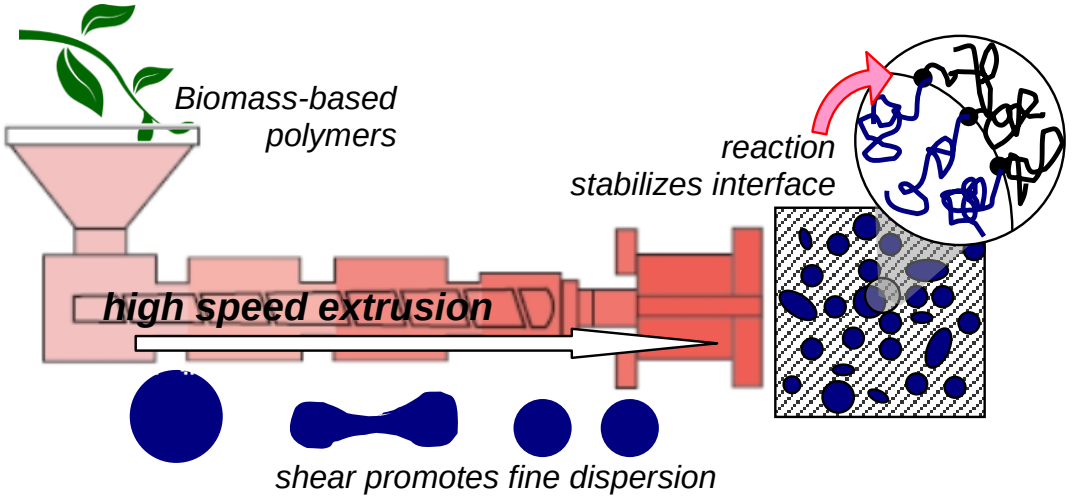
Reactive Compatibilization Schemes for High Speed Extrusion of Polymer Blends



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UMass Lowell

ISBBB Guelph, Ontario

26 July 2018

ISBBB

UMASS LOWELL

Acknowledgements

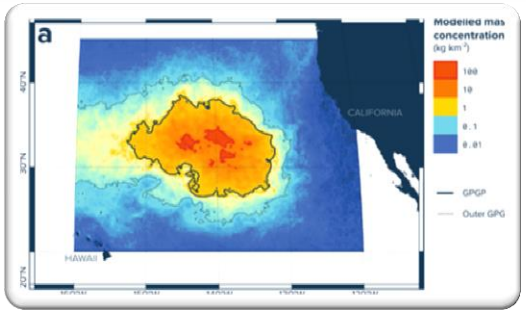
- We gratefully recognize NSF grants CMMI-1350445 and EEC-1342229 for funding this work

- Sobkowicz-Kline research group: JeongIn Gug, Azadeh Farahanchi, Bárbará Calderon, Bin Tan, Hao Pan, James Soule,



- Thanks to Prof. Bob Malloy, Plastics Engineering Department, Technovel for equipment assistance and helpful discussions

Toward a Circular Economy



Lebreton, L., et al. *Scientific reports* 8.1 ( ): 4666.



