



Unlocking the Secrets of High-Water Barrier Stereocomplex Polylactide Blend Extrusion Films

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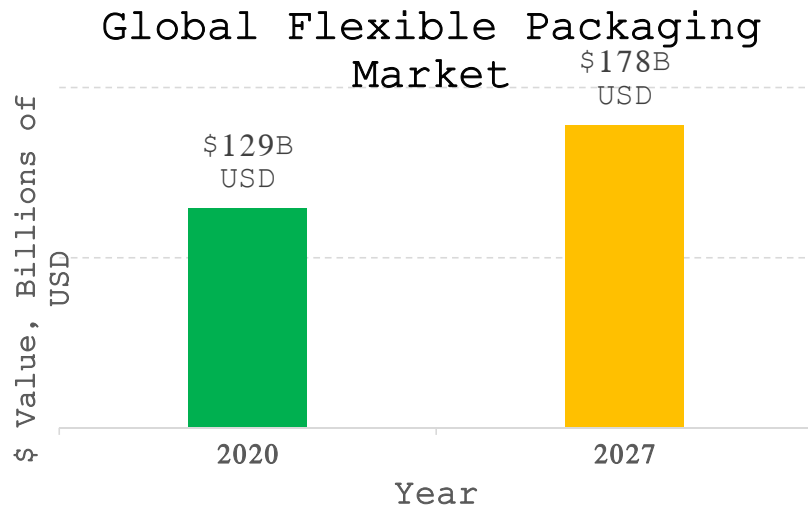


Motivation

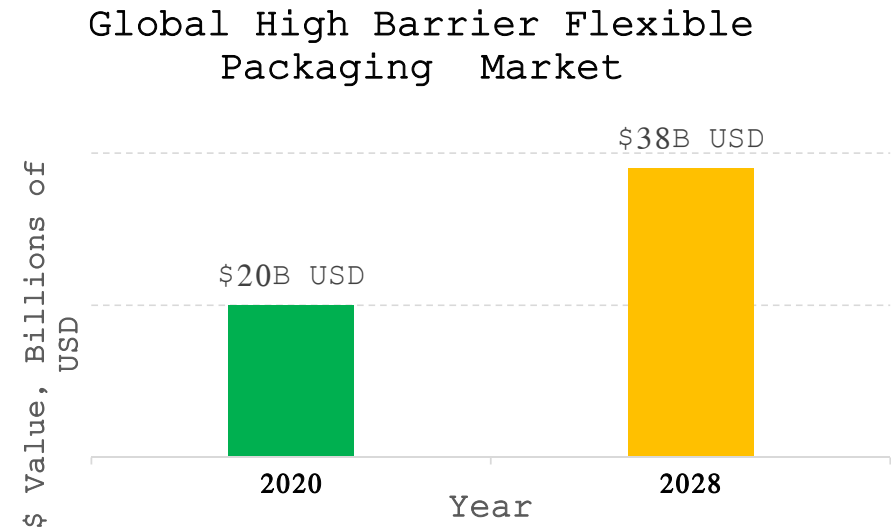
- The flexible packaging market generates tons of waste using single-use plastics.
 - Globally, 139 million metric tons of single-use plastic waste was generated in 2021.
<https://www.cnn.com/2023/02/05/energy/single-use-plastics-volume-grows-climate-intl-hnk/index.html>
- A compostable film with a high oxygen and moisture barrier could help divert soiled single-use plastics to industrial composting.



Background



(Global Packaging Film Market Report 2020, ResearchAndMarkets)



(High Barrier Packaging Films Market Size, Share, Opportunities & Forecast, 2022, Verified Market Research)

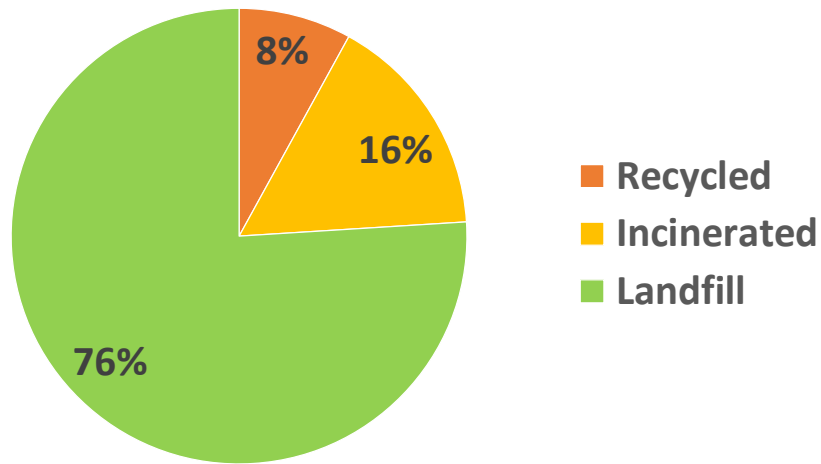
- The US flexible packaging market alone was c. \$34 billion in 2019. (Flexible Packaging Industry Facts and Figures. Available: <https://www.flexpack.org/facts-and-figures>.)
- Non-degradable single-use petrochemical-based plastics dominate the market
 - Concern due to the amount of waste it generates.



