Materials Today: Proceedings 70 (2022) 531–534

Contents lists available at ScienceDirect

Materials Today: Proceedings

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

Fabrication of flexible, and bioresorbable poly-L-lactide acid piezoelectric material with tunable properties

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ARTICLE INFO

Article history:
Available online 18 October 2022

Keywords:
PLLA
Piezoelectric materials
Bioresorbable devices
Printed Electronics

ABSTRACT

There is a clinical need for the development of sensors to measure buildup of pressure on organs, as it is indicative of many underlying ailments. However, electronic devices need to be flexible, and have low Young's modulus to be compatible with human tissues. Although many advances have been made in bioresorbable devices making these devices with safe materials and simple processes remains a challenge. Here, we propose a simple and scalable method of fabricating biocompatible as well as bioresorbable piezoelectric poly-L-lactide acid (PLLA) based films. Films which will be used to fabricate force sensors. Our strategy focuses on material processing to improve crystallinity and orientation of polymer chains to achieve a good piezoelectric response.
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1. Introduction

Monitoring and measuring vital physiological pressures are crucial for monitoring health status and preventing build-up of threatening forces inside organs such as the brain, bladder, heart, etc. Here, in many instances, pressure sensors must be implanted and directly integrated with native soft tissues and organs. To avoid invasive removal surgeries that may cause tissue damage to directly interfaced tissues, devices should be flexible and at the same time biocompatible- and degradable. Due to this huge mismatch between Young's moduli of soft tissues and rigid components, it is a major limitation for current biomedical devices [1,2]. Furthermore, the use of force sensors inside the human body puts stringent requirements on electronics. Therefore, modern piezoelectric biosensors are constructed using new state-of-the-art biodegradable and bioresorbable materials such as PLLA. These are fabricated by advanced microfabrication techniques to avoid toxicity compared to conventional lead-based piezoelectric materials. Biodegradable and bioresorbable electronics involve using materials that are nontoxic, nonimmunogenic, and can be broken down into smaller units over time, leaving behind benign residues. Thus, electronics exhibit transient behavior by serving their function for a prescribed time before being broken down. A key opportunity exists to develop biodegradable electronic materials that can be employed for fabricating flexible and soft biomedical devices.

One of the most promising materials is PLLA. Due to PLLA's biocompatibility, biodegradability, and piezoelectric properties, it has been widely used in medical applications [3]. Its most exciting application relates to the promotion of cell migration, differentiation, growth, protein-surface interaction, and piezoelectricity [4,5]. The piezoelectric properties of PLLA are caused by the internal polarization of the material. Thus, the piezoelectric effect is caused by the molecular structure of the polymer and its orientation. When PLLA undergoes drawing or elongation, it has been shown to exhibit shear piezoelectricity [6]. Due to this internal polarization, PLLA does not require pooling. However, the piezoelectric performance of devices made from PLLA is inferior to devices made from other piezoelectric materials like PVDF. Therefore, research efforts have been focused on enhancing the piezoelectric activity of the material by utilizing methods like electrospinning [7], compression molding [8], and deriving mechanical models based on the constitutive shear (ref). However, all these methods require expensive equipment and lengthy processes. [6,8].

Herein, we demonstrate an easy, scalable, and cost-efficient processing strategy for enhancing the crystallinity and hence the performance of PLLA material. We also study morphology and crystallinity changes caused by this processing.