http://coastalcare.org/2017/03/what-is-the-great-pacific-ocean-garbage-patch/



https://www.patnadaily.com/

Unsustainable Sources

Chemical Extraction

Plastics Production

Product Manufacturing

Sustainable Sources

Compost

End Life

Recycle

Reuse

Product Usage

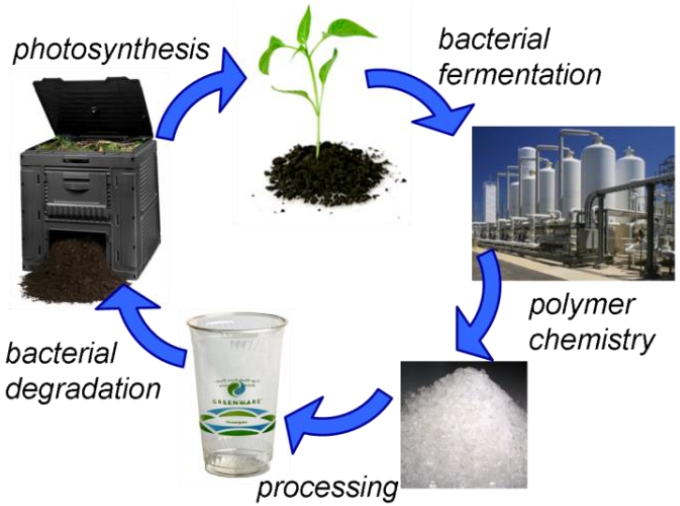
Leakage

Landfill/ incineration

Improving Polymer Sustainability

Closing the loop: end-of-life timeline should match that of useful product life

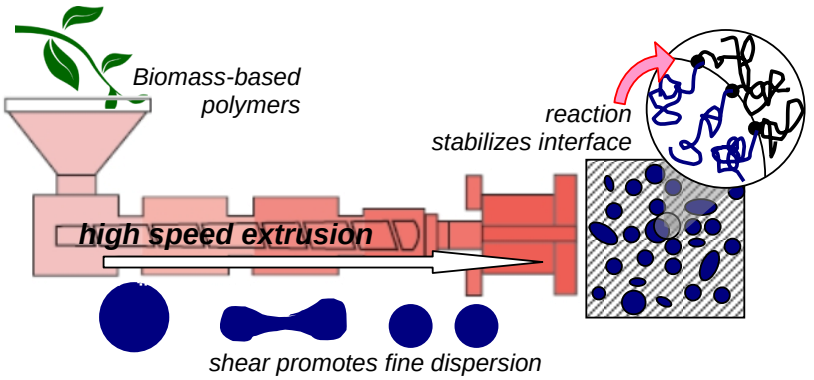
Constraints: Manufacturers need drop-in replacements; end users need product performance



Available Paradigms

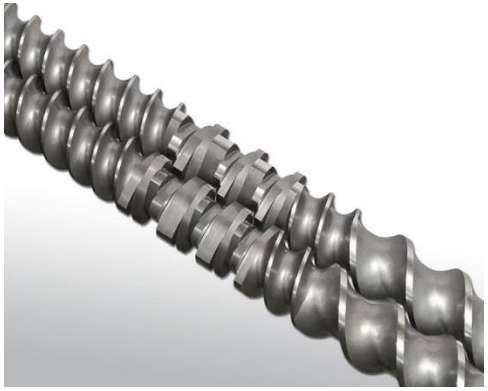
- Mechanical recycling (downcycling?)
- Chemical recycling (energy uses?)
- Compostables
- Reactive extrusion for property modification, hybrid recycling

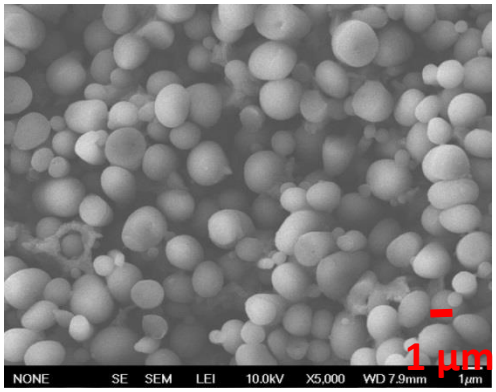


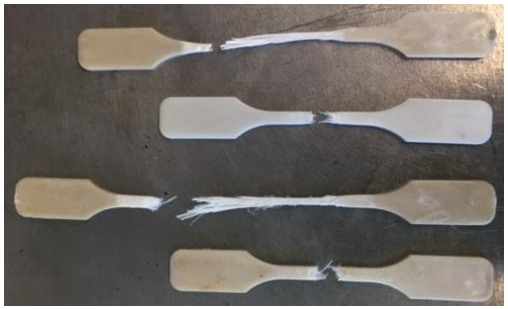


Outline

- Intro to high speed extrusion
- Reactive blending for morphology modification
- Experimental approach
  - Blend 1: transesterification
  - Blend 2: maleic anhydride compatibilizer
- Property improvements stemming from chemistry and morphology
- Simulating reaction kinetics in TSE
- Summary and Outlook