Background, cont.

- 36M million tons of plastic waste generated in the US in 2018.
(Flexible Packaging Industry)

Facts and Figures. Available: <https://www.flexpack.org/facts-and-figures.>)



Reproduced from <https://www.pexels.com/photo/close-up-photo-of-plastic-bottles-2547565/>



Background, Compostable Materials



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Reproduced from <https://www.rts.com/blog/what-is-commercial-composting-and-how-can-cities-manage-organic-waste/>

- Two ASTM standards define what can be declared as being compostable.
 - ASTM D6400-21
 - ASTM D6868-21



Background, Compostable Materials

- Examples of commercially available compostable materials

Polymer	Acronym Certified	
Poly(lactic acid)	PLA	BPI, TUV
Polyhydroxyalkanoates	PHA's	BPI, TUV
Cellulose based plastics	-	BPI, TUV
Poly(glycolic acid)	PGA	BPI, TUV
Poly(Butylene Succinate)	PBS	BPI, TUV
Polybutylene adipate terephthalate	PBAT	BPI, TUV
Poly(vinyl alcohol)	PVOH	BPI, TUV

BPI: Biodegradable plastics institute : TUV: TUV Austria



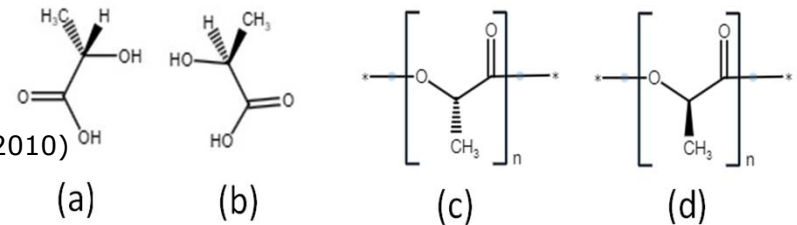
Poly(lactic acid) - PLA

- Compostable polymers are becoming widely used as an alternative to fossil fuel-based polymers.
- Two isomeric forms can be made: L-PLA (PLLA) and D-PLA (PDLA).
 - PLLA is the more predominant of the two.
 - PDLA is mainly used for nucleation or producing sc-PLA.
- Most commercial grades of PLA are based on PLLA.

Barrier Properties

(Chen G. and Steinbuchel A., Eds., *Plastics From Bacteria*. Munster, Germany: Springer, 2010)

- | | | |
|--------|------------|--------------------------|
| • MVTR | 280 - 340 | g/(m ² ·day) |
| • OTR | 590 - 1280 | cc/(m ² ·day) |

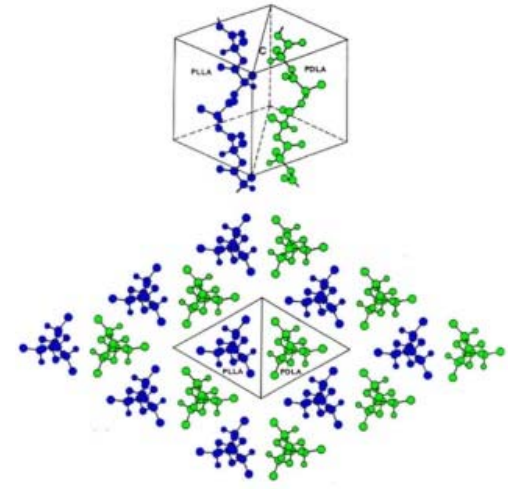


Stereoisomers of L and D lactic acid – (a) L(+)-lactic acid; (b) D(-)-lactic acid; (c) PLLA and (d) PDLA



Stereocomplex PLA (sc-PLA)

- Formed by mixing PLLA and PDLA at specific processing conditions
- Higher melting temperature (230 °C) versus homocrystallite (HC-PLA) (180 °C).
- Improved physical properties over HC-PLA.
- Improved barrier properties over HC-PLA.
 - Not much research has been published.
 - MVTR - 98.1 g/(m²·day)
 - OTR - 283 to 722 cc/(m²·day) for a 25.4-micron film



Reproduced from (Tsuji H., Poly(lactide) stereocomplexes: Formation, structure, properties, degradation, and applications, *Macromolecular Bioscience*, vol. 5, no. 7. Wiley-VCH Verlag, pp. 569–597, Jul. 14, 2005, doi: 10.1002/mabi.200500062.)

