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Title:	Atomistic Modeling and Machine Learning for Bio-advantaged Polymer Design
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Atomistic Modeling and Machine Learning for Bio-advantaged Polymer Design

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Plastic Pollution

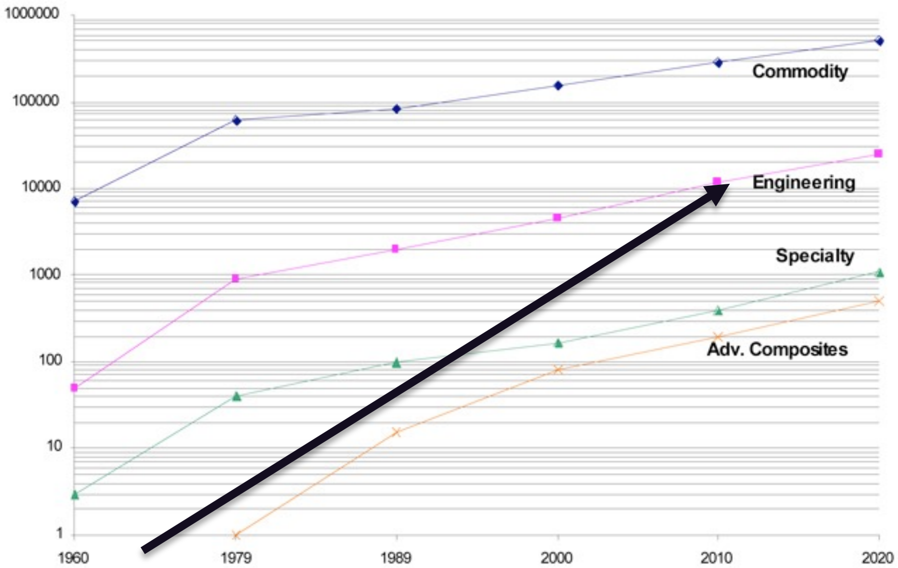
- Single-use plastics constitute more than 40% of total plastics
- Only 9% of the total plastics produced is recycled
- Microplastics are found in the food chain, in our water, and in the air



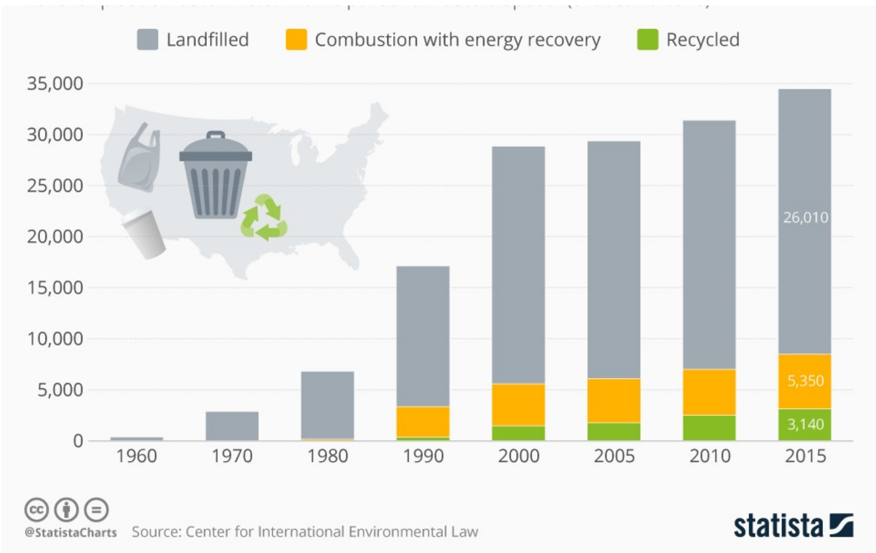
https://www.imperial.ac.uk/news/200553/ocean-plastic-triple-2040-immediate-action/
https://www.ecowatch.com/plastic-pollution-agreement-2636986814.html

Plastic Consumption and Recycling

Plastic consumption, in thousands of tons



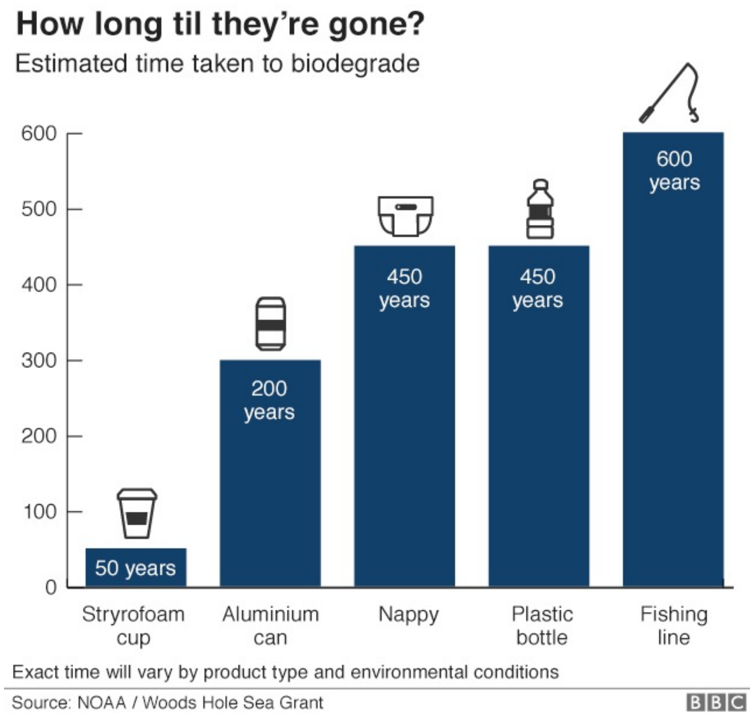
Plastic Recycling

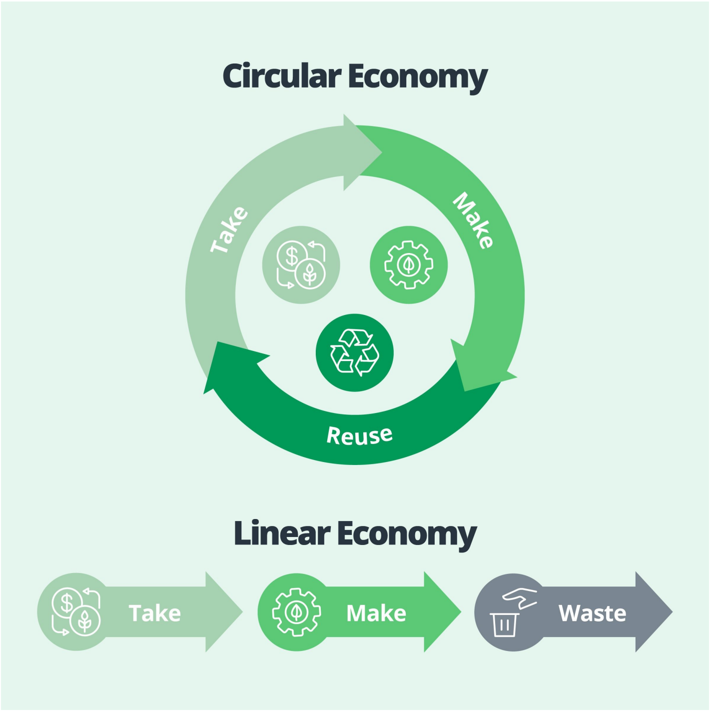


Plastic recycling still has a long way to go

http://www.pardos-marketing.com/hot04.htm
https://www.statista.com/chart/18064/plastic-waste-in-the-us-municipal-solid-waste-disposal/

Overall Objective

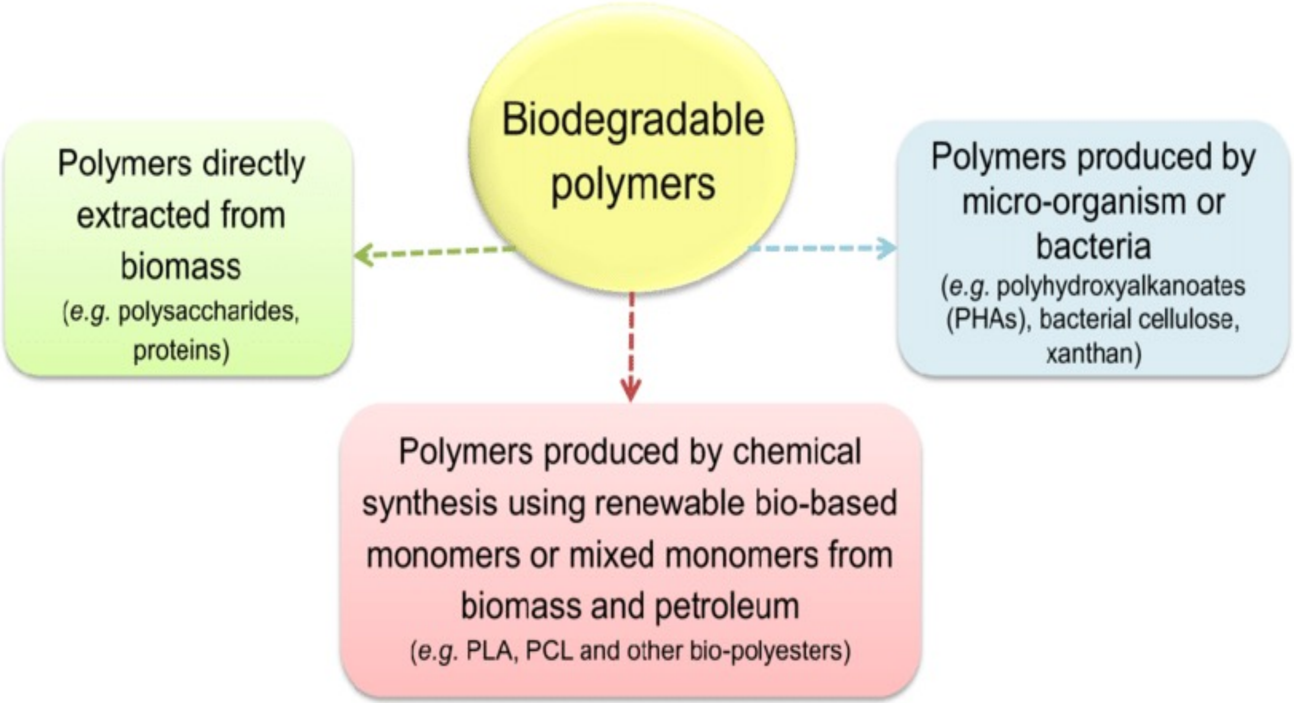




Cannot wait for ~450 years to decompose
Migrate from linear to a circular economy

https://www.bbc.com/news/science-environment-42264788

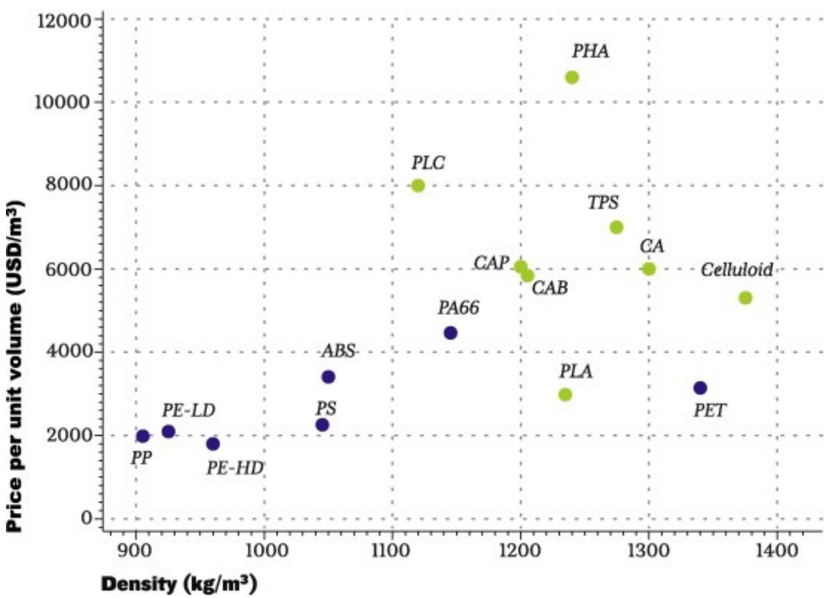
Biodegradable Polymers



Eco-friendly ✓ Easily degradable ✓ Reduces carbon dioxide levels ✓

Limitations of Bio-based Polymers

High cost of production



Materials and Sustainability, **2014**, 156-178

Poor mechanical properties

In-house experiments

Brand name	Materials	Tensile strength (MPa)	Elongation at break (%)	Stress at break (MPa)	Young's modulus (MPa)
GF-0wt%	PHB	13.7	7	12	1050
GF-1wt%	PHBV	8.8	0.7	8.8	1495
GF-8wt%	PHBV	21.6	6.7	19	1103
Ald-0mol%	PHB	7.3	0.4	7.3	1658
Ald-8mol%	PHBV	21.5	1.1	21.5	1920
Ald-12mol%	PHBV	16.9	1.1	16.9	1484
Smith's	HDPE	23.2	206.3	23.2	382.5
Subway	HDPE	26	245.9	26	471
Smith's Produce	HDPE	42.2	77.8	40.2	710.2
Whole Foods Produce	HDPE	23.8	218.2	23.8	463.5
Clothing	LDPE	19.1	434.7	18.5	327.1
Trader Joe's Produce	MATER-Blb	47.7	57.7	47.1	129.3

