Simultaneously Toughening and Strengthening of PLA-b-PCL Copolymer via Pressure-induced-flow Processing at Room Temperature

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Abstract. Biodegradable but brittle polylactide (PLA) can be toughened by copolymerizing with poly caprolactone (PCL). However, the tensile strength and Young’s modulus dramatically decrease compared with pure PLA. On the other hand, melting processing is normally applied for most plastics at relatively high temperatures and may lead to substantial degradation of polymers like PLA-b-PCL copolymer. In this study, we adopted pressure-induced-flow (PIF) processing to manufacture PLA-b-PCL copolymer specimens at room temperature of ~30 °C. Impact toughness, tensile strength and Young’s modulus were simultaneously increased by about 19 %, 151 % and 107 % respectively, when compared with the samples processed via injection moulding. We attributed the remarkable improvements to the multi-layered morphologies generated during PIF-processing which are parallel to the flowing direction. Moreover, the molecular weight and all mechanical properties for PLA-b-PCL were well preserved at such low processing temperature after being reprocessed for ten times.

1. Introduction
Polylactide (PLA), produced from renewable resources, has attracted intensive research attention because of its excellent properties and promising perspective to be alternative of current petroleum-based plastics. However, the application is limited by its intrinsic brittleness, elevated price and degradation during recycling [1-5]. Polycaprolactone (PCL) attracts great interest mainly due to its lower cost and higher toughness than other biopolymers [6-9]. Therefore, through last two decades, toughening PLA by blending or copolymerizing with PCL has become the most promising direction to expand applications of both polymers [10-12]. Previous studies have demonstrated that, generally, with the content of PCL increasing, the toughness of PLA-b-PCL copolymer was improved effectively,
but the tensile strength and Young’s modulus decreased dramatically [13-17]. For this reason, many studies have been dedicated to modify hierarchical structures by tuning types and fraction of component or solidification of each block [18-22]. However, the contradiction between enhanced toughness and impaired strength and modulus always existed.

Pressure-induced-flow (PIF) processing has been demonstrated to be an effective method to enhance together the toughness and strength of semi-crystalline and amorphous polymer, such as toughening of polypropylene (PP) [23] and high impact polystyrene (HIPS) [24]. In addition, the PIF-processing temperature has been adopted slightly beyond glass transition temperature of the material, but much lower than the melting temperature. Therefore, such relatively low temperature processing method shows great advantage in maintaining properties of degradable polymers, such as PLA-b-PCL. Taniguchi et al [25] revealed that PLA-b-PCL showed room temperature processability under hydraulic pressure of 34.5 MPa without polymer degradation. They proposed a greater hard block composition led to a higher modulus, a higher stress-at-break and a lower strain-to-break. However, they did not mention the effect of either pressure or reprocessing times on mechanical properties of PLA-b-PCL.

In this paper, we employed low temperature pressure-induced-flow (PIF) processing to enhance the toughness of PLA-b-PCL and simultaneously avoid sacrificing of tensile strength and Young’s modulus. Moreover, such processing technique can be repeated for more than 10 times without significant degradation and deterioration of mechanical properties for PLA-b-PCL copolymer.

2. Experimental procedure

Materials: PLA-b-PCL copolymer was synthesized according to Ref [20]. Weight average molecular weight ($M_w$) and number average molecular weight ($M_n$) is 150,000 and 80,000 g/mol, characterized by GPC. Content of PCL was about 30 wt.%; PCL ($M_n$ ~ 10000 g/mol), was purchased from Guoyao Chemical Agentia Company of China.

Sample preparation: PLA-b-PCL powder was fitted into the channel-die used in successive PIF-processing [26] (as shown in figure 3a). The PIF-processing was conducted with a compressive equipment at room temperature of about 30°C under a certain pressure (in a range of 150MPa to 550MPa) for 10 minutes. In reproduced samples, PLA-b-PCL specimens were cut into fragments and then formed again by PIF-processing. In all studied samples, no stress whitening or shear band observed through optical microscope observation. Cavitation that frequently observed during stretching was also suppressed due to side constraints according to Ref [27].

Measurements: Notched Izod impact strength test was carried out on a Ceast Pendulum Impact Tester (CEAST RESIL6957 Impactor, Italy), following the standard of ISO-180-2000. Tensile strength test was performed on the Universal Tensile Machine (WDW-20, Shanghai, China) at a cross head speed of 20 mm/min (according to ISO 527). Scanning electron microscope (SEM) (JSM-5600LV, JEOL) was used to observe fracture surface of samples. The weight-average molecular weight and polydispersity were determined by Gel permeation chromatography (GPC), using THF as a mobile phase at a flow rate of 1.0 ml/min, and the column temperature was 35 °C.