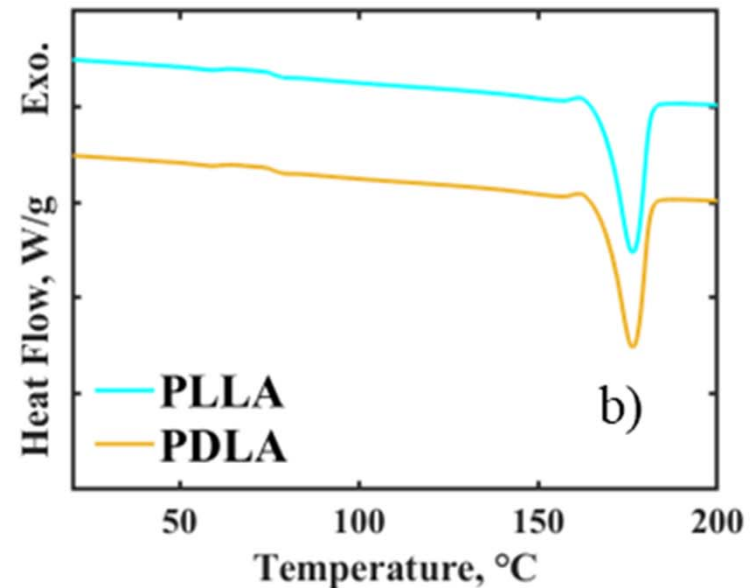
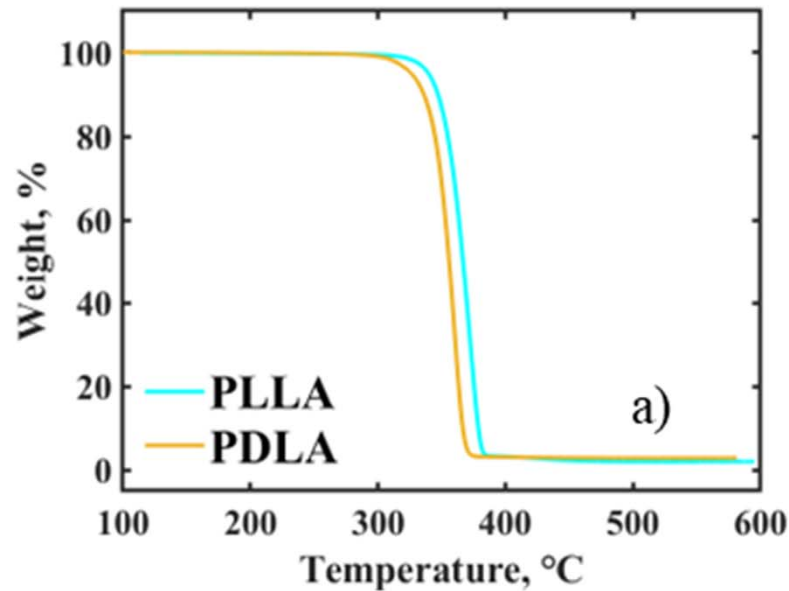


Experimental work

- Resin Data
- Drying
- Extrusion
 - Masterbatch processing - Twin screw extrusion
 - Single screw extrusion
 - PLLA(175K)/PDLA(70K)
 - PLLA(130K)/PDLA(120K)
- Annealing



Resin data



a) TGA of PLLA (130K) and PDLA (120K) resin b) DSC of PLLA (130K) and PDLA (120K) resin



Resin data

Thermal Properties	PLLA (175K)	n	PDLA (70K)	n
$T_{d,1\%}$, °C	318.0 ± 4.5	3	314.4 ± 1.4	3
T_g , °C	77.6 ± 0.6	3	74.8 ± 0.3	3
T_m , °C	177.4 ± 0.5	3	176.5 ± 1.3	3
X_c , %	37.4 ± 8	3	55.9 ± 19.2	3
Melt Flow Rate, g / 10 min (190C/2.16 Kg)	3.5 ± 0.3	8	10 ± 0.9	8
Physical Properties				
Density, g/cm ³	1.25 ± 0.00	9	1.24 ± 0.00	9
M_w , kDa	157.4 ± 6.0	6	37.9 ± 3.1	6
M_n , kDa	86.6 ± 7.2	6	22.4 ± 1.6	6
$\bar{D}$	1.7 ± 0.0	6	1.8 ± 0.1	6

Note: n indicates the number of samples



Resin Drying

Conditions

- 60-80 °C
- 24-30 in Hg
- Min 12 h





Masterbatch Processing



Crystallized in the die during processing.



PLLA(175K) / PDLA(70K) Film



Too high of a processing temperature – could not form a film. (~230 °C)



PLLA(175K) / PDLA(70K) Film



Too low of a processing temperature – could not form a film. (~170-175 °C)



PLLA(175K) / PDLA(70K) Film



Solidified resin in
the extruder





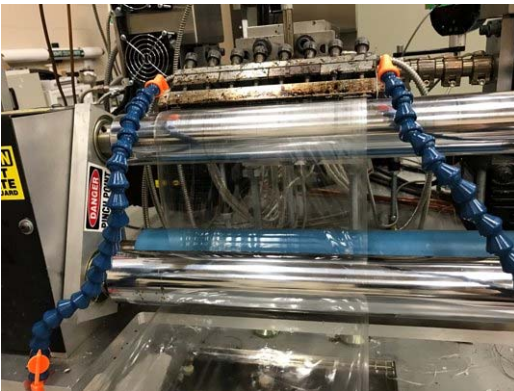
Resin data

Thermal Properties	PLLA (130K)			n	PDLA (120K)			n
$T_{d,1\%}$, °C	302.9	±	5.3	3	319.3	±	5.1	3
T_g , °C	73.9	±	0.8	3	71.9	±	6.6	3
T_m , °C	176.2	±	0.5	3	179.4	±	1.2	3
X_c , %	30.3	±	1.2	3	29.5	±	4.8	3
Melt Flow Rate, g / 10 min (190C / 2.16 Kg)	12.1	±	1.5	13	12.2	±	1.8	13
Physical Properties								
Density, g/cm ³	1.25	±	0.00	19	1.25	±	0.00	12
M_w , kDa	120.0	±	0.42	6	101.0	±	0.4	6
M_n , kDa	70.0	±	1.1	6.0	58.9	±	1.1	6
$\bar{D}$	1.7	±	0.0	6	1.7	±	0.0	6