Conventional Polymers

Polyethylene
terephthalate
(PET)

High density
polyethylene
(HDPE)

Low density
polyethylene
(LDPE)

Polypropylene
(PP)

Polystyrene
(PS)

Cost effective ✓

Thermal stable ✓

High performance ✓

Durable ✓

Tunable properties ✓

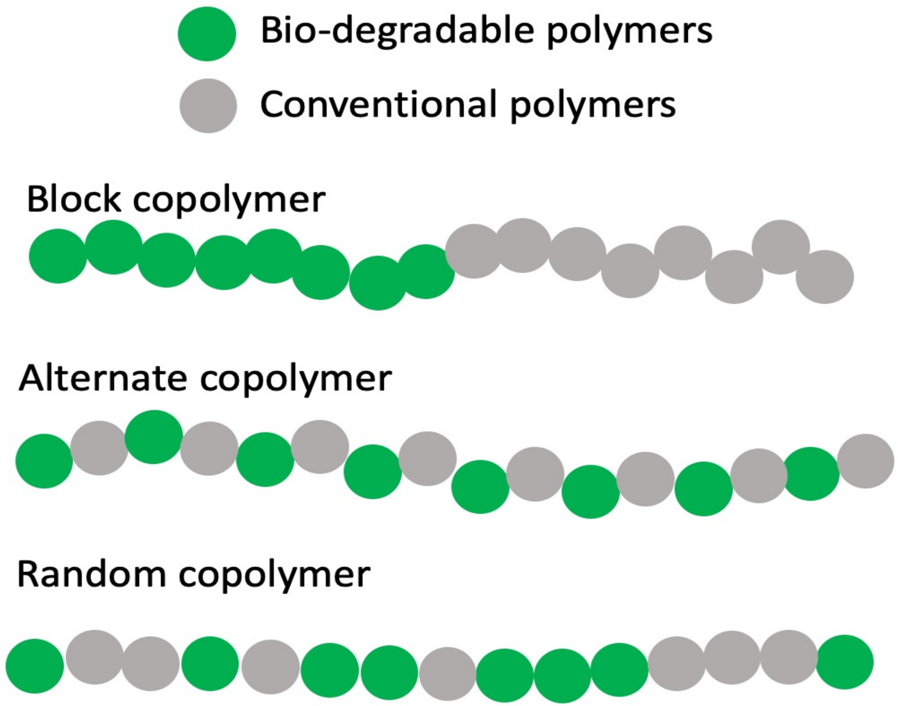
Degradable ✗

Recyclable ✗

Overview of Director's PRD

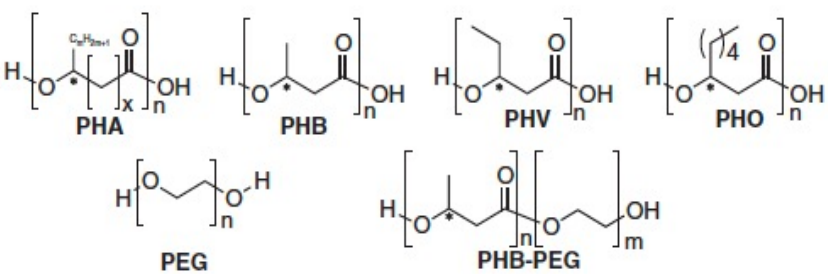
Hybrid polymers

- Bio-based polymers are either or co-polymerize or blended with conventional polymers
- Degradability from bio-based materials
- Improved mechanical strength from conventional polymers



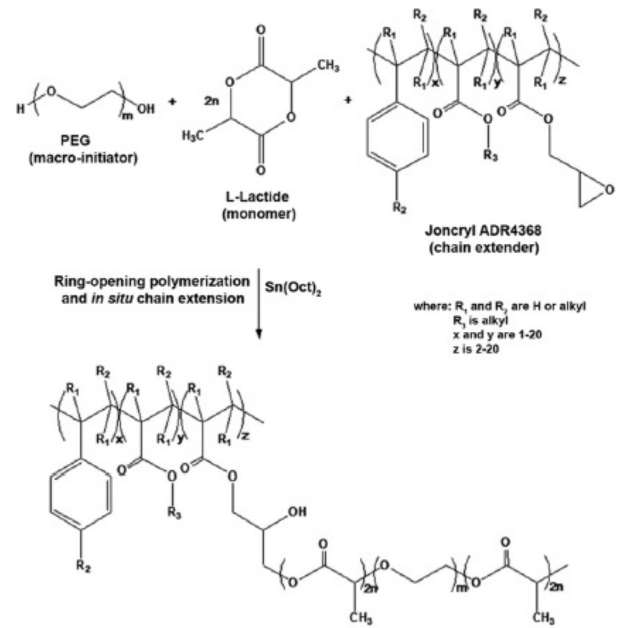
Examples of Hybrid Polymers

Copolymers of polyhydroxyalkanoates and polyethylene glycols: recent advancements with biological and medical significance



Yodthong Baimark*, Wuttipong Rungseesantivanon, and Natcha Prakymoramas

Synthesis of flexible poly(L-lactide)-*b*-polyethylene glycol-*b*-poly(L-lactide) bioplastics by ring-opening polymerization in the presence of chain extender



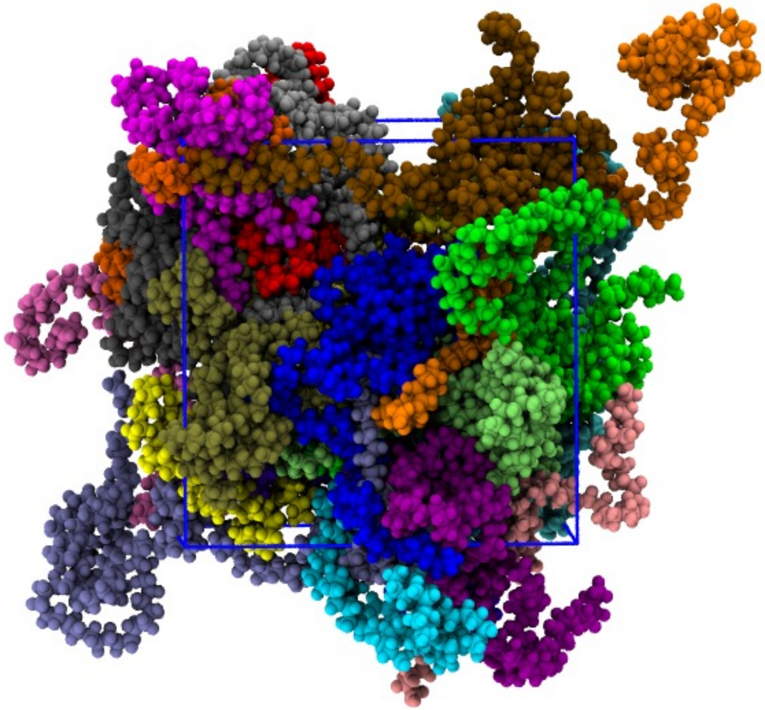
In situ chain-extended PLLA-PEG-PLLA

PolymInt, **2017**, 66, 497-503
e-Polymers, **2020,** 20, 423-429

Molecular Dynamics

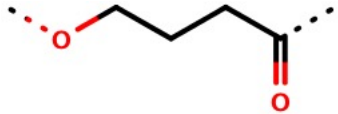
- Molecular dynamics (MD) enable polymer property predictions
- LAMMPS MD package
- Enhanced Monte Carlo (EMC) to generate the amorphous polymer box
- 20 chains and each chain consisting of 100 monomer units
- NPT ensemble; 300 K

Representative snapshot of an amorphous polymer box



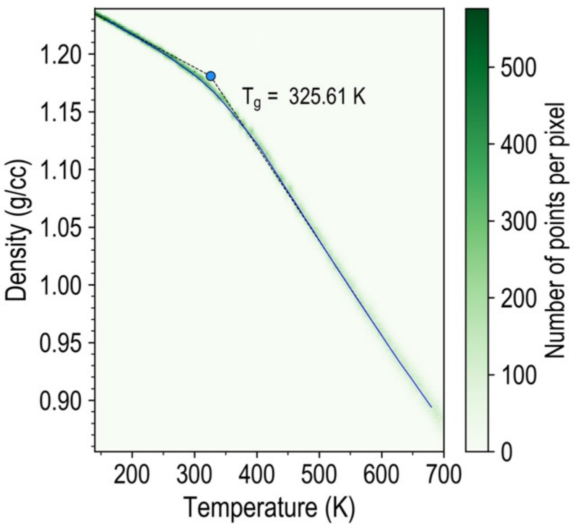
Assessment of Different Force Fields on T_g predictions

poly-4-hydroxybutyrate (P4HB)



Experimental T_g : 225.7 K

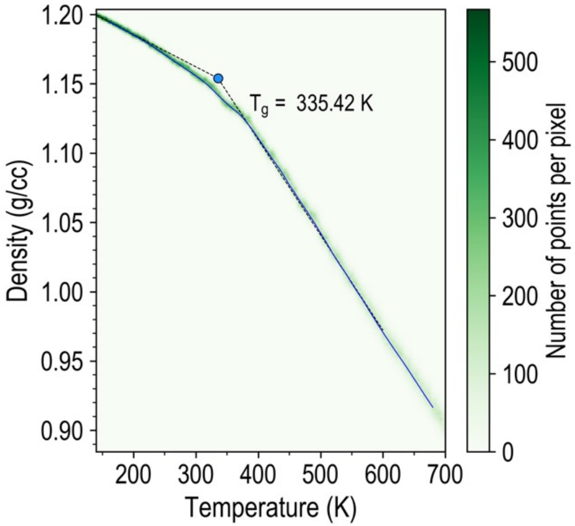
CHARMM General Force Field (CGenFF)



Error: 44.5 %

J. Chem. Inf. Model. **2012**, 52, 12, 3155-3168
J. Chem. Inf. Model. **2012**, 52, 12, 3144-3154

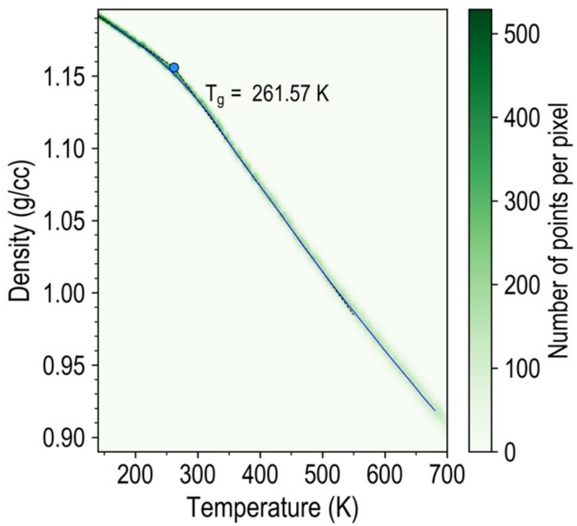
Generalized Amber Force Field (GAFF)



Error: 48.8 %

Journal of Molecular Graphics and Modelling, **2006**, 25, 247260

Polymer Consistent Force Field (PCFF)