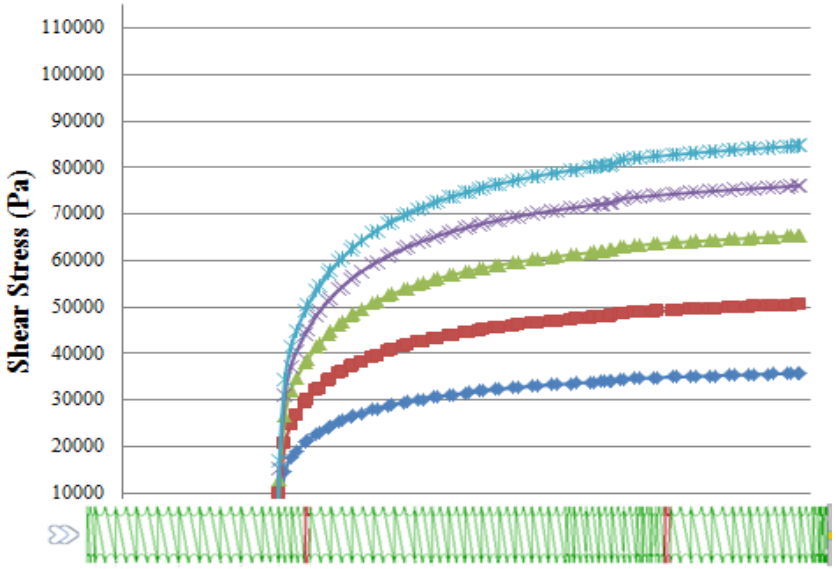


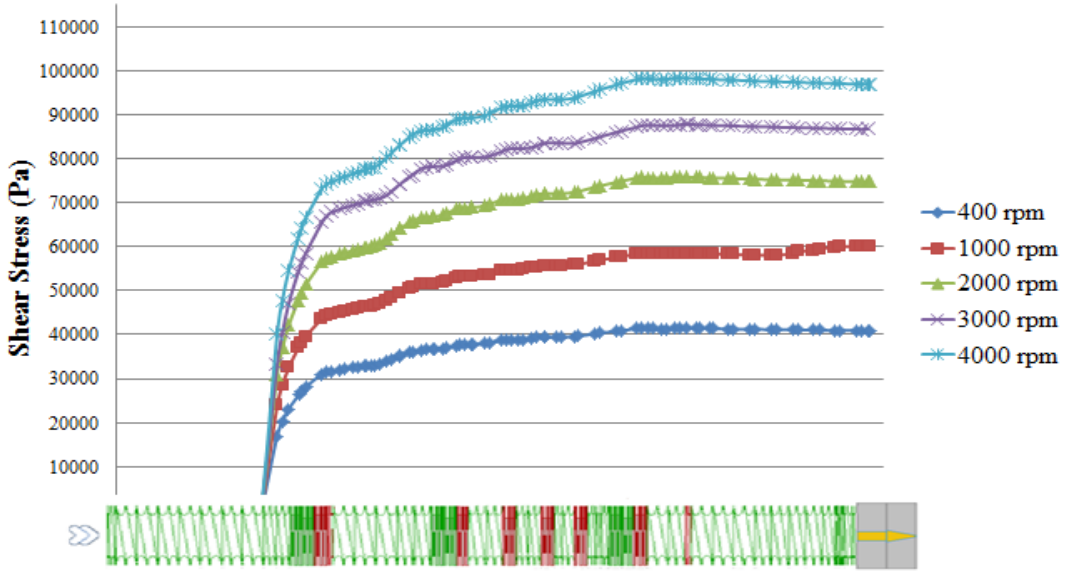




Twin Screw Processing

- TSE as reactor: Process flexibility for blends and composites
  - Imparts high shear stress in short residence time
  - Process factors: specific mechanical energy, temperature, residence time, devolatilization
- Opportunities:
  - Improve properties of bioplastics through blending
  - Hybrid recycling mixed waste streams