Note: n indicates the number of samples



- **PLLA,**
- **PLLA/PDLA (85 / 15, 70 / 30, 50 / 50, 30 / 70),**
- **PDLA**
 - Cast extruded on micro extruder in the pilot plant



Cast extruder die section



Cast extruder flow direction



Cast extruder rewind



Processing Conditions

Processing temperatures	Temperature (°C)
Zone 1	210
Zone 2	220
Zone 3	230
Transfer tube	230
Adapter	230
Feedblock	220
Die	215
Chill Roll	22
Extrusion Settings	Speed (RPM)
Screw	25
Chill roll speed	10 to 20

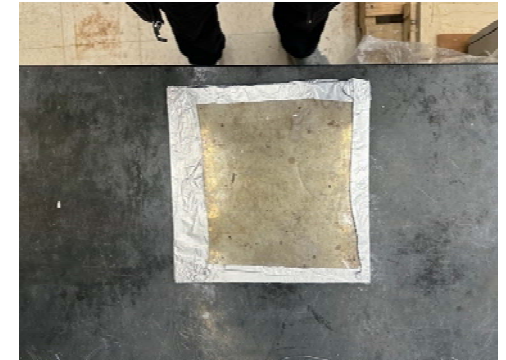


Annealing in a compression molder

- 160 °C



- No pressure applied
- Varying time (5,15,30 min)





Results

- UV transmission
- DSC/WAXD
- Tensile stress versus strain
- Moisture Vapor Permeability coefficient (MVPC)

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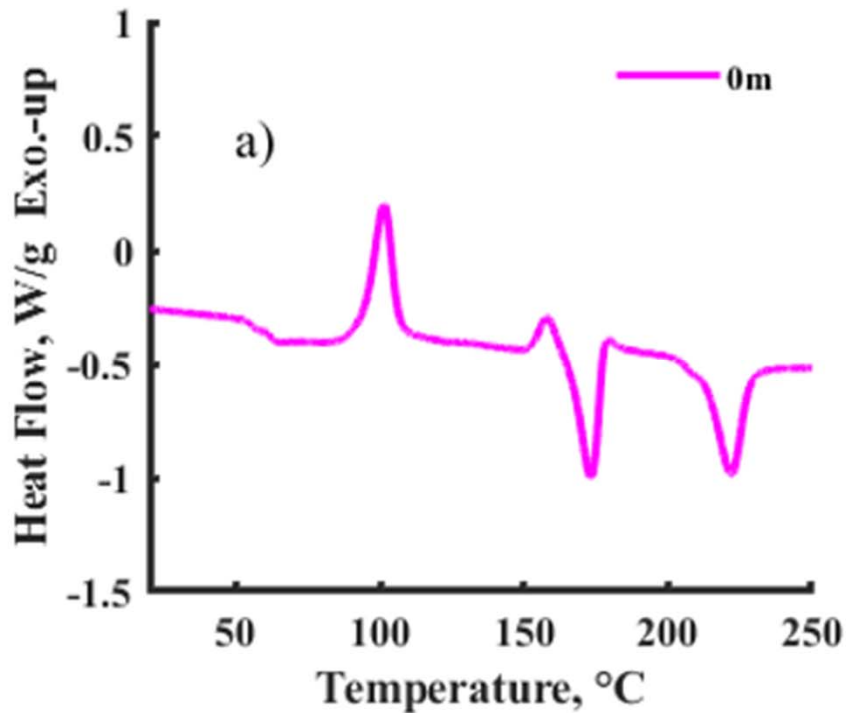
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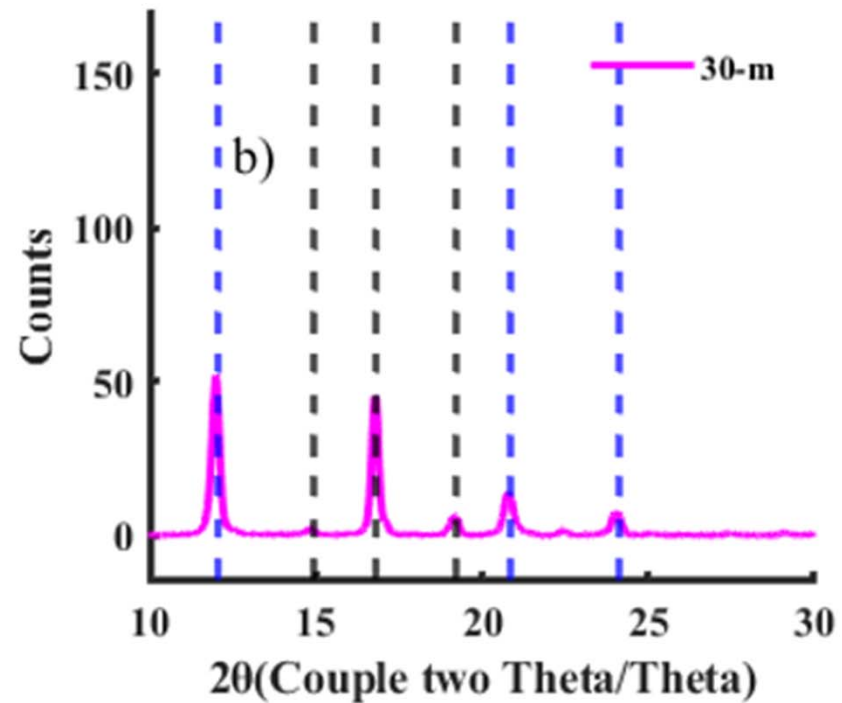
UV Transmission