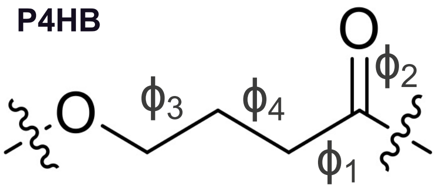
Error: 16.1 %

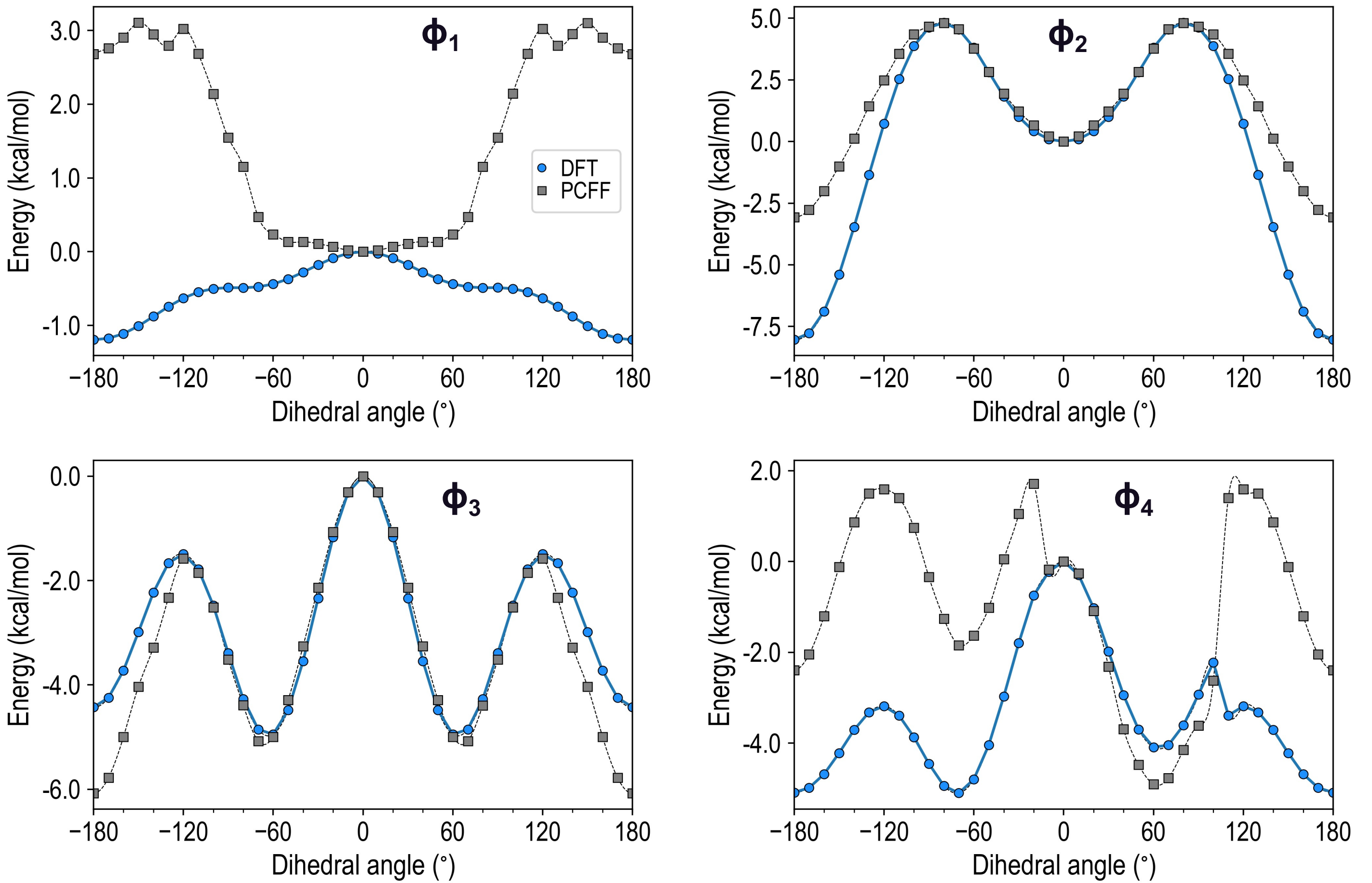
J. Phys. Chem. B 1998, 102, 7338-7364

Comparison of Torsion Potentials Using PCFF

DFT:
B3LYP/6-31+g(d,p)
Using Gaussian16

P4HB



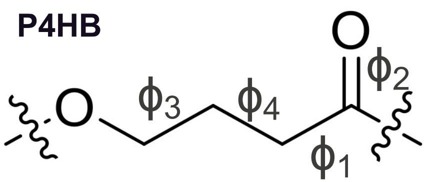


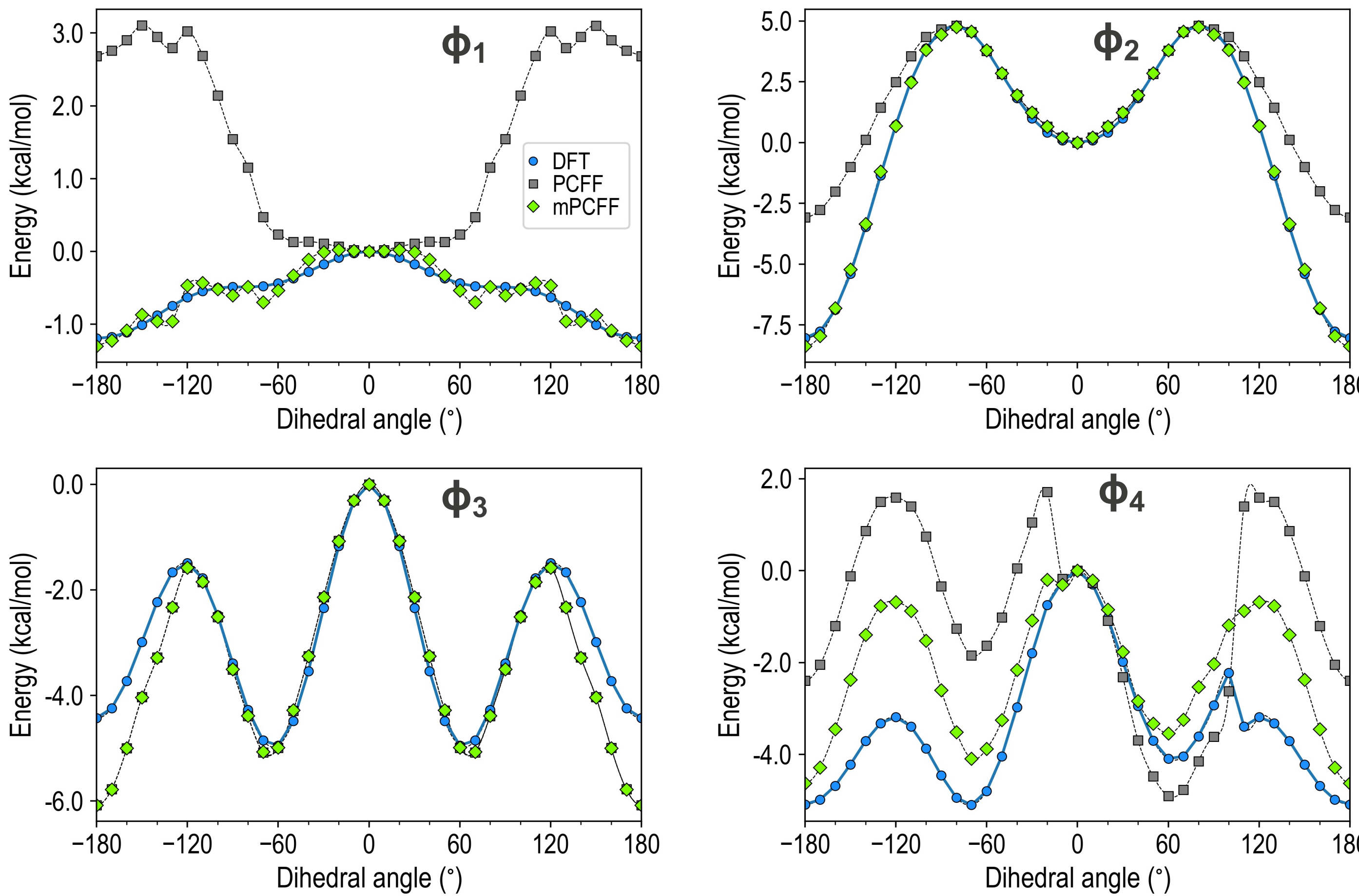
Improved Torsion Potentials : mPCFF

DFT:
B3LYP/6-31+g(d,p)
Using Gaussian16

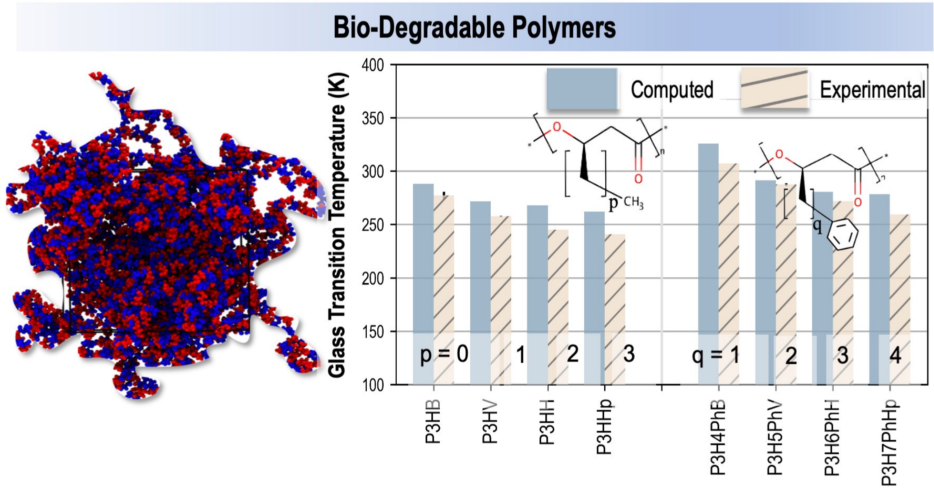
Refitted

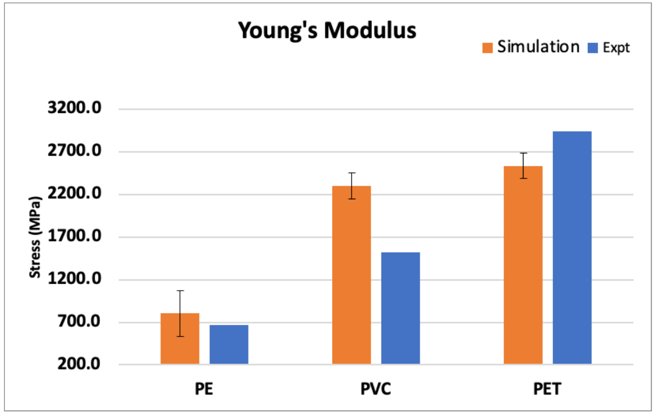
P4HB

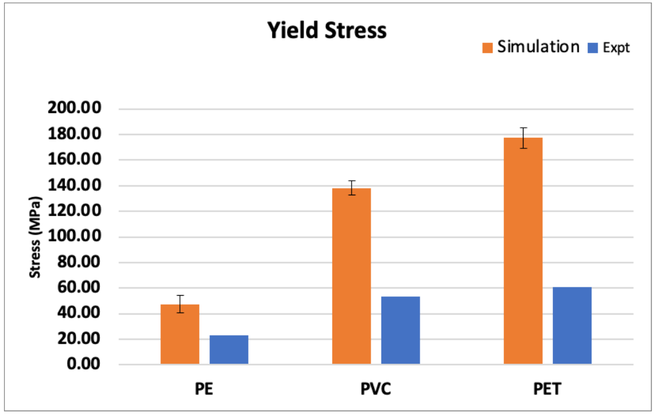




Validation of mPCFF Parameters



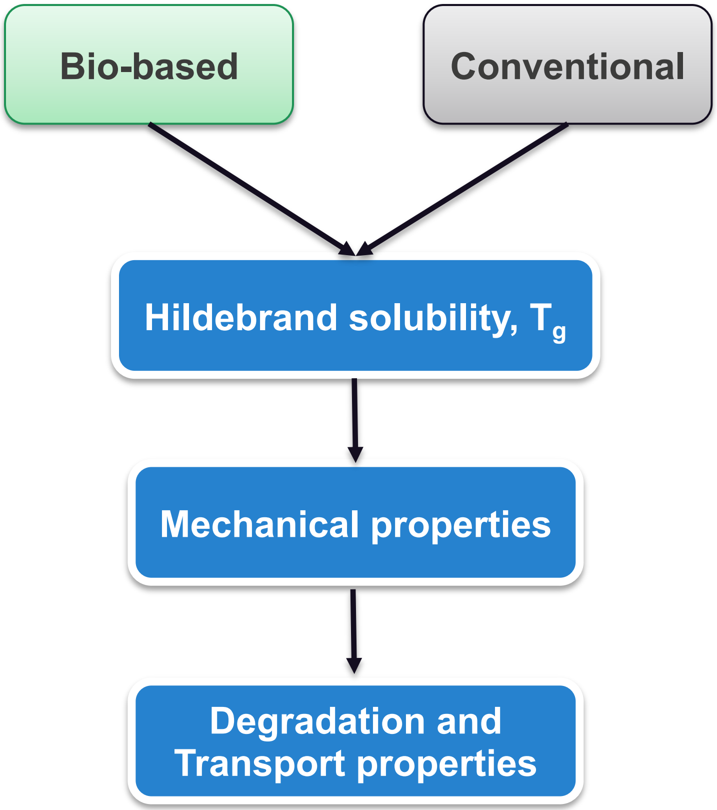




Bejagam, K. K; Iverson, C. N.; Marrone, B. L.; Pilania, G., Phys. Chem. Chem. Phys., **2020**, 22, 17880-17889