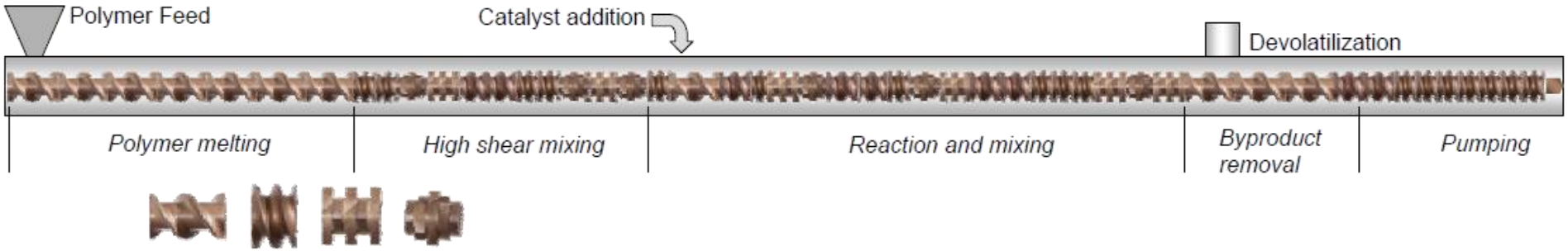




Technovel Ultra-High Speed Extruder

- 15 mm 60:1 intermeshing twin screw extruder rotates up to 4500 rpm
- Fully programmable screw, modular barrel, side stuffer, venting and liquid feed

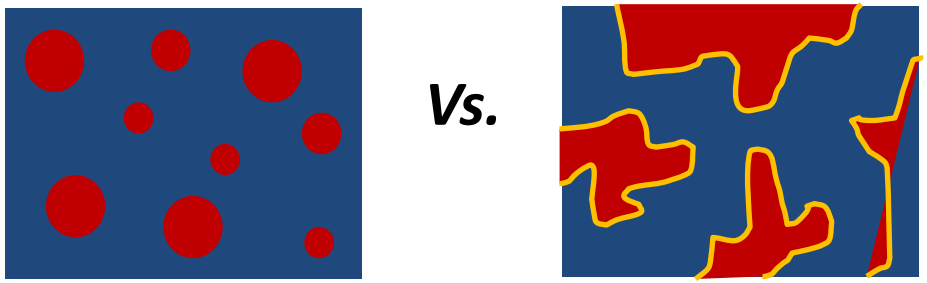




- Objectives:
  - Determine effects of high speeds on interfacial compatibilizing for polymer-polymer blends
  - Compare in situ and ex situ schemes for blend modification