PLLA,
PLLA/PDLA
(85/15, 70/30, 50/
50, 30/70),
PDLA
(%T at 600 nm)





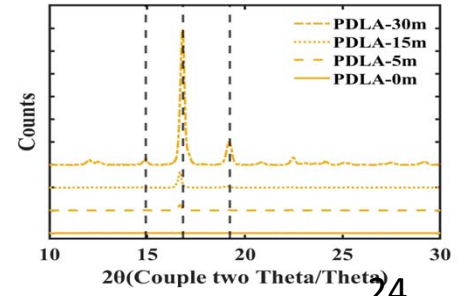
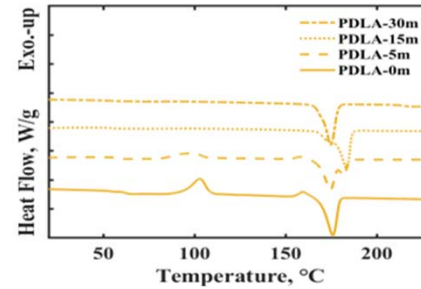
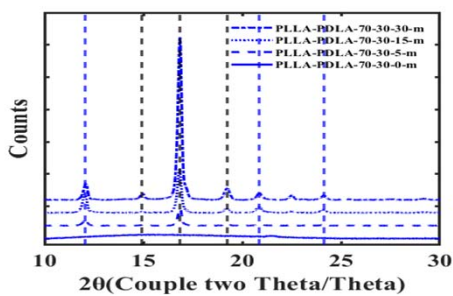
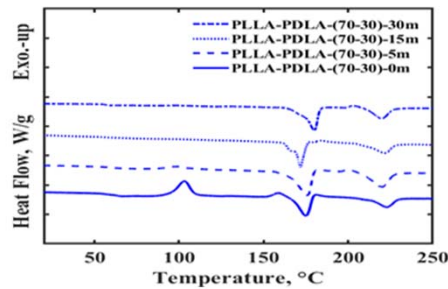
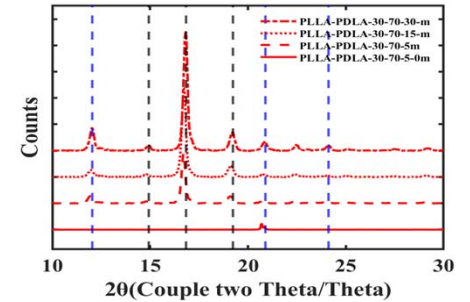
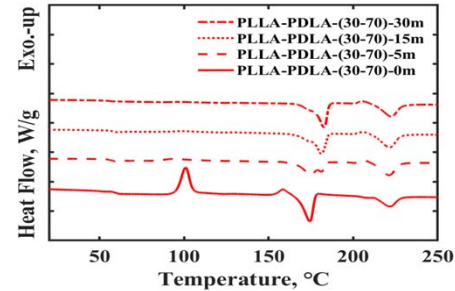
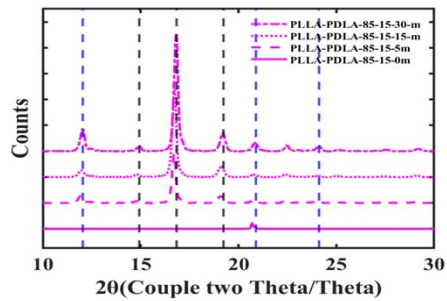
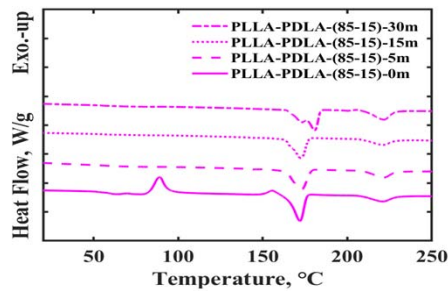
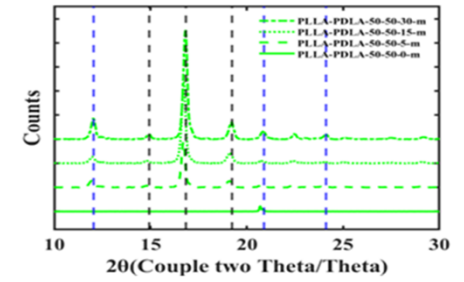
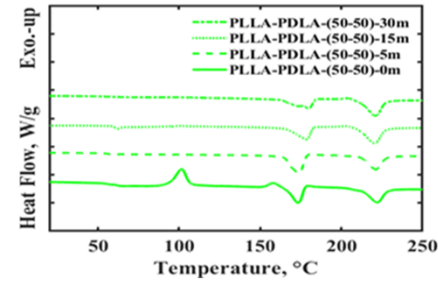
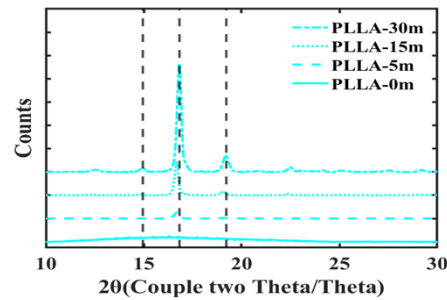
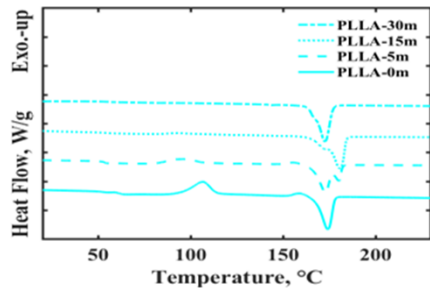
DSC of PLLA/PDLA 50/50
non-annealed