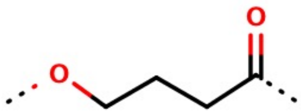
Computational Screening of Hybrid Polymers

- Large number of bio-based and conventional polymers
- Identify the combination based on miscibility
- **Narrow** down the selection with good mechanical properties
- Explore the transport properties and degradation for various packing applications

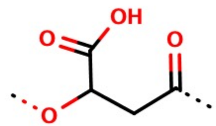


Bio-based Polymers

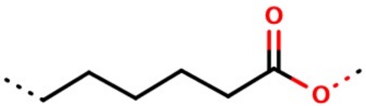
poly(4−hydroxybutyrate)
(P4HB)



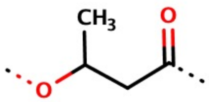
poly(3−carboxy−propionate)
(P3CoxyP)



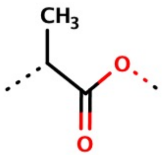
polycaprolactone
(PCL)

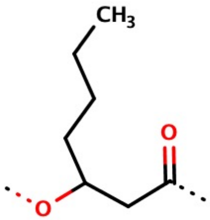


poly(3−hydroxybutyrate)
(P3HB)



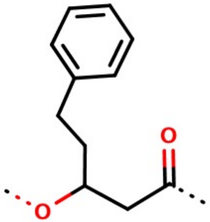
polylactic acid)
(PLA)



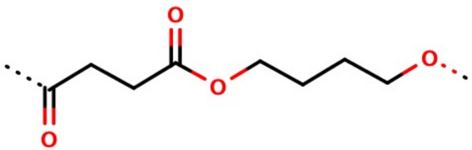


poly(3−hydroxyheptanoate)
(P3HHp)

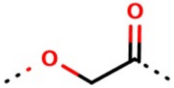
poly(3−hydroxy−
5−phenylvalerate)
(P3H5PhV)



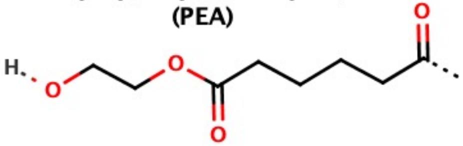
polybutylene succinate
(PBS)



polyglycolide
(PGA)



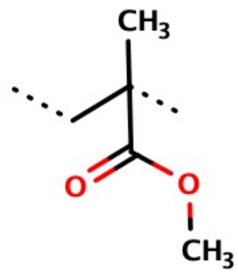
poly(ethylene adipate)
(PEA)



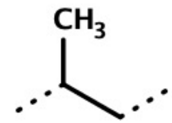
Conventional Polymers

polyethylene (PE)

polymethyl methacrylate (PMMA)

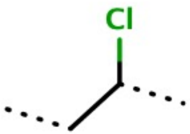


polypropylene (PP)



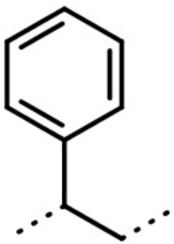
polyvinylidene fluoride (PVDF)

polyvinyl chloride (PVC)

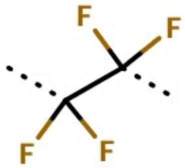


polyoxymethylene (POM)

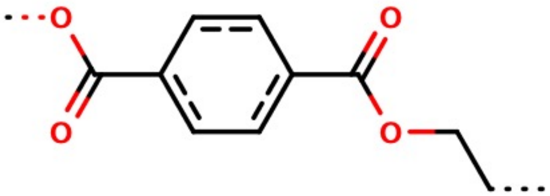
polystyrene (PS)



polytetrafluoroethylene (PTFE)



polyethylene terephthalate (PET)



polyethylene glycol (PEG)

Determining Hildebrand Solubility

Computational Details

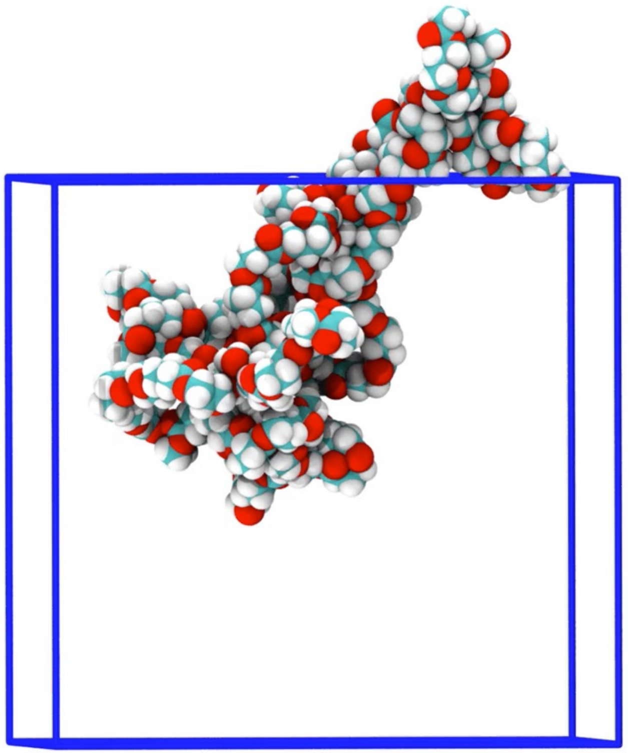
- LAMMPS
- mPCFF parameters
- 20 chains
- Each chain with 100 repeating units
- 300 K

Hildebrand Solubility parameter

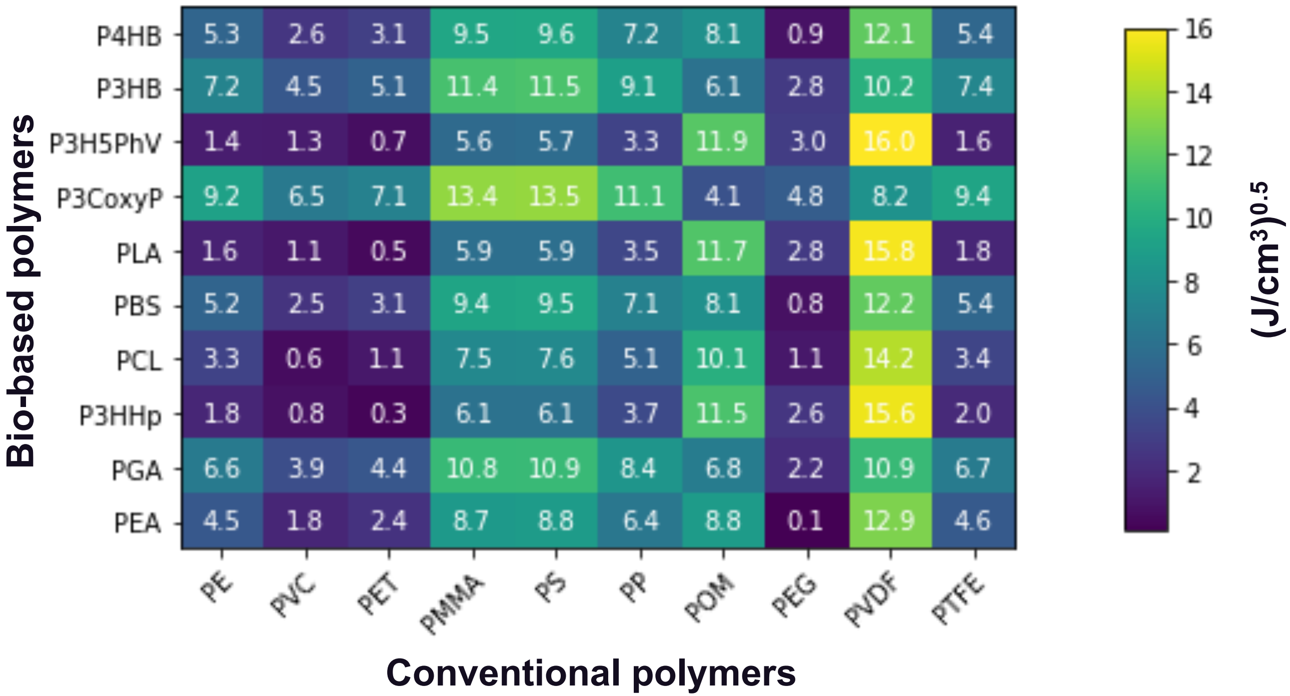
$$\delta = \sqrt{\frac{E_{coh}}{V_M}} \qquad E_{coh} = \sum_{chains} E_{is} - E_{tot}$$

E_{coh} is the cohesive energy

V_M is the molar volume



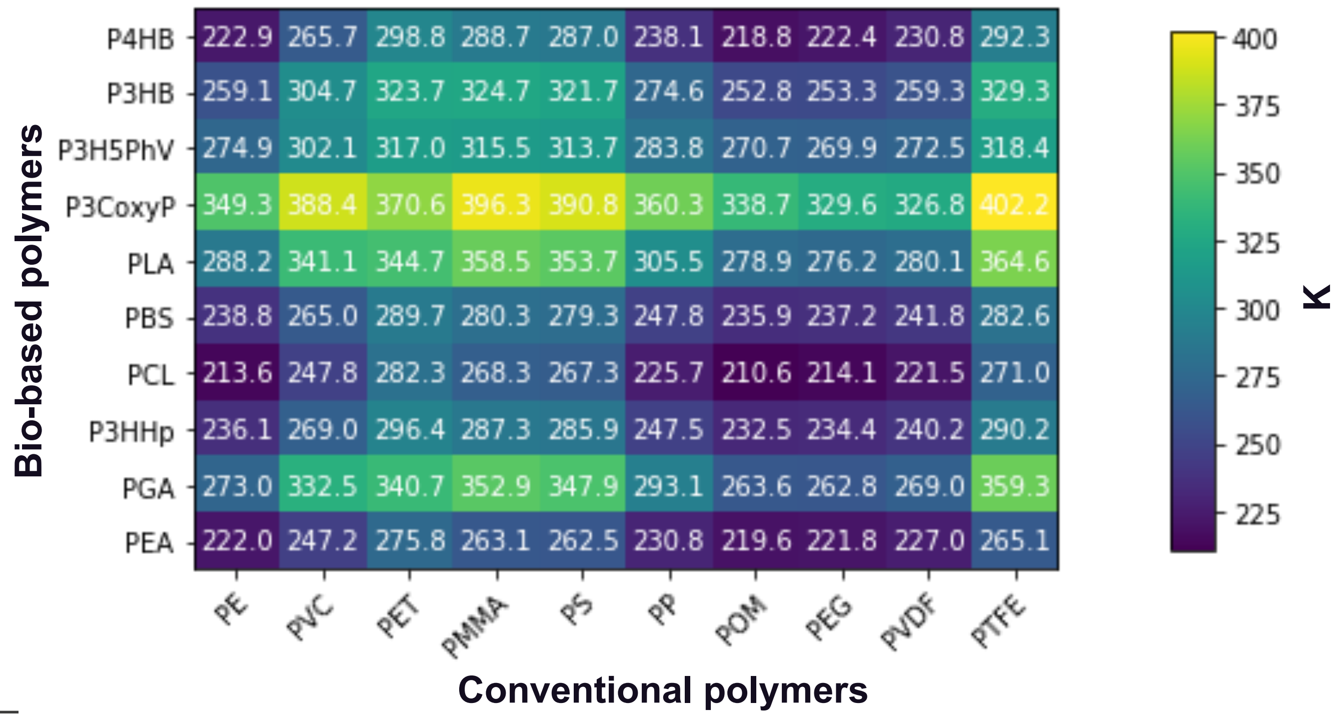
Absolute Differences of Hildebrand Solubility



