Upcycling Plastic into Biodegradable Polymers

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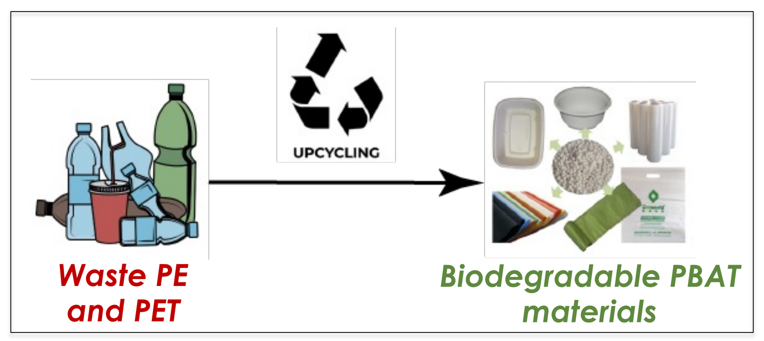
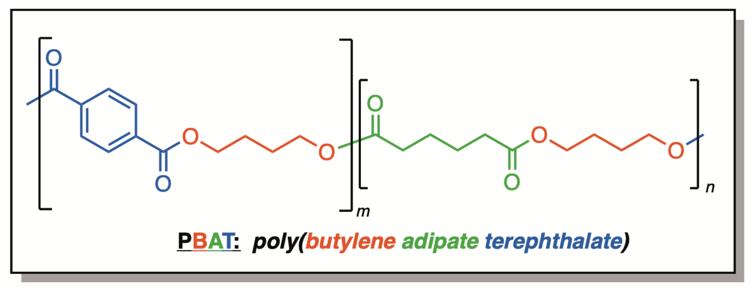
Abstract

Motivated by upcycling waste plastic, we formulated a strategy to create *poly(butylene adipate-co-terephthalate)* **(PBAT)** analogues from post-consumer *polyethylene* **(PE)** and *polyester terephthalate* **(PET)**. PBAT, known for its flexibility, toughness, and biodegradability, is *synthesized from petrochemicals* on the industrial level. However, by adapting *existing chemical recycling methods* for PE and PET which respectively yield *dicarboxylic acids* **(DCAs)** and *bis(4-hydroxybutyl)terephthalate* **(BHBT)**, we demonstrate the synthesis of a PBAT-like polymer with comparable properties. The resultant polymer was characterized by an array of experimental methods and was found to be a robust and rigid material at room temperature. This method offers a pathway to a new range of upcycled, biodegradable materials with tailored physicochemical properties, with the goal of simultaneously repurposing *waste plastic and reducing reliance* on petrochemical feedstocks.