WAXD PLLA/PDLA 50/50
annealed 30 min

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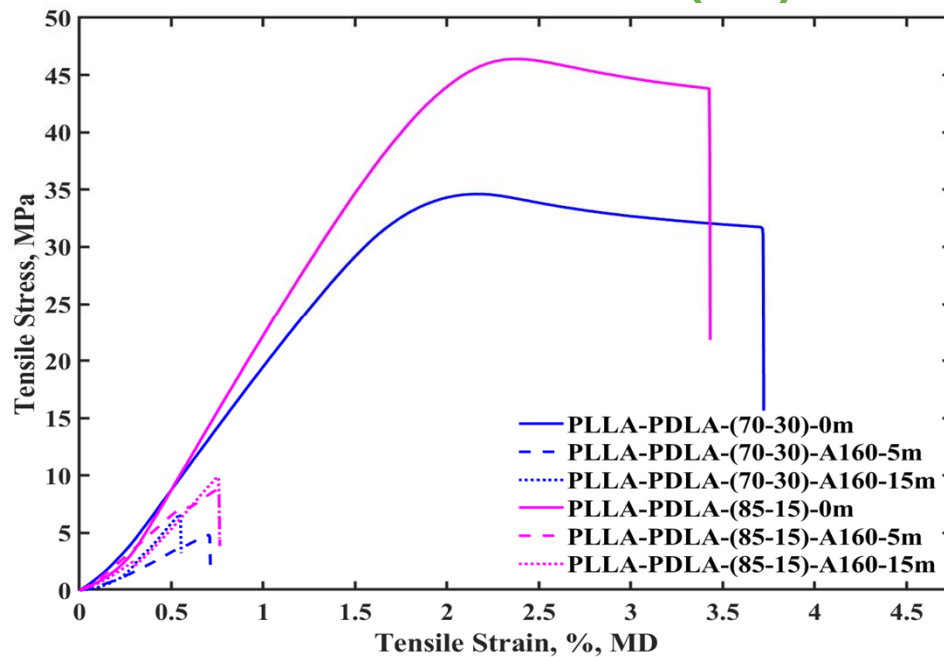
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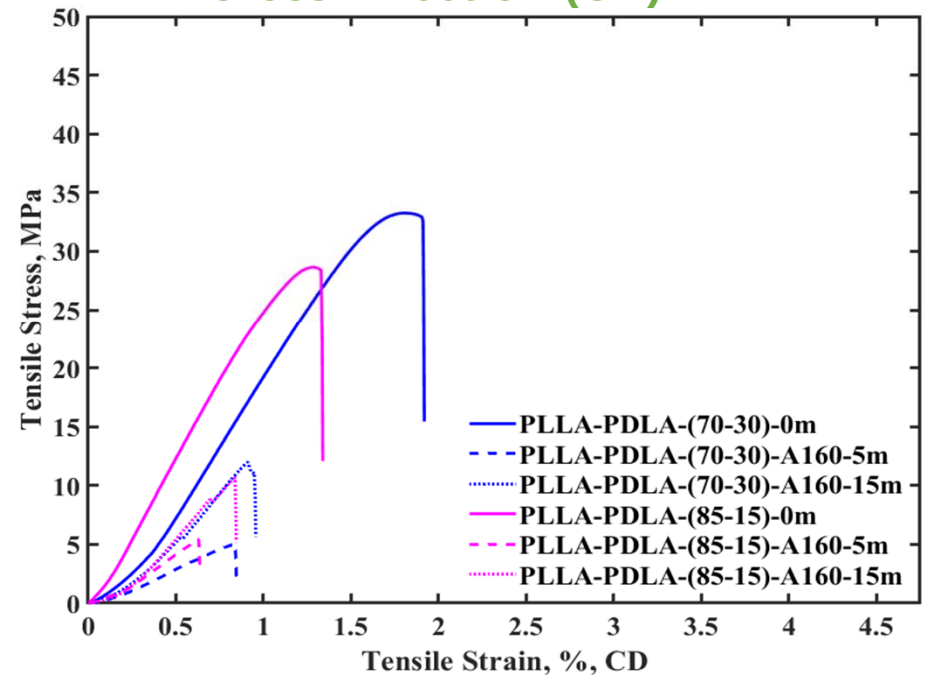
Tensile Stress vs Strain at 160 °C and various annealing times