Polymer combination with low values are preferred

T_g Estimates using Fox Equation

For a 50:50 composition

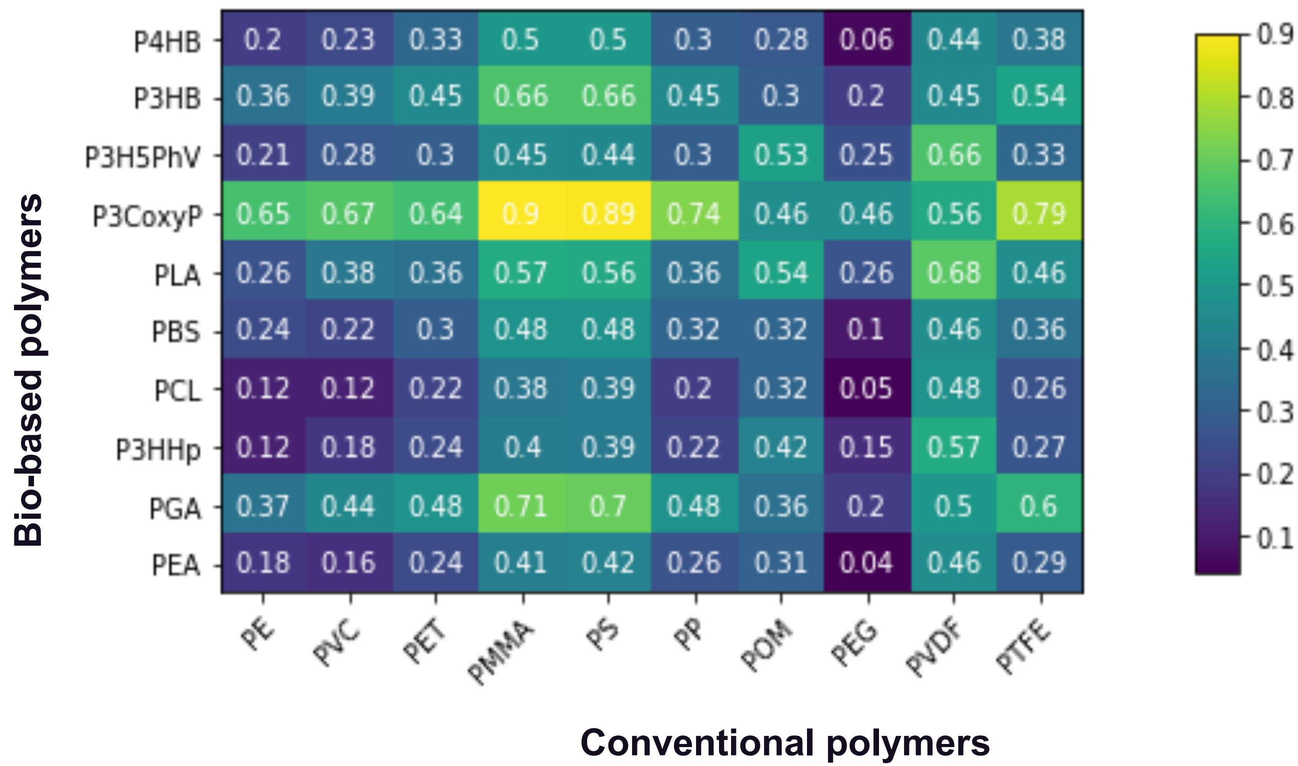


Fox equation

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}}$$

For packing applications, polymers with low T_g are preferred

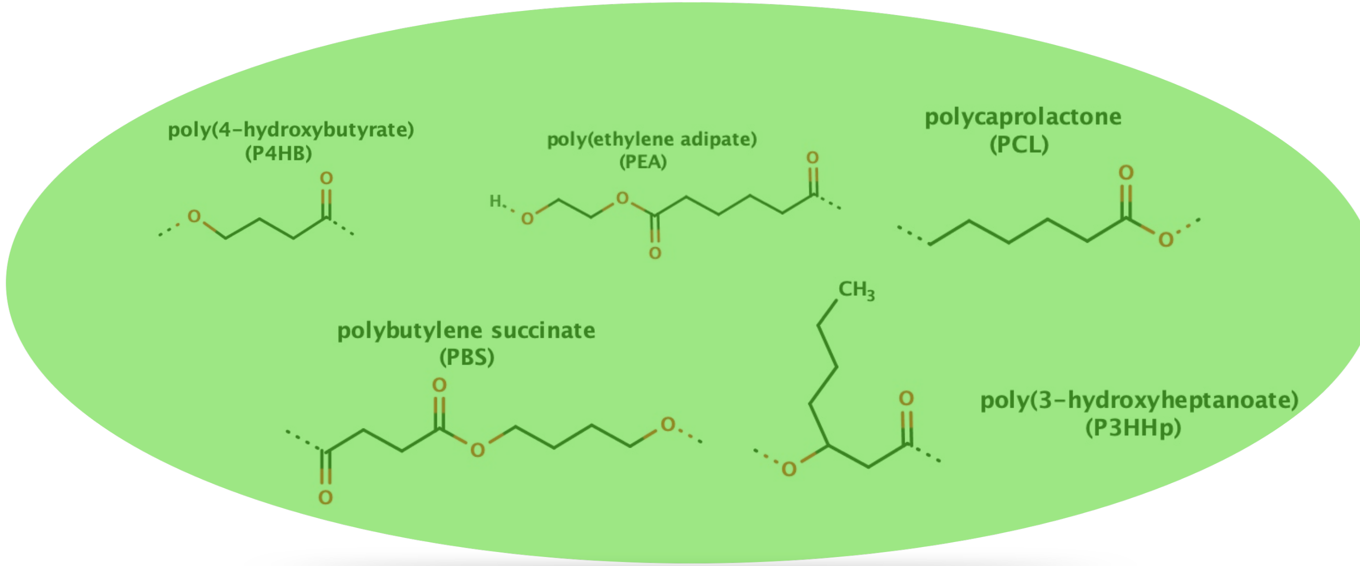
Combining the solubility and T_g

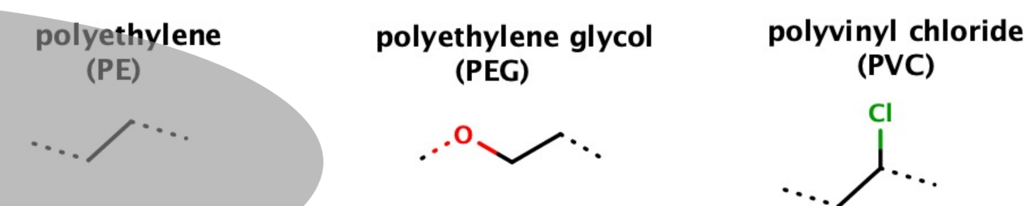


Top candidates with least values are selected for hybrid polymers

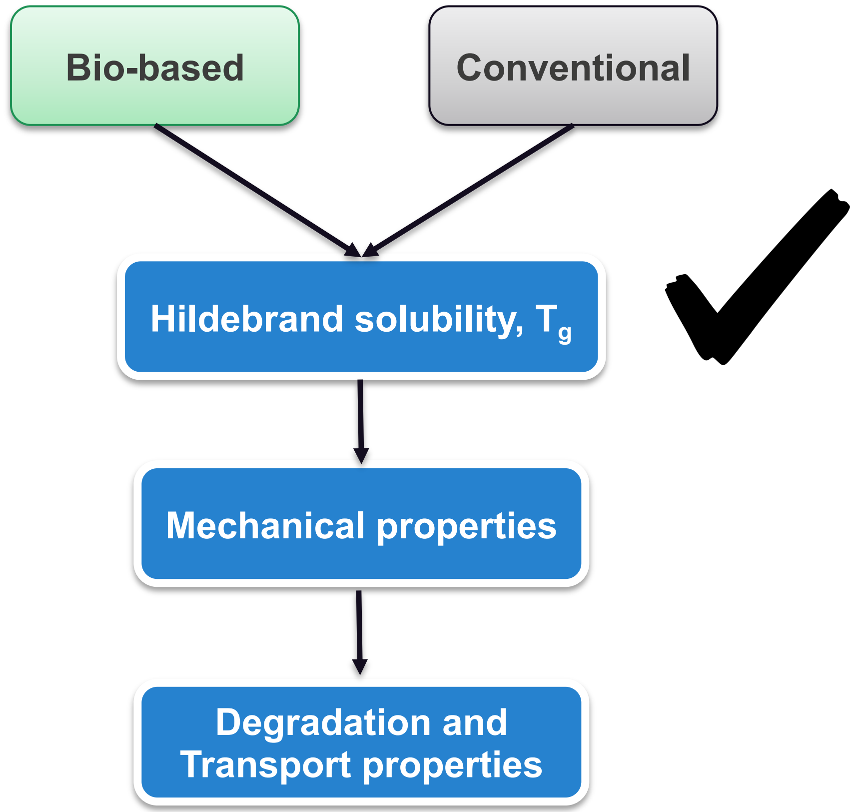
Hybrid Polymers

- **PCL**+PE
- **P3HHp** + PE
- **PCL** + PVC
- **P4HB** + PEG
- **PBS** + PEG
- **PCL** + PEG
- **P3HHp** + PEG
- **PEA** + PEG





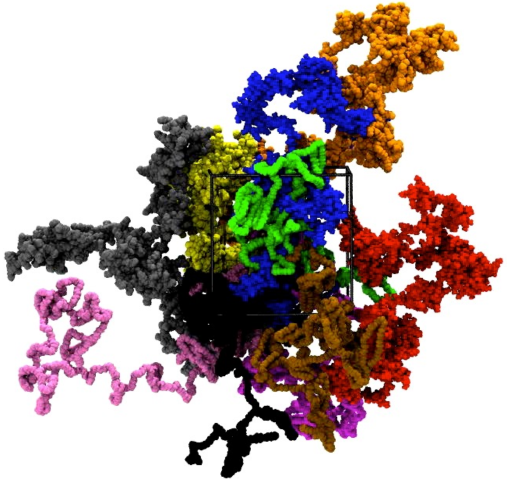
Next Steps…


Bio-based
Conventional
Hildebrand solubility, T_g
Mechanical properties
Degradation and Transport properties

Mechanical Properties

Movie illustrating the evolution of box during deformation simulations

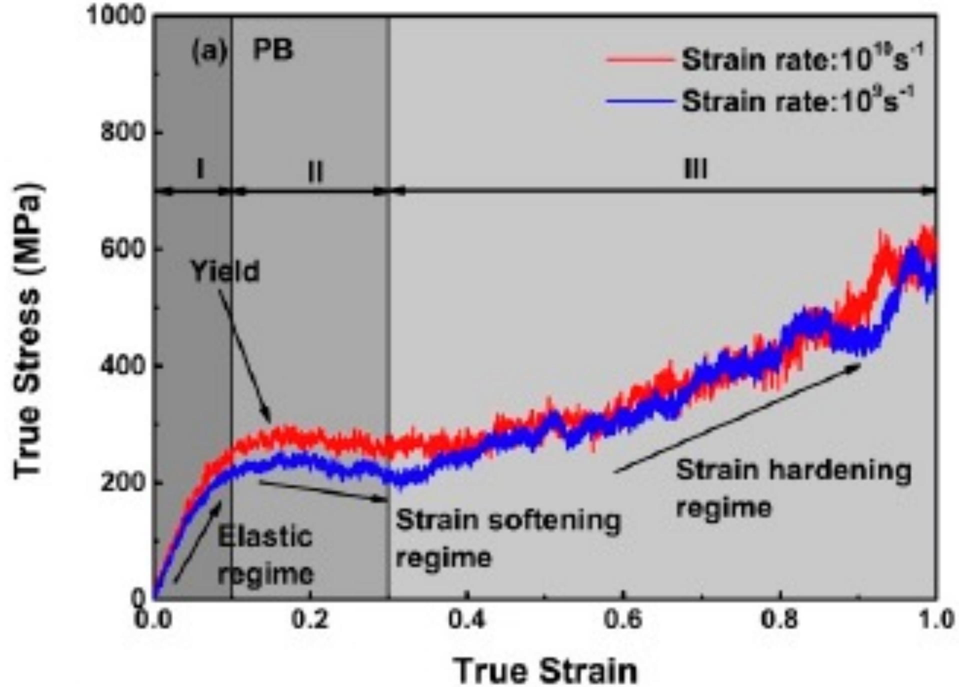
- LAMMPS
- mPCFF parameters
- 10 chains
- Each chain with 500 repeating units
- 300 K
- Deformation simulations
- Average over 5 different configurations
- 3 directions (X, Y, and Z)