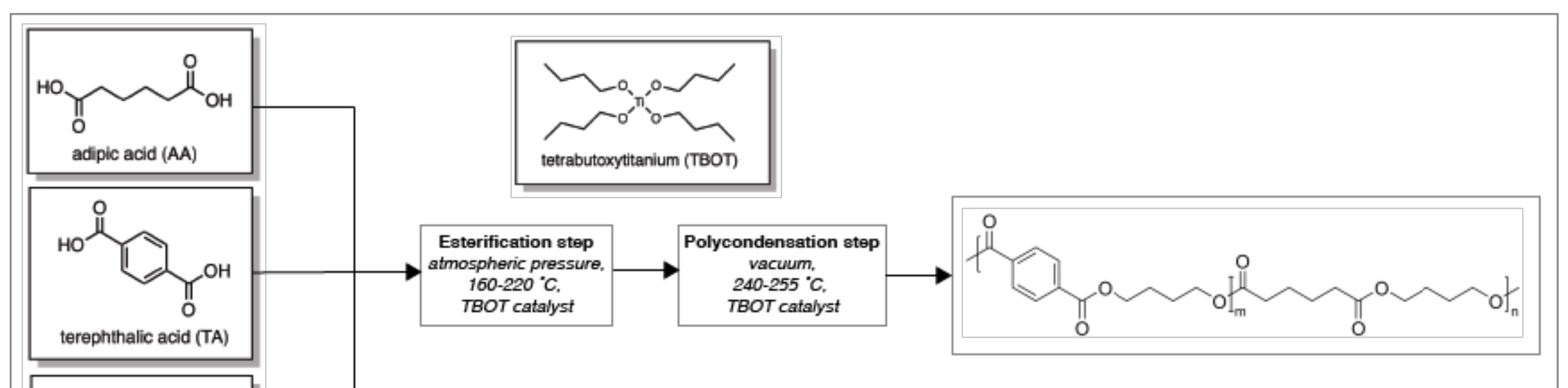




- *Chemical structure of industrial PBAT*

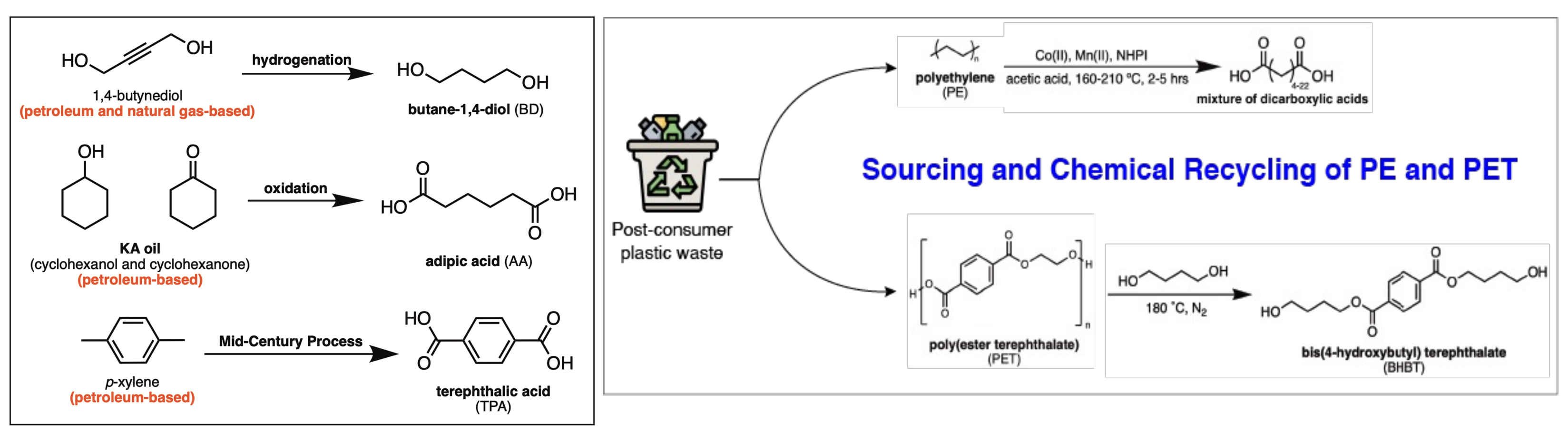
Jehanno, et. al. Critical Advances and Future Opportunities in Upcycling Commodity Polymers. Nature **2022**
Brief Introduction Of PBAT | *ILUCKU Tech In 2024*. https://ilucku.com/brief-introduction-of-pbat/.