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https://doi.org/10.1016/j.matpr.2022.09.553
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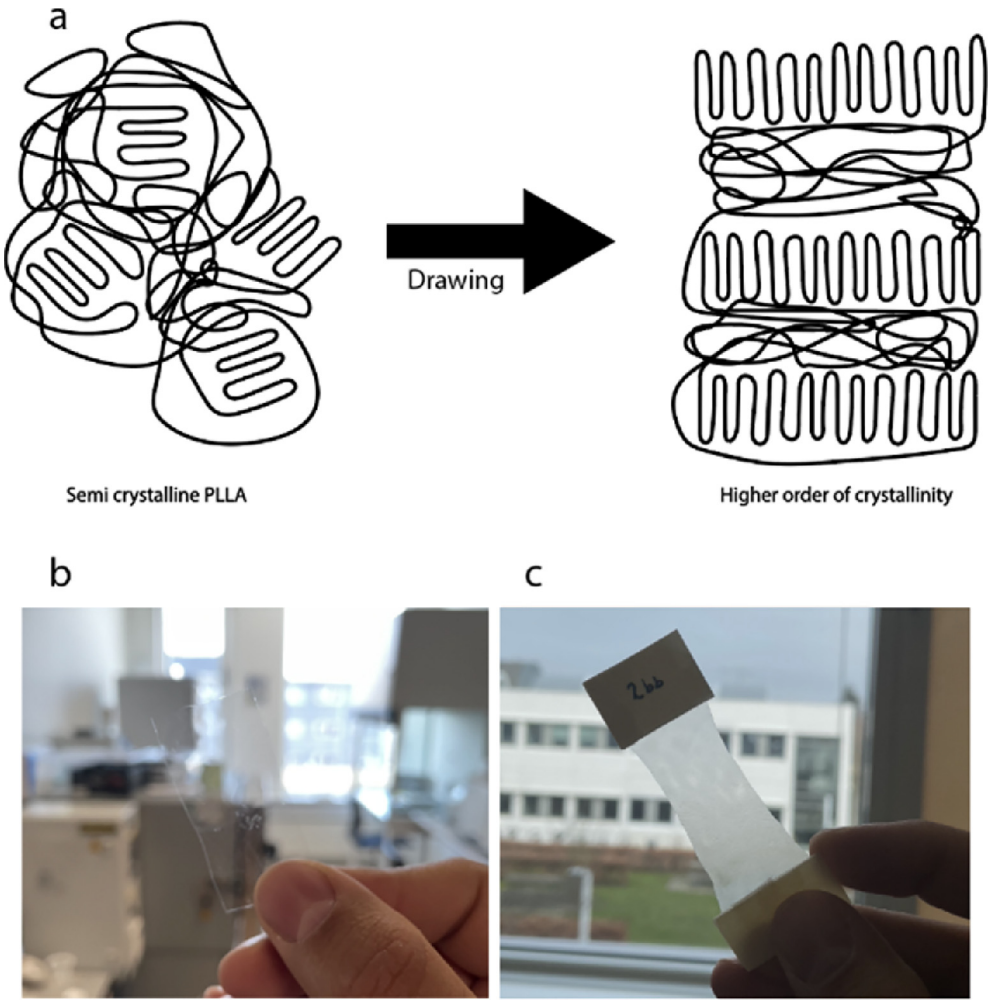

Fig. 1. (a) An illustration showing the micromolecular changes caused by the drawing process in PLLA polymer. (b)Images showing (b) as-synthesized and (c) drawn PLLA films with change in optical transparency.

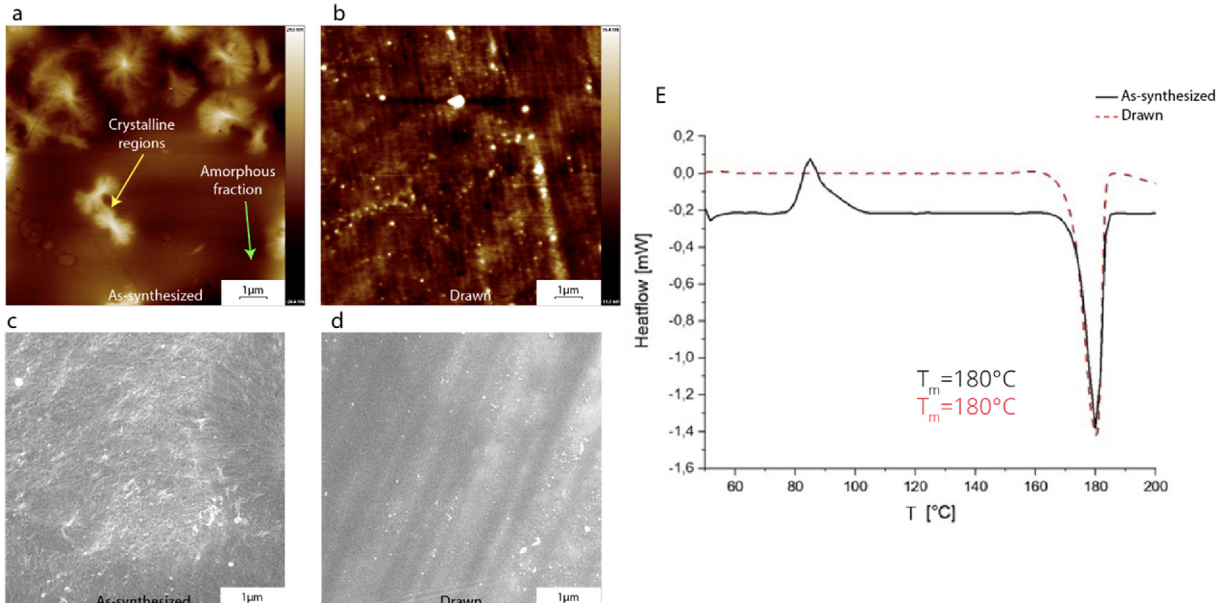

Fig. 2. AFM image of the as-synthesized (a) and drawn (b) PLLA film. SEM image of the (c) as-synthesized (d) and drawn PLLA film. (e) DSC thermograms of drawn (DR = 3) and as-synthesized PLLA films (heating rate of 10 °C /min).

Table 1
Thermal characteristics and crystalline content of drawn (DR = 3) and as-synthesized PLLA films (heating rate of 10 °C /min).