Stress-Strain Profile

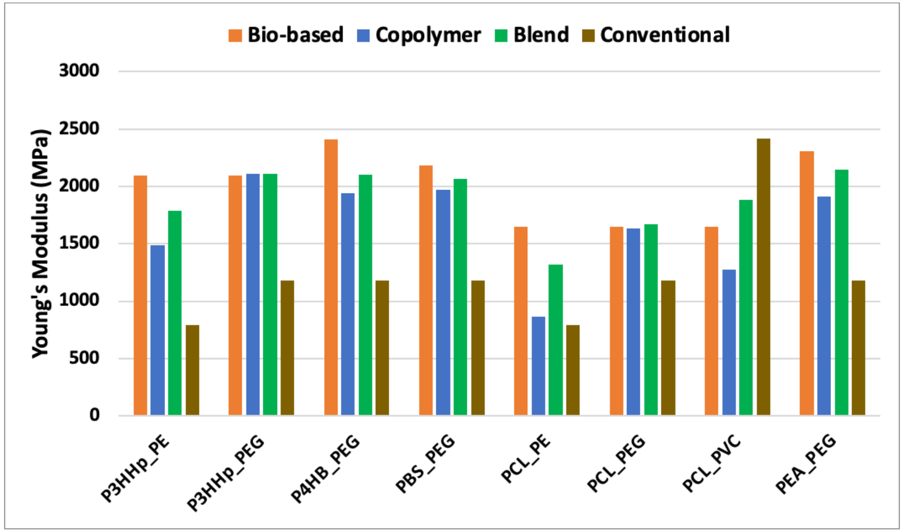
<u>Properties of interest</u>

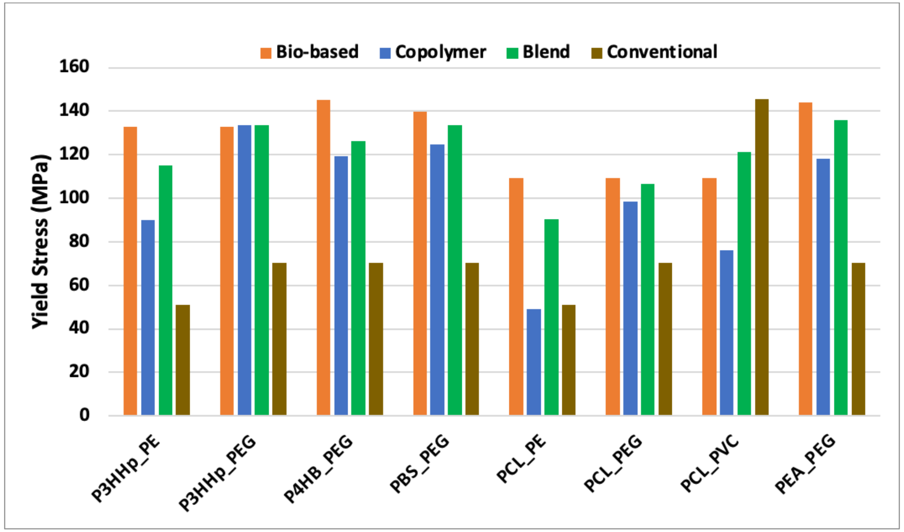
- Young's modulus
- Poisson's ratio
- Yield stress
- Yield strain



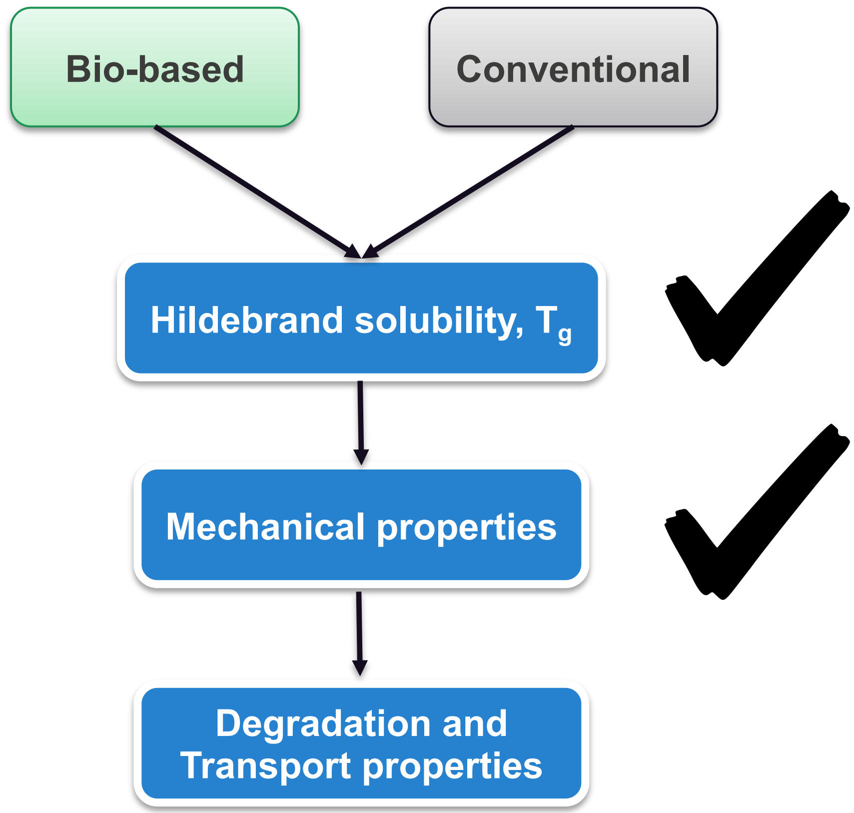
Predictions from Simulations

- 50:50 composition
- Copolymer
- Blend

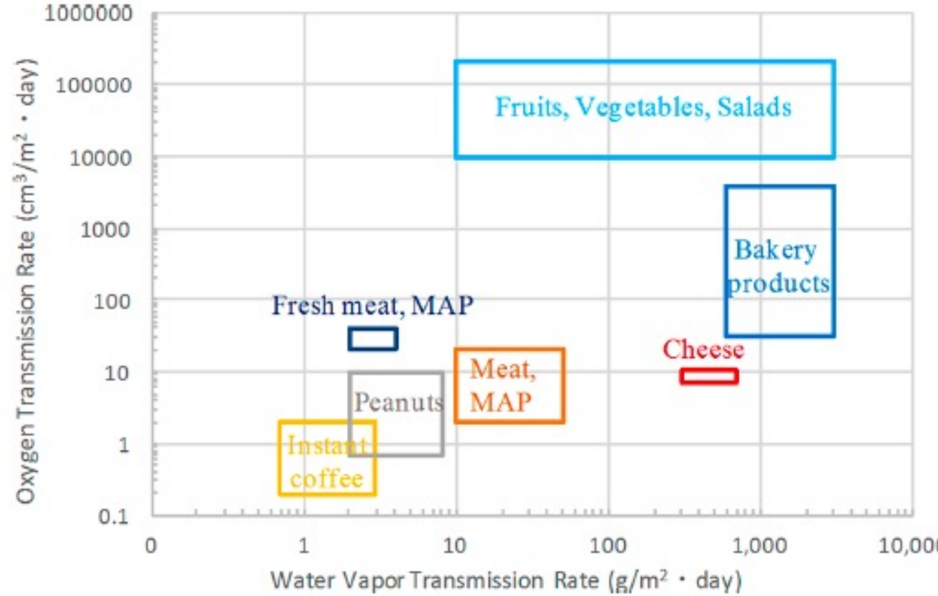




Next Steps…


Bio-based
Conventional
Hildebrand solubility, T_g
Mechanical properties
Degradation and Transport properties