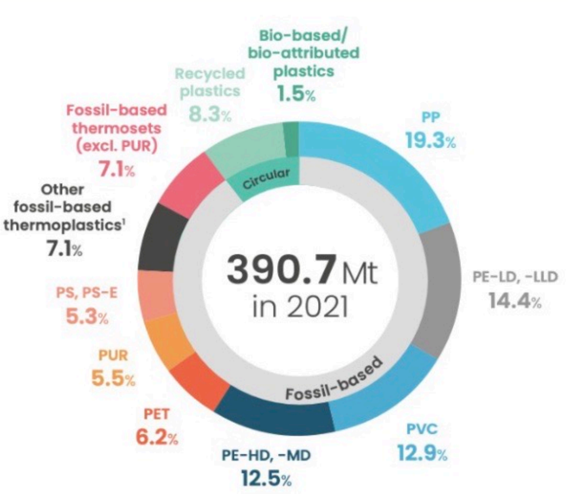
Justification & Motivation



Most common industrial method of PBAT production

The proposed method uses
post-consumer recyclable feedstocks

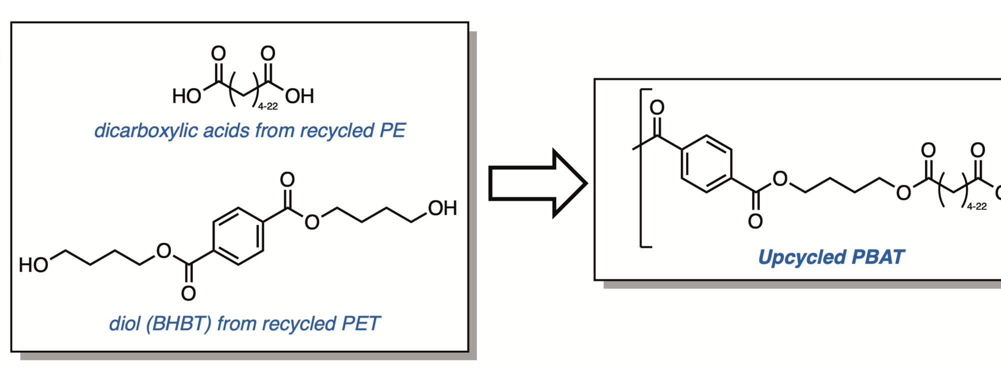




Distribution of global plastics production by type, 2022
- *90.2% petroleum-based*
  - *26.9% PE*
  - *6.2% PET*
- *Only 8.2% was recycled*
- *130 Megatons of PE and PET produced in 2022 alone*

→ Lots of PBAT feedstock!

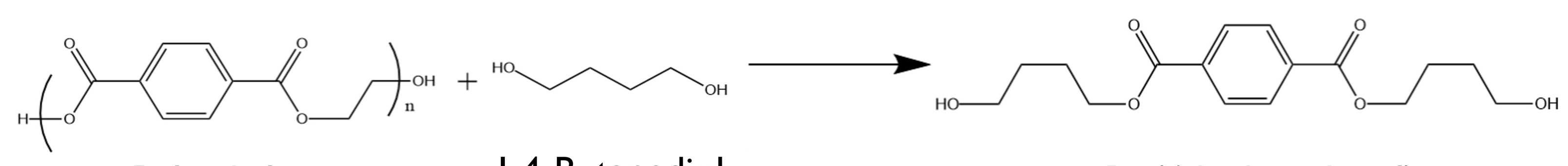
- Methods for the chemical recycling of PE and PET were adapted from previous works
- Degradation products of PE and PET are dicarboxylic acids and BHBT, respectively



Once produced, PBAT is **biodegradable** thanks to its backbone ester linkages, decreasing its environmental impact.

