THz Spectroscopy Analysis of Crystallinity Optimization for Enhanced Piezoelectricity in Biodegradable Poly-L-Lactide Acid

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Abstract— *Our research delves into both the fabrication and analysis of biodegradable Poly-L-Lactic Acid (PLLA) films. Specifically, we investigate how stretching impacts the piezoelectric properties of PLLA films. By employing advanced techniques such as Terahertz Time-Domain Spectroscopy (THz-TDS), we aim to unveil previously undiscovered aspects of PLLA's behavior under strain. This includes quantifying changes in crystallinity and observing alterations in piezoelectric responses and absorption spectra. Our study not only emphasizes the fabrication of PLLA as a biodegradable material but also explores its piezoelectric performance, involving methods such as inducing strain and measuring the piezoelectric output. Through this multifaceted approach, we strive to contribute to the progression of sustainable biomaterials and the design of innovative biomedical devices.*

Keywords—component; formatting; style; styling; insert ***(****PLLA, biomedical applications, THz-TDS, Piezoelectric****)***

I. Introduction

Poly-L-Lactic Acid (PLLA) has attracted significant attention in the field of biomaterials due to its biodegradability and notable piezoelectric properties, positioning it as a promising candidate for diverse biomedical applications, including the development of biodegradable piezoelectric sensors. Notable studies within this domain have highlighted PLLA's potential in sensor fabrication. Here, Yousry, Y.M. et al. Developed a Shear Mode Ultrasonic Transducers derived from Flexible Piezoelectric PLLA Fibers for Structural Health Monitoring [1]. This research exemplifies PLLA's capacity for creating flexible and biocompatible sensors tailored for structural integrity assessment. Additionally, Curry, E.J., et al. contributed to this field by developing a Biodegradable Piezoelectric Force Sensor based on PLLA [2]. Their study further underscores PLLA's versatility in the fabrication of biocompatible sensors capable of measuring mechanical forces in biomedical contexts. These examples highlight the various applications enabled by PLLA's unique properties, showcasing its potential for advancing biomedical technology. Although PLLA holds promise for various applications, it's crucial to grasp how mechanical treatments affect its crystalline structure and piezoelectric behavior [1, 3-5]. This understanding is vital for fine-tuning PLLA's performance to meet practical application needs. In this study, we delve into the enhancement of PLLA's piezoelectric properties through a controlled uniaxial drawing process following solvent casting, aiming to fabricate PLLA films tailored for specific biomedical needs.

The synthesis of PLLA films through solvent casting, followed by mechanical treatment, represents a simple approach for biomaterial engineering, offering opportunities to modulate material properties for enhanced performance in biomedical devices. Previous studies have investigated various methods to enhance PLLA's piezoelectric response, contributing valuable insights into the material's behavior under mechanical stimuli [2, 6]. However, while these studies have provided significant advancements, further exploration is warranted to fully elucidate the complex relationship between mechanical treatments, such as controlled uniaxial drawing, and PLLA's crystalline structure. This ongoing research endeavor aims to deepen our understanding of PLLA's piezoelectric properties and their modulation for biomedical applications [1, 2].

This study seeks to address the following questions: How do different mechanical treatments, particularly controlled uniaxial drawing, affect the crystalline structure and piezoelectric properties of PLLA films? What insights can be gained from Terahertz Time-Domain Spectroscopy (THz-TDS) regarding the molecular dynamics and structural alterations induced by mechanical stretching?

Understanding the relationship between mechanical treatments and PLLA's piezoelectric behavior is crucial for the development of advanced biomedical devices with improved performance and longevity. By elucidating the structural changes underlying PLLA's piezoelectric response, this study contributes to the optimization of PLLA-based materials for applications ranging from tissue engineering to biomedical sensors.

II. Experimental Section

Poly-L-Lactic Acid (PLLA) granules, PURASORB PL 24 from Corbion, were dried overnight at 80°C before use. Chloroform served as the solvent for PLLA dissolution. For PLLA film preparation, 10 grams of PLLA granules were dissolved in 50 grams of chloroform and stirred for 8 hours at room temperature. The solution was refrigerated overnight. While cold, the solution was poured into a Petri dish, the solution was air-dried overnight. The resulting PLLA film was cut into rectangular pieces (50x50 mm) and subjected to uniaxial drawing with draw ratios of 50-100%. After stretching, the films were thermally treated at 90°C for 8 hours and then quenched in an ice bath for 7 hours. The combined thermal treatment and quenching process serve to optimize the mechanical performance and structural integrity of the PLLA films, ensuring their suitability for various biomedical applications.

THz-TDS analysis was performed using the Toptica TeraFlash system, which covers a THz spectrum from 0.1 THz to 6 THz. To ensure consistent conditions, all samples were introduced into the system after purging with dry air to reduce relative humidity. The THz spectrum of each sample was recorded at room temperature, with dry air as the reference. Each measurement consisted of 1000 averages within a 200 µs time window.