Machine Direction (MD)



PLLA/PDLA (70/30) and PLLA/PDLA(85/15)

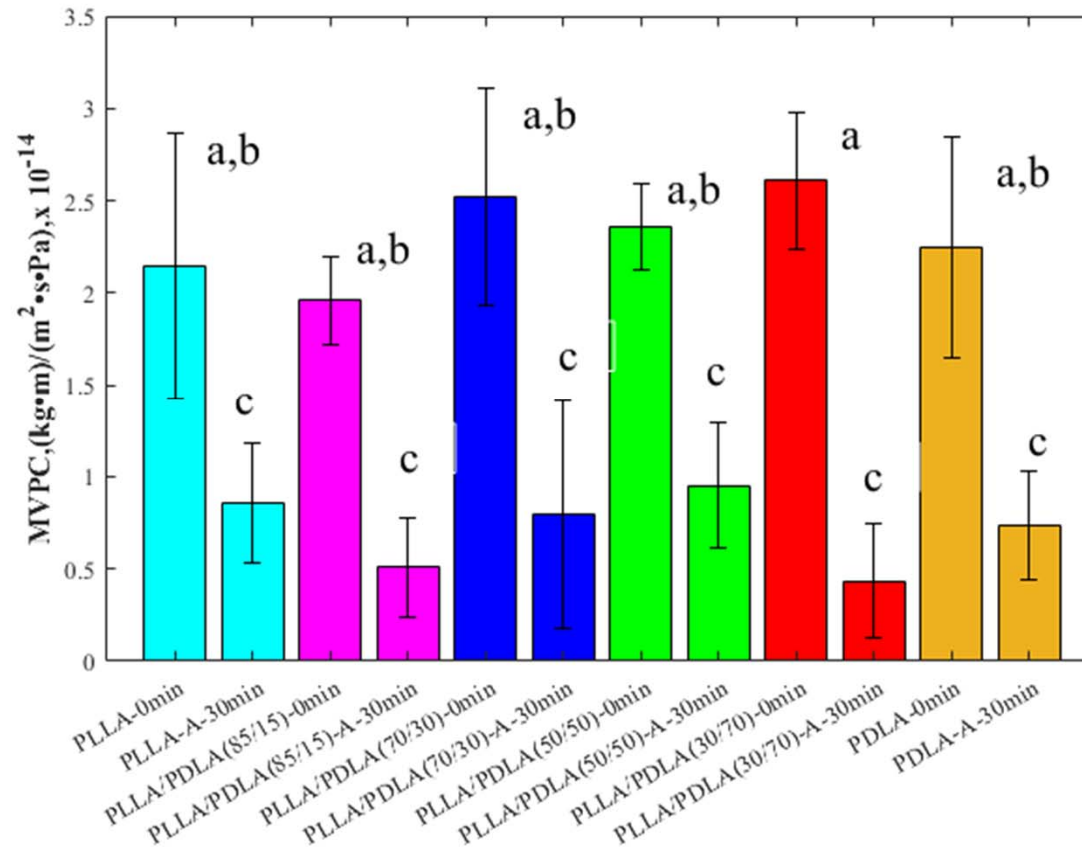
Cross Direction (CD)



PLLA/PDLA (70/30) and PLLA/PDLA (85/15)