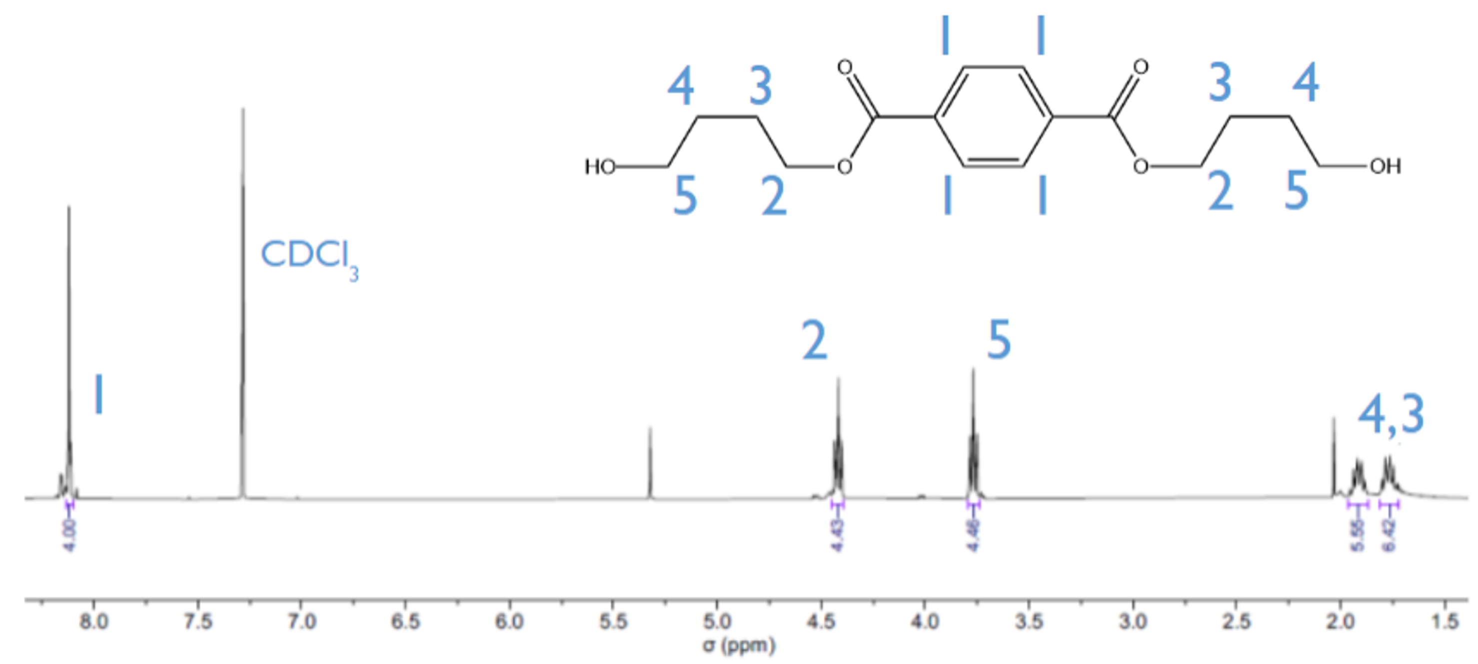
Jian et. al. *Adv. Industrial and Engineering Polymer Research*. **2020**, 3 (1), 19-26.
1,4-Butanediol Production And Uses. chemcess.com/14-butanediol-production-and-uses/.
Fukushima et. al. *Science*. **2022**, *378* (6616), 207-211.
Wischert et. al. ACS Catalysis **2013**, *4* (1), 53–62.
Plastics - The Facts 2022, PlasticsEurope. **2022**, 1-81.

Depolymerization of PET into BHBT

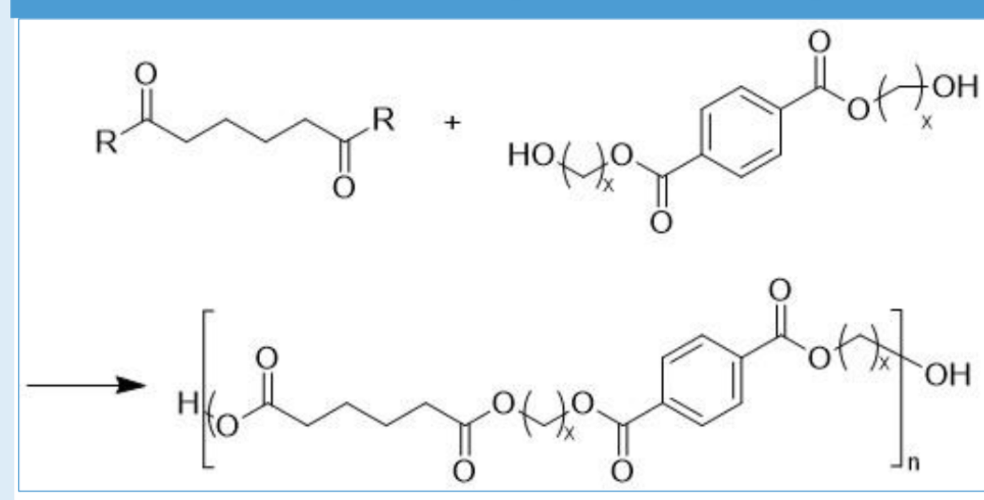


Dry 4.00 g (20.8 mmol, 1.00 equiv.) of post-consumer polyethylene terephthalate pellets. Add mixture of 1.45 g (10.4 mmol, 0.50 equiv.) of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 29.4 mL (333 mmol, 16.0 equiv.) of 1,4-butanediol. Heat at 190°C for 6 hours. Extract into dichloromethane and wash with 0.5 M HCl. Dry by stirring of $MgSO_4$, then isolate via rotary evaporation.