Sample	T_g [°C]	Tm [°C]	ΔH_f [J/g]	Xc [%] (±Std)
As-synthesized PLLA film	79.74	180	−35.86	28.43 (±1.52)
Drawn PLLA film (DR = 3)	–	180	−47,95	41.15 (±2.80)

2. Materials and method

The PLLA granules were purchased from Corbion (PURASORB PL 24) and dried at 80 °C in a vacuum oven overnight. 10 g of PLLA granules were dissolved in 50 g of chloroform (Merck). The mixture was stirred for 4 h at room temperature. After complete dissolution, the container was stored in a fridge overnight at 4 °C to prevent bubble formation. The cold solution was poured into a glass Petri dish and left to dry for 4 h at room temperature. The casted PLLA film was then peeled off from the cast and cut into rectangular pieces of 24x40 mm. Following this step, the precut films were uniaxially drawn to a draw ratio (DR) of 3. The films were then fixed and annealed for 8 h at 90 °C. Later, the films were quenched in an ice bath for 2 h. The atomic force microscopy (AFM) images were obtained using Bruker Dimension Edge atomic force microscope. Here, the film was taped to a firm substrate using double sided tape, to ensure good contact to the AFM stage. The scanning electron microscope (SEM) images were obtained using FEI Magellan 400 SEM. A 5 nm Ti coating was applied using Cryofox Explorer 500 GLAD to enhance the quality of the images obtained by SEM. Differential Scanning Calorimetry (DSC) was done using DSCM Toledo, USA.

3. Results and discussion

The piezoelectricity is proportional to the product of the crystalline content (X_c) and orientation coefficient (Fc) of the polymer. Drawing is a common processing technique used for polymers to achieve higher crystalline content [9]. To accommodate the extension caused by drawing, the amorphous fraction of the material will tend to align with direction of the drawing. This also realigns any crystalline regions embedded within the amorphous matrix, as illustrated in Fig. 1a. Images of the PLLA film before and after uniaxial drawing are shown in Fig. 1b and c. It can be observed that the transparent and as-synthesized PLLA film transforms to an opaque film due to the alignment of the amorphous fractions into a higher order of crystallinity. The transition of the transparency in the film can be explained by surface scattering. The crystallinity in the film affects the optical transparency because of the scattering taking place when light passes from amorphous to crystalline regions [10,11]. Thus, change in optical transparency of PLLA films indirectly confirms that processing of films through uniaxial drawing leads to higher crystallinity.

To understand the transformation of PLLA films after the drawing process, AFM and SEM were used. The semicrystalline nature of the as-synthesized PLLA film is observed in Fig. 2a. Both amorphous and crystalline regions can be distinguished as labelled. A clear morphological change is observed after the drawing process as seen in Fig. 2b. The amorphous and crystalline regions have merged with no clear boundaries. The observed parallel grain boundaries, indicate alignment with the drawing direction. SEM micrographs are shown in Fig. 2c and d. In Fig. 2c, the semicrystalline nature of PLLA is seen. Although, it was not easy to distinguish the amorphous from crystalline regions. This could be due to the coating layer applied to the surface before imaging, resulting in less structure details. Although a clear change in morphology after treatment was observed SEM. Here, the same grain boundaries are observed in Fig. 2b is seen in Fig. 2d.

DSC provides a rapid method for determining polymer crystallinity based on the heat required to melt the polymer. The DSC analysis for the as-synthesized and drawn films is shown in Fig. 2e. the as-synthesized PLLA film exhibits both glass temperature (T_g) and melting temperature (T_m), due to the semicrystalline structure of the material. The presence of T_g and T_m in the DSC diagram confirms the semicrystalline nature of PLLA. However, after processing only T_m is present, due to annealing process (90 °C). This indicates that PLLA can be crystallized. Therefore, the crystalline content (X_c) was calculated for both the drawn and as-synthesized PLLA film to quantify the crystalline changes due to the processing (Table 1.). The calculation is done by calculating ΔH_f from the data obtained by the DSC and used in the following equation:

$$X_C(\%) = (\Delta H_f / \Delta H_f^o) \cdot 100$$

[12].

Here, ΔH_f is the calculated heat of fusion (see tab.1) and ΔH_f° is the heat of fusion for the 100 % crystalline form of PLLA. From this, we calculated an increase in crystallinity from 28.48 % to 41.15 % for DR = 3.

4. Conclusions

We presented a strategy for material processing to increase the crystalline content of the PLLA films. The developed process is easy, scalable, and cost-efficient. The crystalline content was obtained by DSC measurements and the changes were calculated. Here, a clear change in thermal behaviour of the drawn and as-synthesized PLLA was seen and the crystalline content (X_c) showed an increase of 12.72 %. To support these changes, the morphological changes were studied using AFM and SEM.

CRediT authorship contribution statement

Youssif Merhi: Conceptualization, Data curation, Formal analysis, Writing – original draft, Writing – review & editing. **Shweta Agarwala:** Conceptualization, Writing – review & editing.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The project is funded by Independent Research Fund Denmark Grant 1032-00182B on Bioresorbable Force Sensor using Biodegradable Piezoelectric Material. We thank Hamed Abdolmaleki for his help in carrying out DSC measurements.

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