Polymer Melt Blending

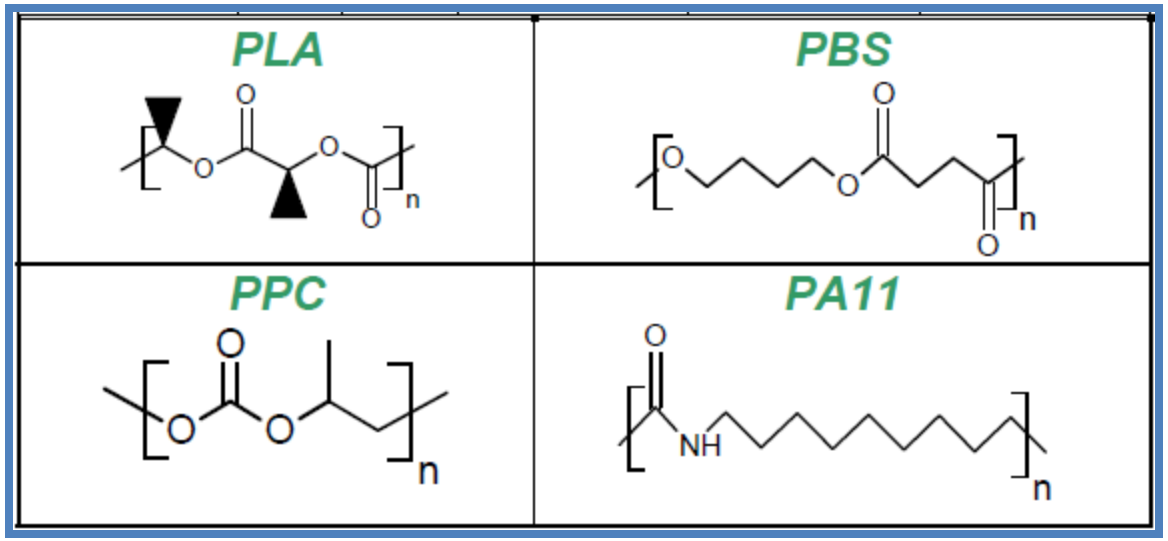
- Why high speed melt blending for Bioplastics?
  - Combine properties: e.g., strong and tough
  - High shear results in large interfacial area
  - Introduce interfacial reactions to compatibilize phases
  - Ease of processing in terms of cost & time



- Blend characteristics
  - Most polymers immiscible & incompatible → weak interfaces
  - Morphology equilibrium between droplet breakup, coalescence
  - Bioplastics often shear sensitive → exploit for interchange reaction

Condensation Polymers for Reactive Blending

Polymer	Tg [°C]	Tm [°C]	Modulus [GPa]	Tensile strength [MPa]	Impact strength [J/m]
PLA	60	180	3.8	48	16.0
PBS	-32	130	0.58	34	2400
PA11	42	190	1.5	36	74.8
PPC	37	150	1.78	42	<10



- Poly(lactic acid) and Poly(butylene succinate): linear semicrystalline polyesters
- Polyamide 11: engineering thermoplastic from castor oil
- Poly(propylene carbonate): produced from carbon dioxide
- Synergistic blends prepared for balanced properties

Experimental Approaches

- Two routes for reactive extrusion:
  - Route A: trans reactions by catalyst addition
  - Route B: ...tive polymer; blend/react in second step
- Process design for modifying morpholo...ce
  - Screw de...
  - Screw speed and mass feed rate for controlled SME
- Simulate ...ction kinetics coupled w...l fluid flow