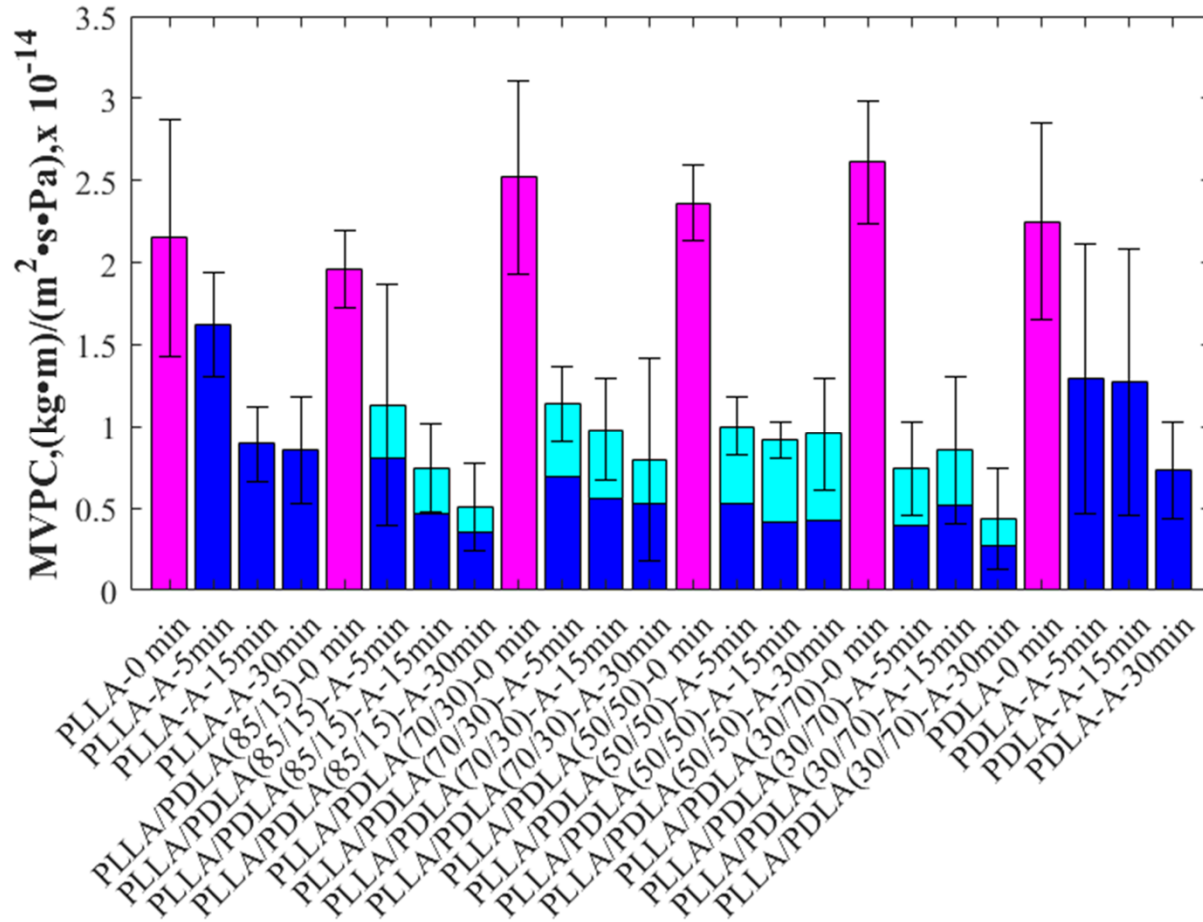
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The magenta bars represent amorphous samples; the blue bars represent the hc-PLA crystalline portion, and the cyan bars represent the sc-PLA crystalline portion.



Summary

- Can produce sc-PLA on a single screw extruder without making a masterbatch first.
- Annealing improves barrier properties of all sc-films at all annealing times tested.
- Introducing sc into the structure decreases the annealing process time to 5 min or less for all blends, whereas HC needs 15+ min to crystallize and improve the barrier.
 - As little as 15 % PDLA will decrease the time needed for increased X_c .
- Overall, X_c matters the most for barrier improvement and is not necessarily the split between HC- X_c and sc- X_c .
- Brittleness is an issue that needs to be addressed.



Summary

- Full paper available at RSC Green Chemistry Journal:

<https://pubs.rsc.org/en/Content/ArticleLanding/2024/GC/D3GC04805E>

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Unlocking the secrets of high-water barrier stereocomplex polylactide blend extrusion films†

James F. Macnamara, Jr.,^a Maria Rubino,^a Matthew Daum,^a Ajay Kathuria^b and Rafael Auras^{a*}

Consumers, companies, and governments are becoming more interested in compostable materials as the amount of waste generated from single-use petrochemical-based and non-biodegradable plastics has grown exponentially since 1960. A drawback to compostable flexible option films is the lack of equivalent moisture barrier performance to maintain a comparable shelf life of food products compared with traditional petrochemical-based versions. Stereocomplex PLA (SC-PLA), a combination of the stereoisomers L-PLA (PLLA) and D-PLA (PDLA), offers a potential solution to this problem. This study presents a viable and novel method to cast extrude SC-PLA films without using a masterbatch. For comparison, several blend compositions were produced, including 85/15, 70/30, 50/50, and 30/70 PLLA/PDLA and homo-complex PLLA and PDLA films. The samples were then annealed at 160 °C for 5, 15, and 30 min to understand the effect on the crystallinity (X_c), moisture vapor permeability coefficient (MVPC), and functional and mechanical performance. As expected, the X_c increased for all the samples upon annealing. We observed increased crystallization kinetics in the blended samples, which crystallized in 5 minutes, which can be ascribed to the nucleation effect, while the PLLA and PDLA started crystallizing between 15 and 30 minutes. PDLA acted as a nucleating agent at levels as low as 15% to induce crystallization in ≤ 5 minutes in the blended samples. We observed a correlation between the crystallization trend of various compositions and MVPC, with the blended annealed films having a significantly better moisture barrier than all the non-annealed films. The increased X_c reduces the strength properties due to higher brittleness associated with the higher X_c . Further optimization is needed to produce fully viable films for commercial applications; however, this work shows pathways to unlock the creation of PLA films with high barriers to water.

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1. Introduction

were sent to landfills.³ This lack of recycling has concerned



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- Dr. Maria Rubino



- Dr. Matthew Daum



- Dr. Ajay Kathuria





Questions?



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Thank you