Resulted in a yield of approximately 5 g of bis(4-hydroxybutyl) terephthalate. Product structure was confirmed via ^1H NMR, as shown below.



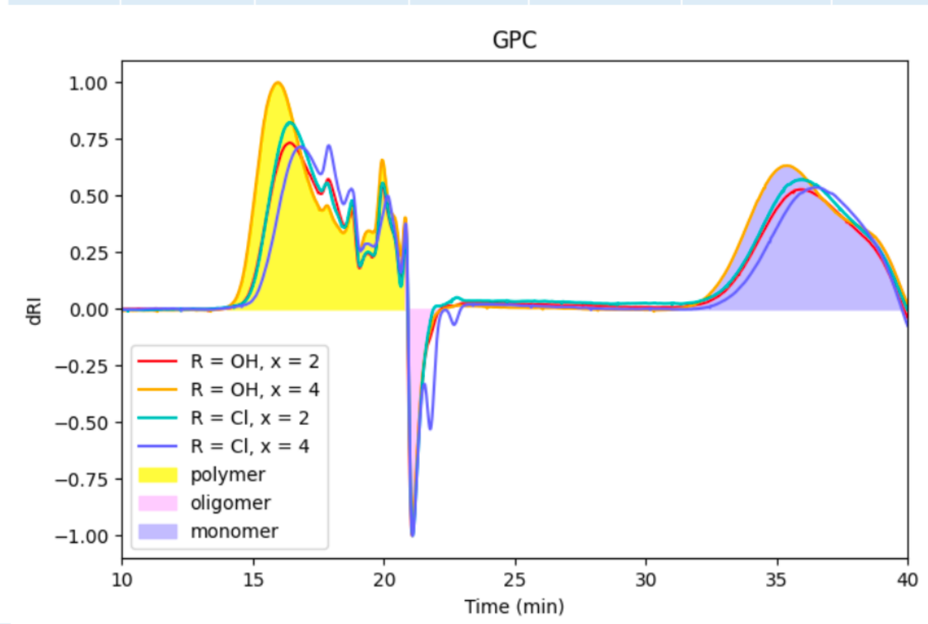
Attempts at Polymerization of PBAT



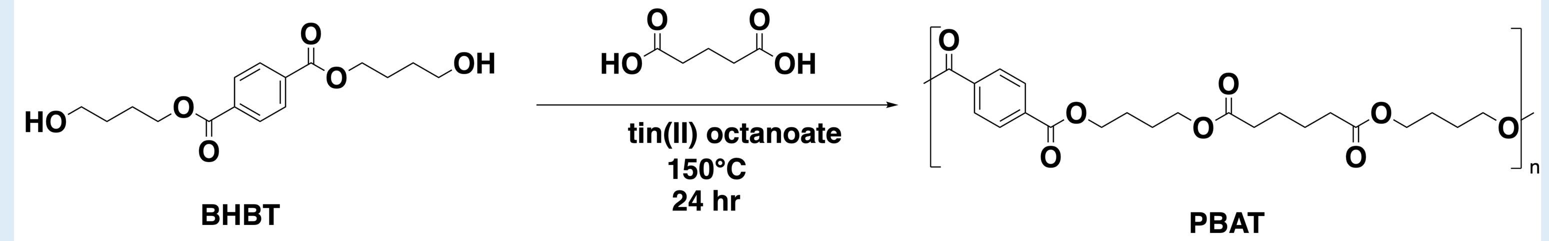
Condensation with adipic acid (R = OH) produced PBAT with greater Mn and in greater yield than adipoyl chloride (R = Cl). Polymerization with the diacid could be performed neat. The length of terephthalate aliphatic segments (x) did not significantly affect the degree of polymerization or yield. Ability to polymerize without solvent is a desirable characteristic of the diacid synthesis.