Importance of Transport Properties

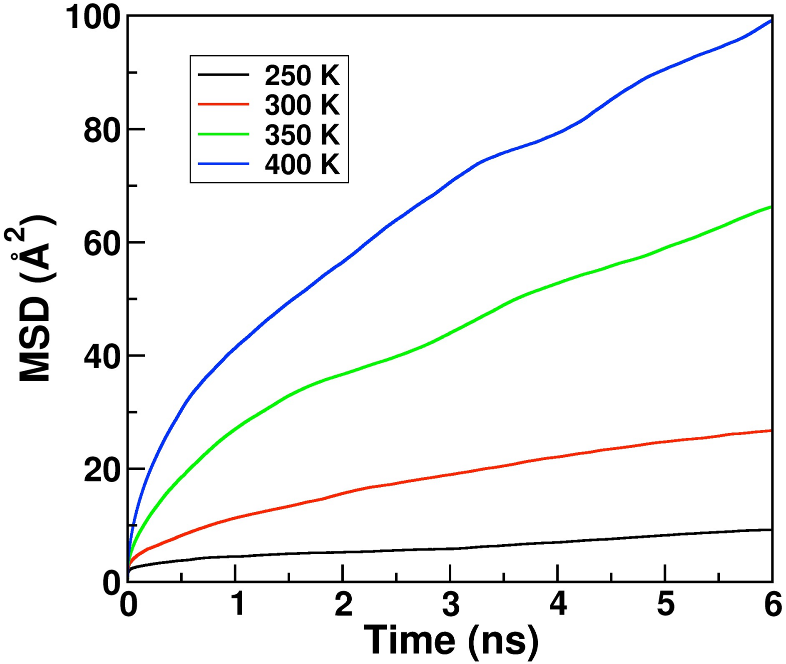


ACS Sustainable Chem. Eng. **2018**, 6, 49−70

Water Transport Properties

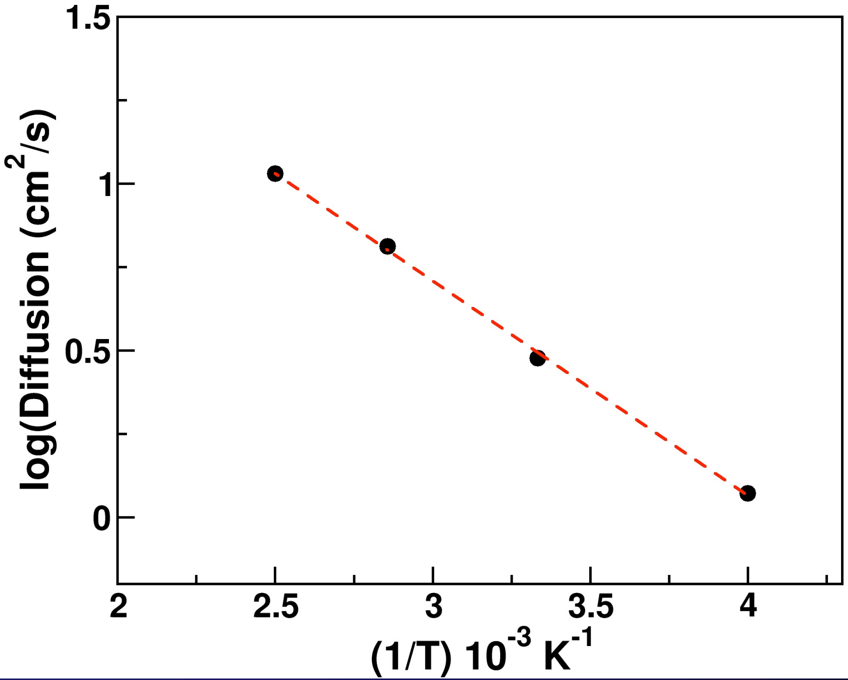
Polypropylene

Mean square displacement at various temperatures

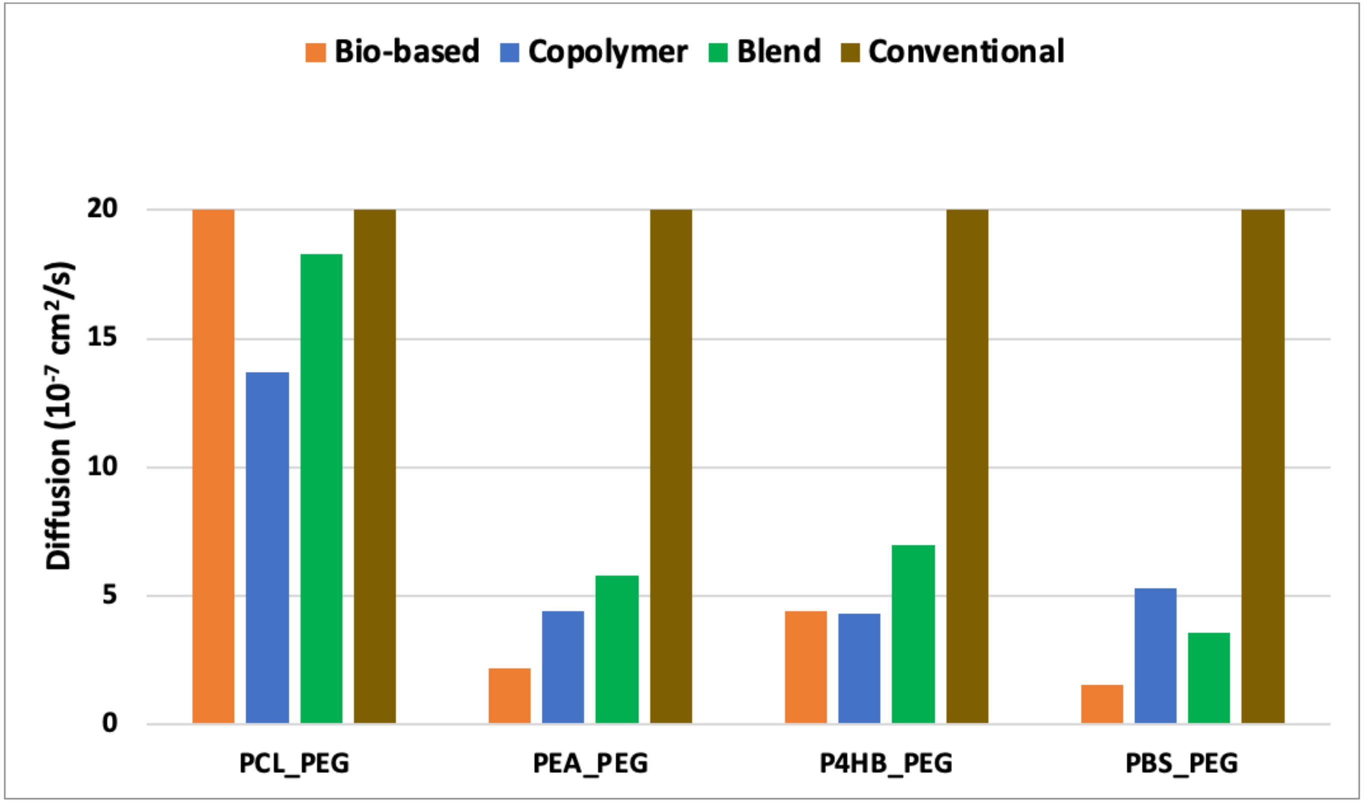


Arrhenius equation

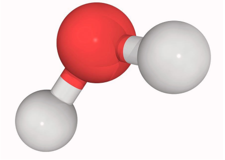
$$D = D_0 \, e^{\left(\frac{-Q}{k_B T}\right)}$$



Transport Properties of Hybrid Polymers

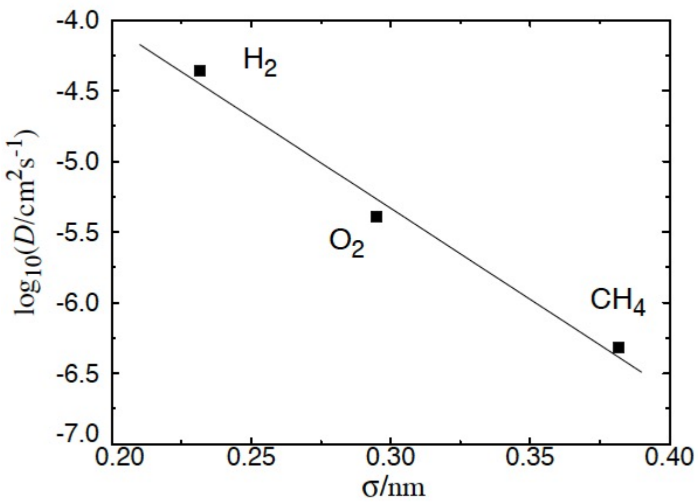


Water molecule

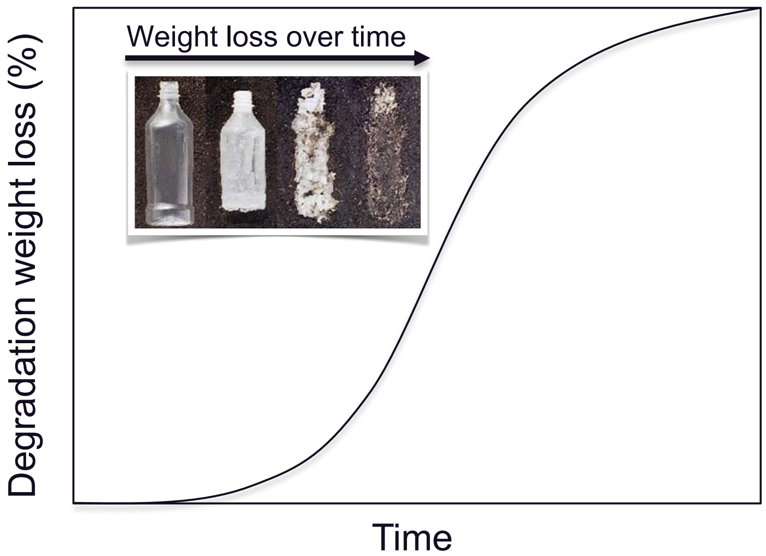


Future Plan

Transport properties for different small molecules



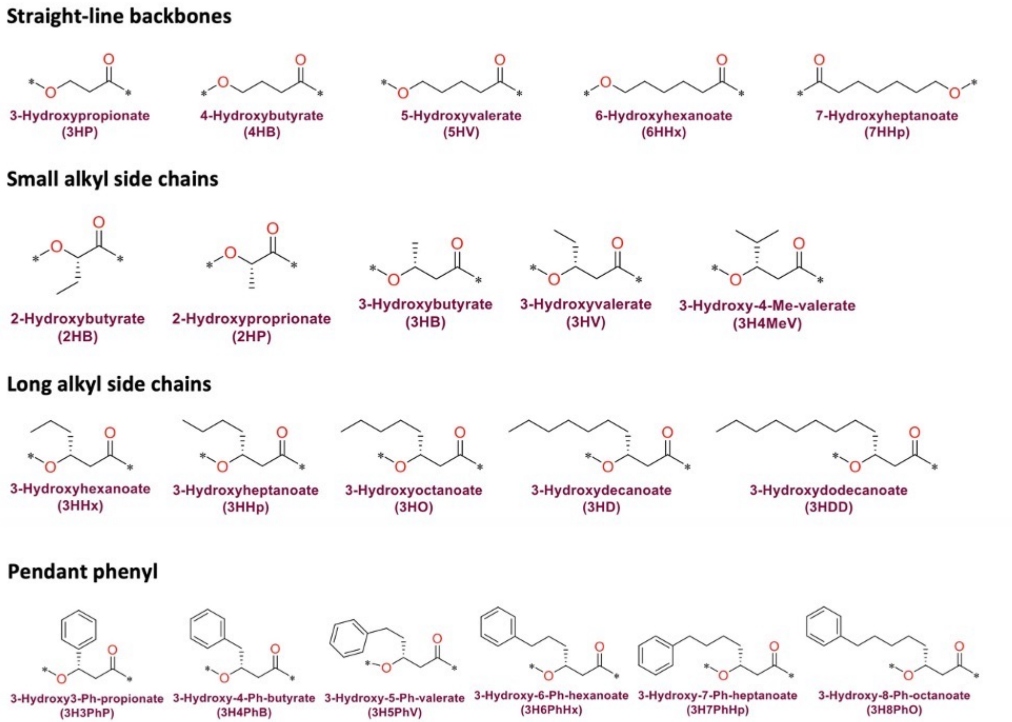
Degradation properties



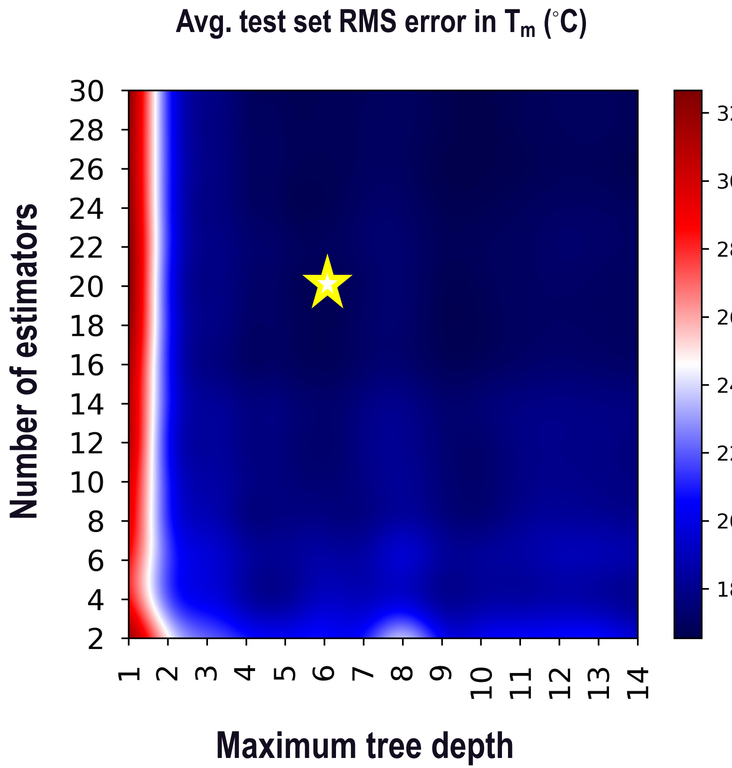
Down select the top polymer candidates and pass on to the experimental collaborators for testing our predictions