Initially, each of the respective strained films was cut at a 45-degree angle from the strain direction before conducting the cyclic strain test. Using the ESM303 MARK-10 apparatus, each sample underwent 30 strain cycles, maintaining a consistent 10% strain throughout. Precise measurements of voltage and current outputs were conducted using the Keithley 6517B electrometer.

III. CRYSTALINITTY ANALYSIS USING THZ-TDS

Our study investigates the intricate relationship between molecular dynamics and optical responses, focusing on absorption spectra and refractive index using THz-TDS. The refractive index exhibits a direct correlation with applied strain during uniaxial stretching, indicating the film's responsiveness to molecular changes triggered by stretching (Figure 1A), including alterations in crystal, dipole orientation, and refractive index variations. These changes reflect the extent of birefringence induced by mechanical stress, with unprocessed films maintaining a more consistent refractive index, suggesting isotropy [7, 8].

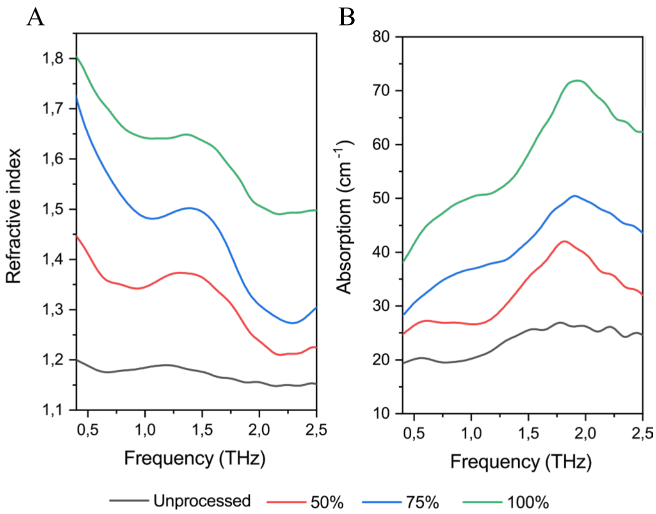

Figure 1 A) refractive index and B) absorption spectra of unprocessed, 50%, 75%- and 100% strained samples parallel to the electric field polarization.

Additionally, our analysis extends to absorption spectra obtained through THz-TDS, revealing distinctive peaks dependent on sample crystallinity (Figure 1B). Here, we observe a subtle red shift in the peak position, transitioning from 1.82 THz (in the 50% strained sample) to 1.91 THz in both the 75% and 100% strained films. Furthermore, a clear correlation between peak sharpness and strain is observed indicating a more specific molecular vibration. Furthermore, these peaks exhibit notable sensitivity to sample rotation, providing insights into angle-dependent behavior under varying degrees of stretching. The absence of discernible peaks in unprocessed samples suggests a uniform molecular arrangement, indicative of reduced crystalline structures and predominantly amorphous composition.

Furthermore, the observed correlation between peak intensity and applied strain in absorption spectra suggests a direct influence of crystallinity changes on the material – indicating a correlation between absorption intensity and the content of crystallinity. This correlation underscores the understanding that higher levels of crystallinity lead to enhanced piezoelectric output, a well-established phenomenon corroborated by previous research and theoretical considerations [9].

IV. PIEZOELECTRIC PERFORMANCE INDUCED BY STRAIN

Building upon the foundational insights from our crystallinity optimization analyses, our research further investigates piezoelectric performance, specifically focusing on studying the piezoelectric output resulting from applied strain, Figure 2. Through comprehensive studies, we enhance the existing understanding and provide valuable perspectives on how these materials behave in real-world applications.

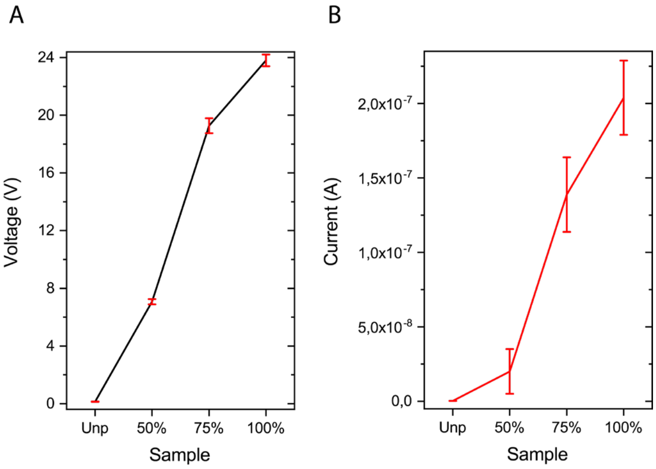

Figure 2 Both A) Voltage and B) Current output due to applied strain of unprocessed, 50%, 75%- and 100% strained samples. Both the voltage and current values are an average of 30 cycles.