R	x	n	Time	Catalyst	Base	Δ
Cl	2	0	1h	∅	TEA	0° C
Cl	4	12.2	1h	∅	K_2CO_3	0° C
OH	2	12.8	24h	$Sn(oct)_2$	∅	150° C
OH	4	18.0	24h	$Sn(oct)_2$	∅	150° C

GPC regions of polymer, oligomer, and monomer via various starting reagents. Left shift of polymer peak maxima obtained from adipic acid demonstrates increased n given by these schemes.



Successful Polymerization & Characterization

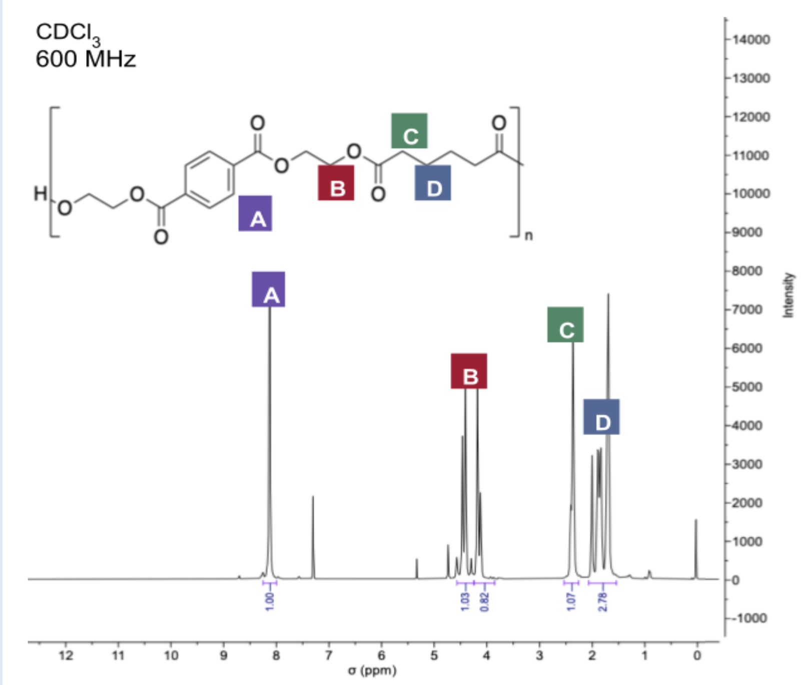


Successful polymerization was conducted via distillation and the use of Lewis acid catalyst, tin(II) octanoate.

Molecular weight data was obtained via GPC for this product:

Mn (g/mol)*	Mw (g/mol)**	PDI***
34980	41620	1.19

*Number Average Molecular Weight , **Weight Average Molecular Weight ,***Polydispersity



^1H NMR analysis matches expected results compared to literature.

Further characterization showed similar behavior to virgin PBAT material, demonstrating viable way to make sustainable PBAT.

