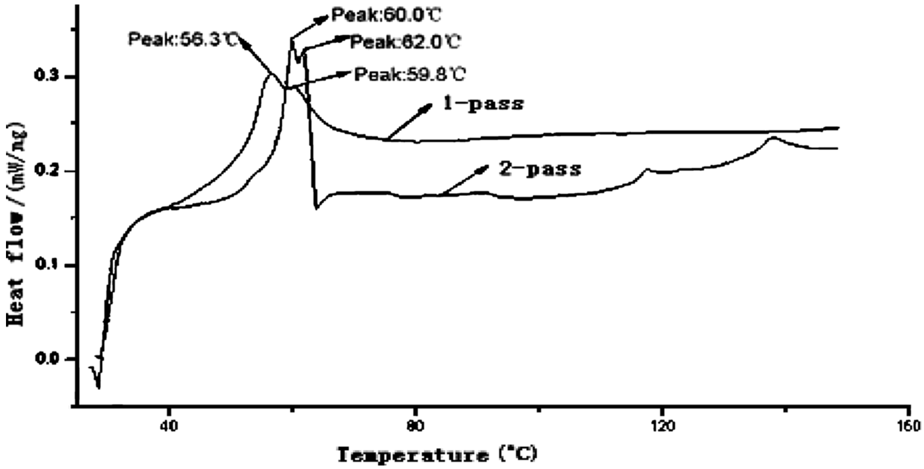


Figure 4.
DSC heating curves for extruded PDLLA specimens.

MPa and 2.3 to 5.8 GPa, representing an increase of 115% and 152% respectively.

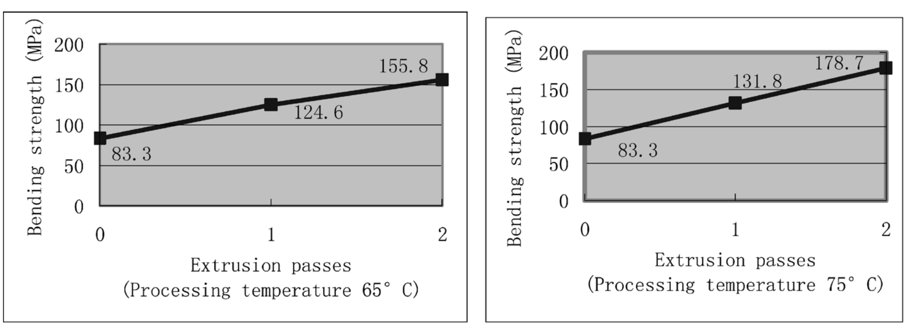
During ECAE, specimens undergo large shear plastic deformation, which orientates the molecular chains and grains and changes the structure. Compared to other processes, ECAE is carried out at a lower temperature, so is better for processing PDLLA and leads to less molecular weight loss.

3. Conclusion

(1) Equal-channel angular extrusion is very effective in increasing the bending strength of poly(DL-lactic acid). Two ECAE passes at 75 °C increased the bending strength of PDLLA from 83.3 to 178.7 MPa.

(2) SEM micrographs showed that the PDLLA interior is a fibrillar structure and thus is suitable for application in bone fracture fixation to prevent brittle fractures.

(3) DSC indicated that with increasing number of extrusion passes, the T_g of PDLLA increased by more than 2 °C, and thus the hot resistance increased. These properties can improve the strength attenuation of PDLLA in the body.



(a) ECAE at 65 °C (b) ECAE at 75°C

Figure 5.
Bending strength of PDLLA under different processing conditions.

The above results clearly show that ECAE processing is effective in changing the morphology. The ECAE process can effectively force the PDLLA structure to undergo orientation. This orientated structure leads to an improvement in the mechanical properties. Further work is needed to determine the best processing conditions under which to perform ECAE of PDLLA.

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