Machine-learning Melting Temperature (T_m) model

Diverse chemistries



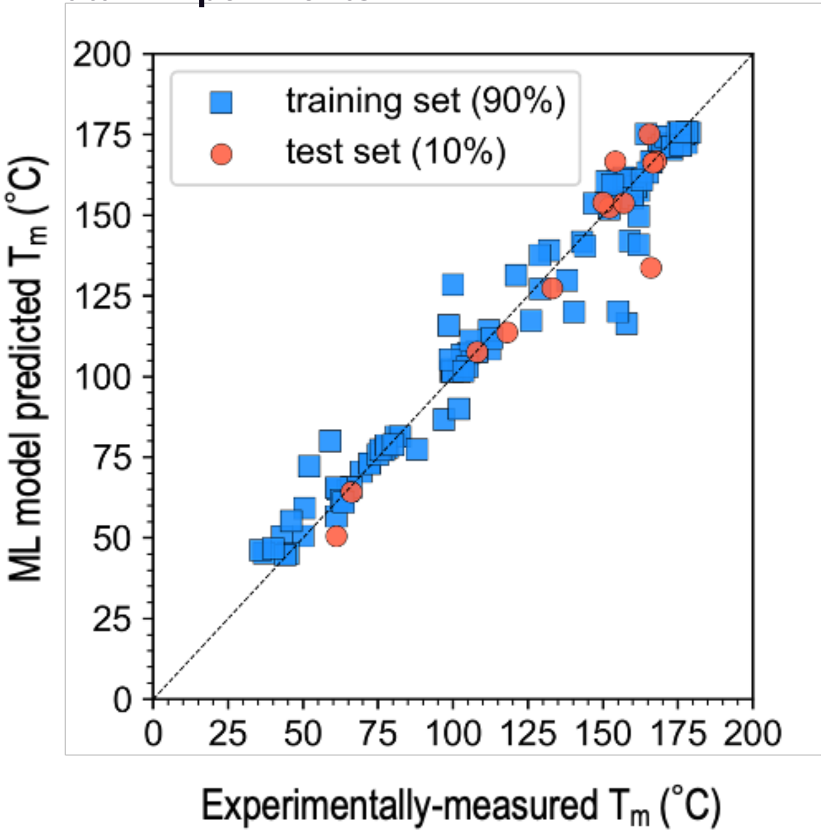
Random Forest method



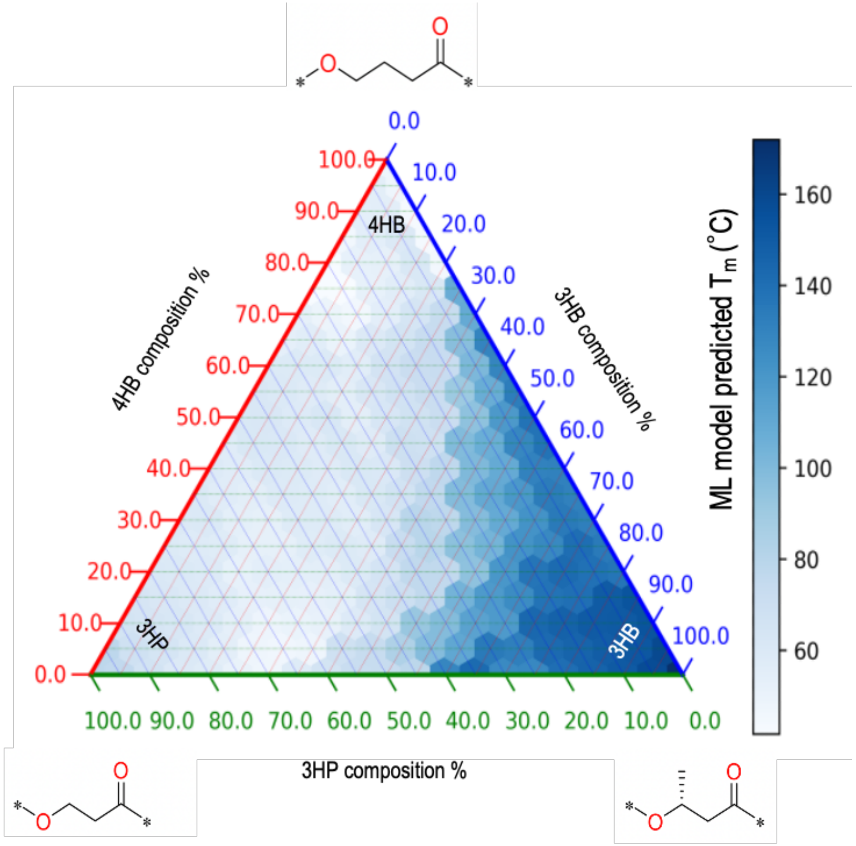
Karteek K. Bejagam, Jessica Lalonde, Carl N. Iverson, Babetta L. Marrone, and Ghanshyam Pilania (Manuscript ready to submitted)

ML Predictions

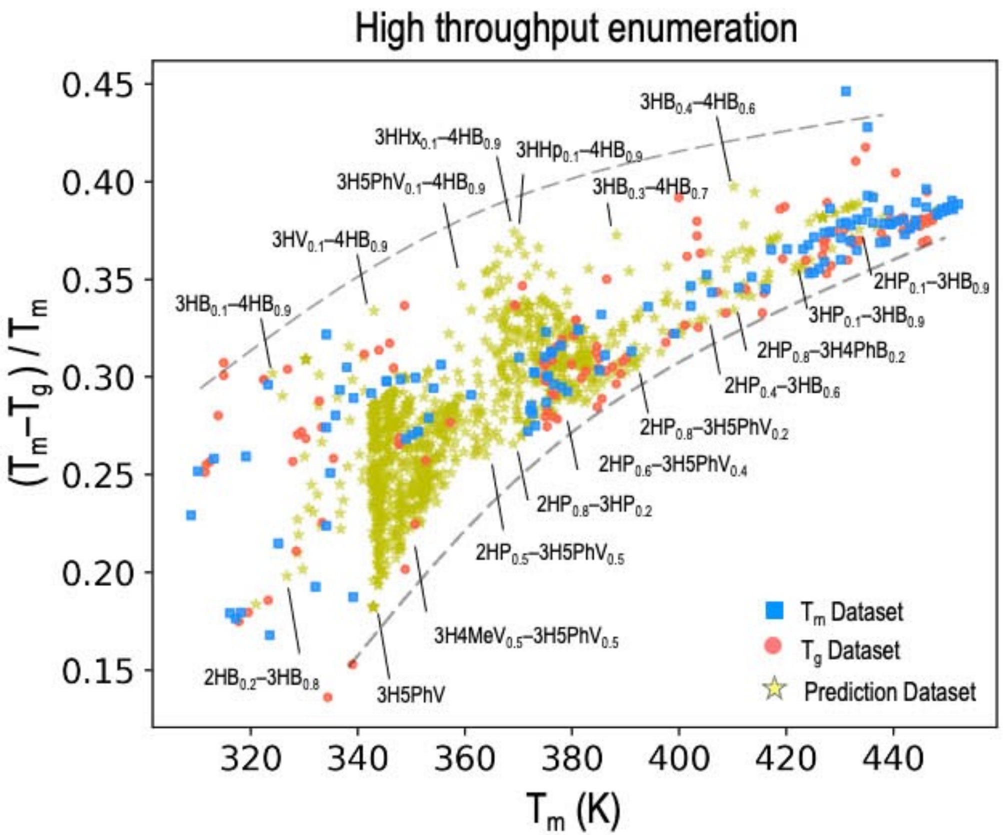
Descriptors : RDKit
Data : Experiments



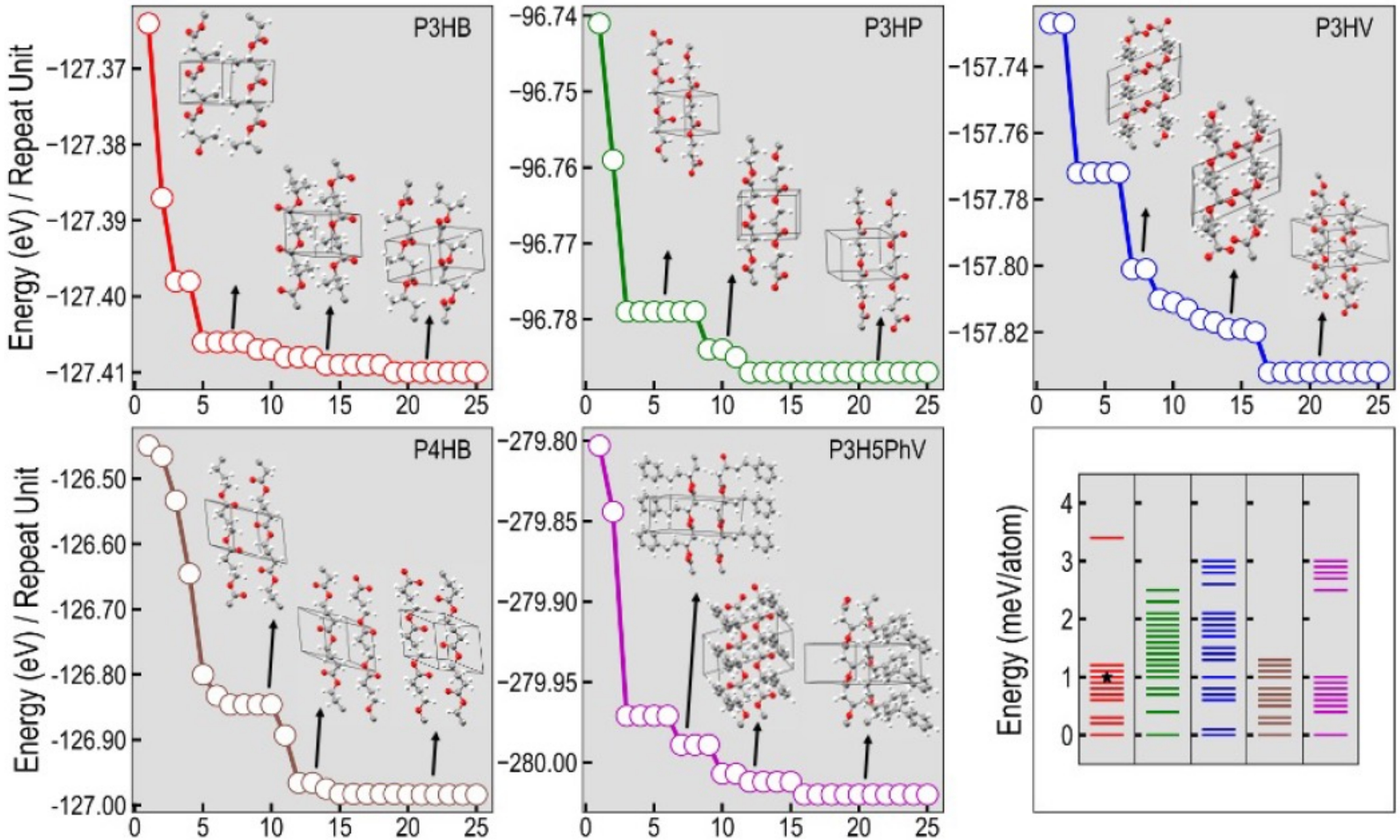
Predictions for multicomponent mixtures



Polymer Design



Crystal Structure Predictions



Vinit Sharma, **Karteek K. Bejagam**, and Ghanshyam Pilania (Manuscript under preparation)

Publications and Conference Talks

Publications:

1. **Karteek K. Bejagam**, Carl N. Iverson, Babetta L. Marrone, and Ghanshyam Pilania Glass Transition Temperature Predictions of Binary Copolymers and Blends of Polyhydroxyalkanoate Biopolymers: Compositional and Configurational Dependence Macromolecules, **2021**, 54, 12, 5618-5628 (LA-UR-20-30478)
2. **Karteek K. Bejagam**, Nevin S. Gupta, Kwan-Soo Lee, Carl N. Iverson, Babetta L. Marrone, and Ghanshyam Pilania, Predicting the Mechanical Response of Polyhydroxyalkanoate Biopolymers Using Molecular Dynamics Simulations (Manuscript ready to submitted)
3. **Karteek K. Bejagam**, Jessica Lalonde, Carl N. Iverson, Babetta L. Marrone, and Ghanshyam Pilania, Machine Learning for Melting Temperature Predictions in Polyhydroxyalkanoate-based Biopolymers (Manuscript ready to submitted)
4. Vinit Sharma, **Karteek K. Bejagam**, and Ghanshyam Pilania Predicting Crystal Structure and Chemistry of Bio-polymers Using Evolutionary Algorithms (Manuscript under preparation)
5. Nevin S. Gupta, Kwan-Soo Lee, Shounak Banerjee, **Karteek K. Bejagam**, Ji Hyeon Kim, Chi Hoon Park, Joseph H. Dumont, Ghanshyam Pilania, Carl N. Iverson, Babetta L. Marrone Soil Degradation of Polyhydroxybutyrate and Polyhydroxybutyrate-co-Polyhydroxyvalerate films: A Computational and Experimental Study (manuscript under preparation)

Conference talks:

1. **Karteek K. Bejagam**. In the quest for "Green Polymers". Presented at CPMU Silver Jubliee meeting, Bangalore, India. (LA-UR-20-30343)
2. **Karteek K. Bejagam**, Carl N. Iverson, Babetta L. Marrone, and Ghanshyam Pilania Computational aided design of bio-polymers by mining the PHA chemical space. Presented at ACS spring Meeting 2021, Los Alamos, New Mexico, United States. (LA-UR-21-23600)
3. **Karteek K. Bejagam**, Carl N. Iverson, Babetta L. Marrone, and Ghanshyam Pilania Design of Bio-Polymers by Mining the PHA Chemical Space. Presented at International Conference on Biopolymers and Bioplastics, Los Alamos, New Mexico, United States. (LA-UR-21-26177)

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LABORATORY DIRECTED RESEARCH & DEVELOPMENT

HIGH PERFORMANCE COMPUTING

Thank you for your attention