European Polymer Journal 90 (2017) 54–65

Contents lists available at ScienceDirect

European Polymer Journal

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

Structure evolution and orientation mechanism of long-chain-branched poly (lactic acid) in the process of solid die drawing

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ARTICLE INFO

Keywords:
Long chain branched poly (lactic acid) (LCB-PLA)
Solid die drawing
Structure evolution
Orientation mechanism

ABSTRACT

Highly oriented long-chain-branched poly (lactic acid) (LCB-PLA) was prepared and the structure evolution was studied in the process of solid die drawing by compared with poly (lactic acid) (PLA). During drawing, samples underwent not only die drawing process but also free drawing process. Drawing speed presented a prominent effect on the free drawing process, while die thickness showed a more obvious influence on the die drawing process. For PLA, free drawing process mainly contributed to its final orientation degree and crystallinity, and thus the mechanical properties of PLA were greatly influenced by drawing speed. However, for LCB-PLA, die drawing process made a greater contribution to the final orientation degree and crystallinity, and its mechanical properties were mainly affected by die thickness. Under the same drawing condition, the tensile strength and modulus of LCB-PLA were always higher than those of PLA, and reached up to 228 MPa and 7.2 GPa, respectively, which basically met the requirement for born fixation materials. Samples which only underwent die drawing showed obvious "sandwich" structure, and the thickness of the oriented skin layer for LCB-PLA was thicker than that for PLA, suggesting that shear-induced orientation can be easily retained due to the enhanced entanglement between long branched chains. After drawing, LCB-PLA samples showed smaller lamellae size ($L_{lateral}$) but larger long period (L_{ac}) compared with PLA, suggesting that the low chain mobility restricted the motion of chain slipping of LCB-PLA and thus resulted in the fragmentation of neighboring crystal lamella by chain stretched-out.

1. Introduction

Poly (lactic acid) (PLA, $-[CH(CH_3)COO]_n-$), a linear aliphatic thermoplastic polyester which is produced from lactic acid by converting sugar or starch obtained from renewable sources (e.g., corn, wheat, or rice), has been a focus of research during recent decades because of its potential applications in the fields of biomedical products [1]. But the brittleness and unsatisfied mechanical strength of PLA greatly limit its wide applications as bone screws, bone fixation plate, stent and so on.

Molecular orientation can greatly improve the mechanical and physical properties of PLA. Long Yu et al. produced two types of oriented PLA films (one amorphous and one semi-crystalline) by using an extruder and sheet die [2]. The maximum draw ratio was 200%, and the tensile strength and modulus can reach up to 121.1 MPa and 3.9 GPa respectively. Yuan et al. fabricated PLLA fibers through a two-step melt-spinning method (melt extrusion and hot drawing) [3]. During the hot drawing process, the maximum draw

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http://dx.doi.org/10.1016/j.eurpolymj.2017.03.005
Received 22 January 2017; Received in revised form 3 March 2017; Accepted 4 March 2017
Available online 06 March 2017

ratio of 589% and tensile modulus of 3.6–5.4 GPa were obtained for the fiber. PLA fiber was also prepared by Bhuvanesh Gupta et al. by using dry-jet-wet spinning method [4]. The draw ratio plays an important role in the structural development of the fiber and the maximum draw ratio of 1000% was achieved. Anyway, due to the very low viscosity and low melt strength of PLA, ultra-drawing and high orientation for PLA is very difficult, and thus the enhancement of the mechanical property through molecular orientation is limited.

Solid die drawing is an effective way to obtain molecular orientation for polymer in solid phase. During this process, a billet of polymer is heated to a temperature below its melting point before drawn through a fixed shape die by an axial load. Then the billet is constrained to follow the shape of the die, which has a reduced cross section, and therefore it undergoes axial extension. When the billet is drawn out of the die exit, the material also undergoes free drawing and further axial extension of the material occurs. Compared with other orientation processes, such as free solid drawing [5,6] and electrospinning [7,8], through solid die drawing process, not only high production rates and high orientation can be achieved without complex processing apparatus, but thick section samples including tubes, tapes, etc. can also be produced [9,10]. Although the development of the die drawing process on polyolefin is highly successful, die drawing of PLA and its structure evolution during the process have been scarcely reported.

In our previous study, in order to enhance the melt strength and thus obtain high orientation degree, long-chain-branched PLA (LCB-PLA) was prepared through a two-step ring-opening reaction with anhydride and epoxy during processing [11]. The topological structure of LCB-PLA was made of linear chains, star-like chains with three arms and tree-like chains with two generations, and during hot stretching, the maximum draw ratio as high as 1200% can be achieved [12]. Because the molecular entanglements play a key role in shear-/strain-induced orientation and crystallization, the unique molecular architecture of the LCB-PLA provides an opportunity to study its effects on the processing-induced orientation and structure developments.

In this study, highly oriented PLA and LCB-PLA were prepared through solid die drawing technology. The influence of drawing conditions, such as the die thickness and drawing speed, on the microstructure and mechanical properties of LCB-PLA was studied in comparison with PLA. During solid die drawing, sample can be divided into three distinct zones as shown in Fig. 1, including undeformed part (Region I), the part which deformed within the die (Region II) and the part drawn out of the die where a substantial free drawing can occur (Region III). Because the structure evolution of sample was quite different in the above mentioned three regions, it is necessary to discriminate the contributions of die drawing and free drawing outside the die to the formation of oriented structure of LCB-PLA and PLA during die drawing processing.

2. Experimental section

2.1. Materials

Poly (lactic acid) (PLA) (NatureWorks® PLA Polymer 3052D) was supplied by Nature Works Co., USA. The molecular weight (M_w) was about 1×10^5 and the molecular weight distribution index (M_w/M_n) was about 1.21. Pyromellitic dianhydride (PMDA)(AR) was obtained from Sinopharm Chemical Reagent Co. Ltd, China. Pentaerythritol polyglycidyl ether (PGE) (AR) was obtained from Energy Chemical Reagent Co. Ltd, China.

2.2. Preparation of highly oriented LCB-PLA

LCB-PLA was prepared according to our previous work. After dried at 70 °C for 5 h in a vacuum oven, PLA pellets were added in a Haake internal melt mixer (Rheocord 90, Germany) at 180 °C. When they were totally melted, PMDA was added to react with PLA for several minutes, and then PGE was added into the mixture. After mixing for about 50 min, the reaction was completed and the

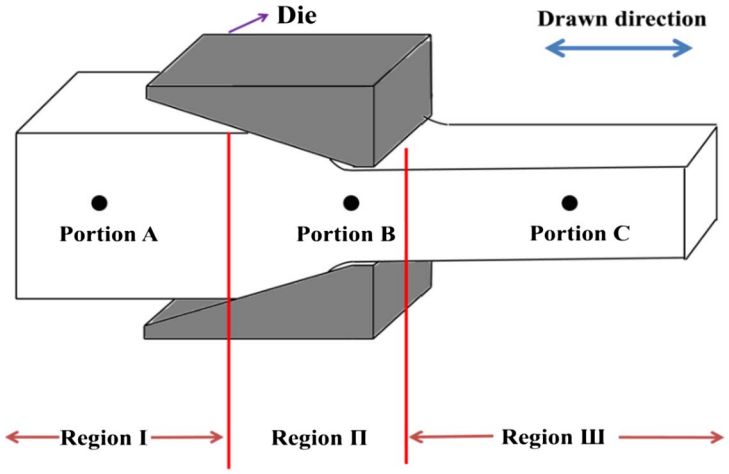

Fig. 1. Schematic diagram of PLA samples drawn through a die.