Similar to the correlation observed with THz spectroscopy, we observe a proportionality between both the voltage- and current output and the applied strain. As depicted in Figure 2A, there is a noticeable increase from 0.14V (±0.012 V) for the unprocessed samples to 7.10V (±0.18V) for the 50% strained samples, followed by 19.28V (±0.52V) for the 75% strained samples, and finally, 23.81V (±0.41V) for the 100% strained samples. These findings are echoed in the current measurements illustrated in Figure 2B. Specifically, we observe a rise from 3.023E-10 A (±6.01632E-11 A) for the unprocessed samples to 2.0032E-08 A (±1.50142E-08 A) for the 50% strained samples, followed by 1.39E-07 A

(±2.50791E-08 A) for the 75% strained samples, and finally, 2.038E-07 A (±2.49191E-08 A) for the 100% strained samples.

V. Discussion

The findings presented in this study shed light on the complex interplay between mechanical strain, crystallinity, and piezoelectric performance in PLLA films. By integrating simple fabrication techniques with advanced analytical methods such as THz-TDS and piezoelectric measurements, we have gained valuable insights into the behavior of PLLA after mechanical strain.

The observed changes in the refractive index and absorption spectra reveal the structural alterations induced by mechanical stretching. Notably, the transition from a more amorphous state to crystalline phases, evidenced by shifts in peak positions and intensities, underscores the importance of crystallinity in determining PLLA's optical and mechanical properties. These findings corroborate previous studies highlighting the significant role of crystalline domains in enhancing piezoelectricity in polymer materials.

Moreover, our study establishes a clear correlation between crystallinity and piezoelectric output, as evidenced by the voltage and current measurements under applied strain. The progressive increase in voltage and current with higher levels of strain suggests that the piezoelectric response of PLLA is directly influenced by its crystalline content. This correlation underscores the potential of controlled mechanical treatments, such as uniaxial stretching, in optimizing PLLA's piezoelectric performance for various biomedical applications.

Overall, our study contributes to the growing body of research aimed at harnessing the unique properties of PLLA for sustainable biomaterials and biomedical device applications. By elucidating the mechanisms underlying PLLA's piezoelectric behavior and its modulation through mechanical strain, we pave the way for the development of innovative and environmentally friendly solutions in healthcare, sensing, and wearable technology.

VI. Conclusion

This research demonstrates the potential of biodegradable PLLA films as versatile materials with tunable piezoelectric properties. Through a combination of simple fabrication techniques, advanced spectroscopic analysis, and piezoelectric measurements, we have elucidated the intricate relationship between crystallinity, molecular dynamics, and piezoelectric performance in PLLA. Our findings underscore the importance of controlled mechanical treatments in optimizing PLLA's properties for biomedical applications, offering new avenues for the design of sustainable biomaterials and biomedical devices. Future research directions may involve further optimization.

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References

1. Yousry, Y.M., et al., *Shear Mode Ultrasonic Transducers from Flexible Piezoelectric PLLA Fibers for Structural Health Monitoring.* Advanced Functional Materials, 2023. **33**(15): p. 2213582.
2. Curry, E.J., et al., *Biodegradable Piezoelectric Force Sensor.* Proceedings of the National Academy of Sciences, 2018. **115**(5): p. 909-914.
3. Curry, E.J., et al., *Biodegradable nanofiber-based piezoelectric transducer.* Proceedings of the National Academy of Sciences, 2020. **117**(1): p. 214-220.
4. Merhi, Y. and S. Agarwala, *Fabrication of flexible, and bioresorbable poly-l-lactide acid piezoelectric material with tunable properties.* Materials Today: Proceedings, 2022. **70**: p. 531-534.
5. Ando, M., et al., *Film Sensor Device Fabricated by a Piezoelectric Poly(L-lactic acid) Film.* Japanese Journal of Applied Physics, 2012. **51**(9S1): p. 09LD14.
6. Lee, S.J., A.P. Arun, and K.J. Kim, *Piezoelectric properties of electrospun poly(l-lactic acid) nanofiber web.* Materials Letters, 2015. **148**: p. 58-62.
7. Zhu, Z., et al., *Study of Crystallinity and Conformation of Poly(lactic acid) by Terahertz Spectroscopy.* Analytical Chemistry, 2022. **94**(31): p. 11104-11111.
8. Wei, L., et al., *Application of terahertz spectroscopy in biomolecule detection.* Frontiers in Laboratory Medicine, 2018. **2**(4): p. 127-133.
9. Hirata, J., et al., *Evaluation of Crystallinity and Hydrogen Bond Formation in Stereocomplex Poly(lactic acid) Films by Terahertz Time-Domain Spectroscopy.* Macromolecules, 2020. **53**(16): p. 7171-7177.