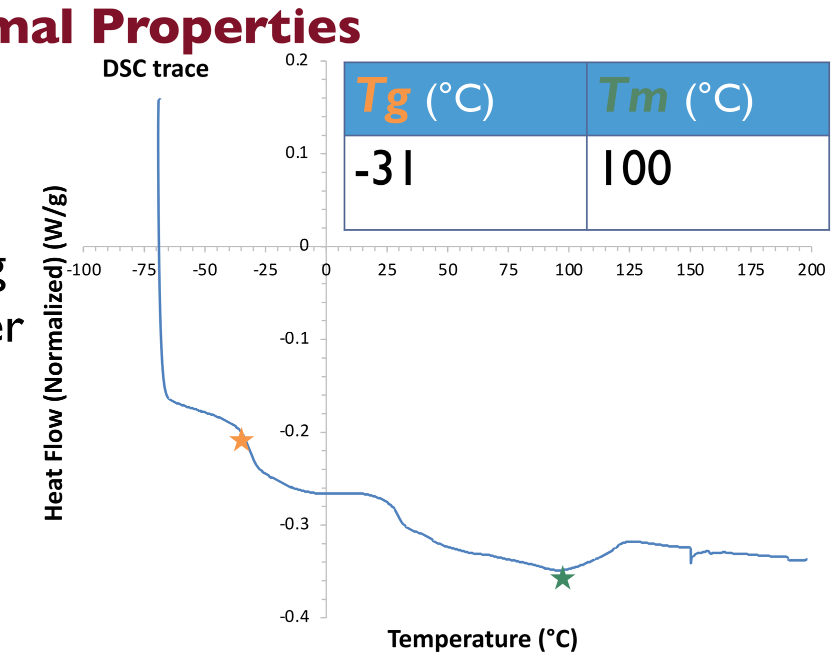
Pholharm., et. al; *IOP Conf. Series Mat. Sci. Res.* **2019**, *529(1)*
Davachi, S. M., et. al., **2023**, *8*, 1710-1722.

Polymer Properties & Mechanical Testing

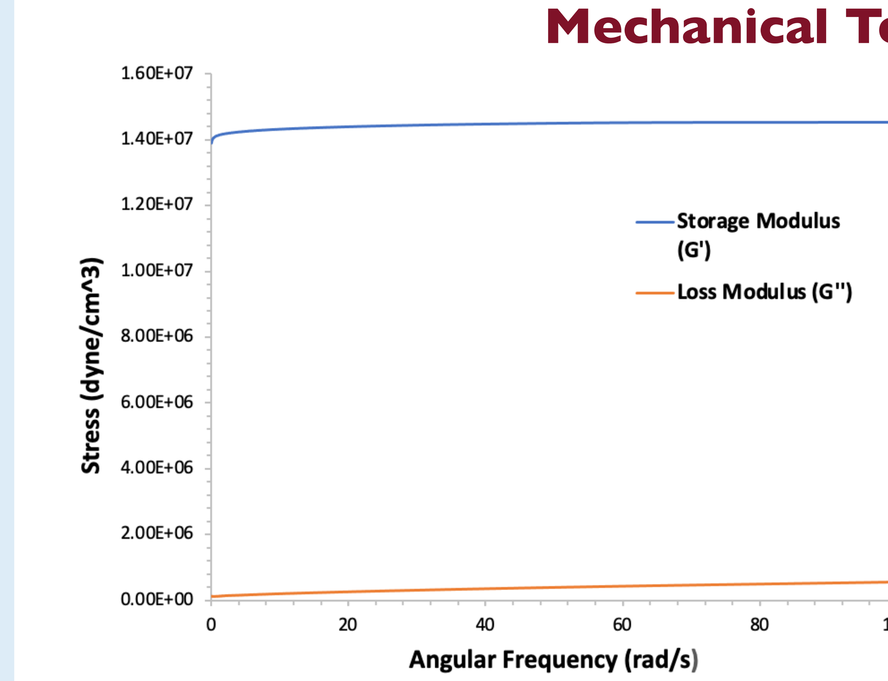
Thermal Properties

- Thermal properties match expected behavior for PBAT
- Glass transition and melting temperature was slightly lower than reported in literature
  - *Tg:* 4°C lower
  - *Tm:* 25°C lower
- Thermogravimetric Analysis
  - Multistep degradation (aliphatic then aromatic regions)

Tg (°C)	Tm (°C)
-31	100



Mechanical Testing



- Material too brittle for tensile strength testing
- Oscillatory rheology
  - G' > G'' indicates little to no elastic character

Davachi, S. M., et. al. *ACS Omega*, **2023**, *8*, 1710-1722.
Correa-Pacheco, Z. *Polym.* **2020,** *12(1)*, 38.
Zhang, M., et. al. *J. Hazard. Mat. Adv.* **2023**, *10*, 100260.