3. Results and discussion

3.1 The effect of pressure on mechanical properties and morphologies
Figure 1. Impact of PIF-processing pressure on mechanical properties of PLA-b-PCL (30 wt. % PCL content) copolymer with and without PIF-processing: (a) impact strength, (b) tensile strength, (c) Young’s modulus and (d) strain. (The samples were all processed at 30 °C for 10 min.)

The mechanical properties of PLA-b-PCL copolymer with and without PIF-processing are shown in figure 1. In general, there is a conflict between toughness and strength, which means that by a single processing, the toughness increasing with loss of tensile strength [27]. Here, the PIF-processing method is suggested to be a promising technique that can enhance toughness and strength simultaneously, which is extremely essential for expanding application field of biomaterials. It can be seen that the toughness of PLA-b-PCL copolymer increased by 190 % indicated by the impact test (as shown in figure 1a). Simultaneously, tensile strength, Young’s modulus and tensile strain increased by 151 %, 107 % and 92 % respectively (as shown in figure 1b, c, d) compared with PLA-b-PCL specimens processed via injection moulding. In addition, PIF-processing was performed at lower processing temperature (~30 °C), which may be important to avoid significant degradation problem during processing compared with traditional melt processing.

Impact post-fractured surface of PLA-b-PCL copolymer (30 wt. % PCL content) with and without PIF-processing were studied by SEM, as shown in figure 2. The fractured surface of injection molded samples exhibited smooth and isotropic morphologies. However, after PIF-processing, the fractured surface showed rougher features compared with the original as shown in figure 2a. Many of oriented grooves along flow direction (FD) can be found, furthermore grooves became deeper and longer with higher pressure as shown in figure 2(b, c, d), which indicated that more energy was dissipated upon impact. Such oriented grooves along FD implied that oriented structures were generated during PIF-processing. According to our previous researches on PP [26] and PLA/PEG blends [28], with PIF-processing, crystalline lamellae fractured and subsequently reoriented along FD direction.
3.2 The effect of repeating processing times on molecular weight and mechanical properties

In order to investigate on the maintenance of molecular weight and mechanical properties for PLA-b-PCL copolymer during PIF-processing, we conducted a series of repeating processing (as shown in figure 3a). The PLA-b-PCL copolymer was first cut into fragments (as shown in figure 3b) and then was reprocessed via exactly the same PIF-processing. The pieces of PLA-b-PCL were not transparent, but it showed good transparency after reprocessing as shown in figure 3c. After recycled for ten times, the copolymer is still processable at ambient temperature.

The molecular weight and mechanical properties of reprocessed samples were studied in figure 4. The results showed that with increasing reprocessing times the weight-average molecular weight (Mw) reduced slightly and polydispersity gradually broadened (see figure 4a). Mechanical properties including impact strength, tensile strength and Young’s modulus are shown in figure 4(b, c, d) respectively which showed only modest and negligible decline. It indicated that PLA-b-PCL copolymer reprocessed by PIF-processing maintained good mechanical performances and the plastic was fully recyclable. Similar outstanding material has been denominated as baroplastic owing to its excellent processibility under low temperature [29].

![Figure 2](image)

**Figure 2.** Impact post-fracture surface of PLA-b-PCL copolymer (30 wt. % PCL content) with and without PIF-processing characterized by SEM: (a) original sample, (b, c, d) samples via PIF-processing under the pressure of 240, 440, 540 MPa respectively.

![Figure 3](image)

**Figure 3.** Reprocessed copolymer samples (30 wt. % PCL content). (a) schematic diagram of PIF-processing, (b) sample pieces after being cut, (c) the samples reprocessed for 2, 4, 6, 8, 10 times respectively. (The samples were all processed at 30 °C under 440 MPa for 10 min.)
Figure 4. The molecular weight, polydispersity and mechanical properties of PLA-b-PCL (30 wt. % PCL content) copolymer after cutting and reprocessing. (a) molecular weight and polydispersity, (b) tensile strength, (c) Young’s modulus and (d) impact strength versus PIF-processing times. (The samples were all processed at 30 °C under 440 MPa for 10 min.)

4. Conclusions
The impact toughness of PLA-b-PCL was enhanced notably via a physical pressure-induced-flow (PIF) processing at relatively low temperature of ~30°C (much below $T_m$). Simultaneously, the tensile strength and Young’s Modulus were not sacrificed but also got a raise, which might expand the application of PLA-b-PCL. Furthermore, the PLA-b-PCL copolymer samples were able to reprocess for ten times without significant decrease of molecular weight or mechanical properties. Such unique behavior may reduce the cost of manufacturing of polymers, avoid serious degradable problems in processing and promote recycling of materials.

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