Chemistry

Processing

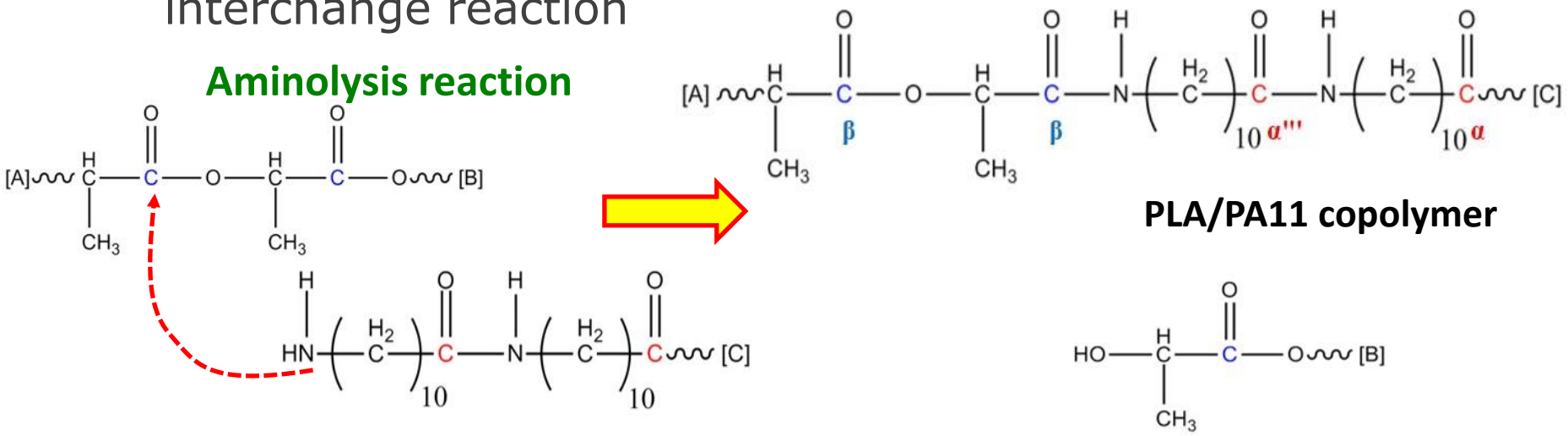
Simulation

Characterizations:

- **Spectroscopy/titration → chemical reaction**
- **Microscopy → morphology**
- **Mech/thermal props → performance**

Transesterification Reaction Scheme

- Polyester-Polyamide
  - PLA → Biodegradable, brittle
  - PA11 → Biomass-based, tougher
  - Toluene sulfonate transesterification catalyst to promote interchange reaction

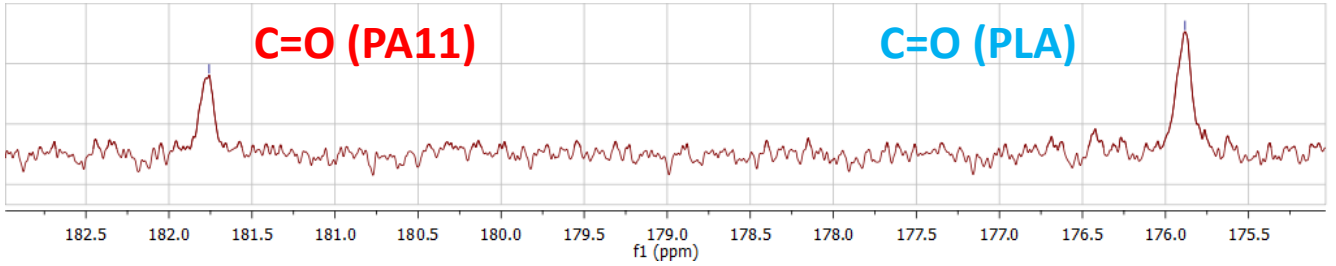


- Non-specific catalyst: homopolymer reaction can also take place
- Challenge: control extent of reaction in extruder

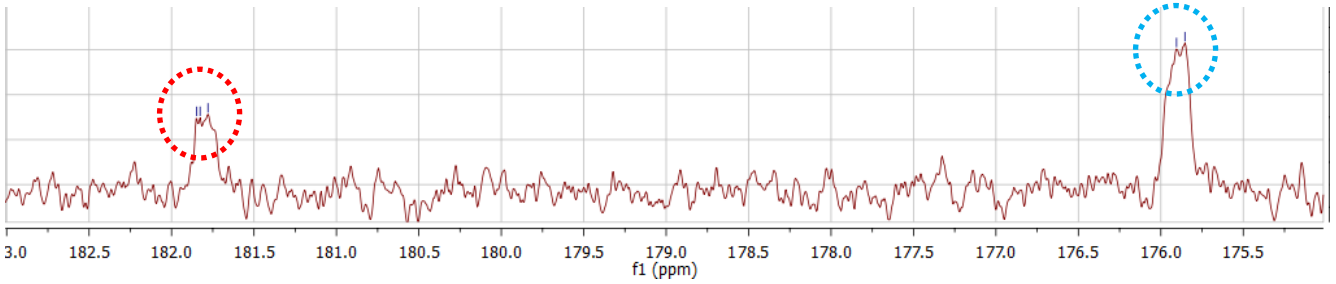
Spectral Evidence of Interchange Reaction

- Peak splits observed when TsOH catalyst added
- Split attributed to aminolysis, i.e. amine ends of PA11 attack ester bonds of PLA

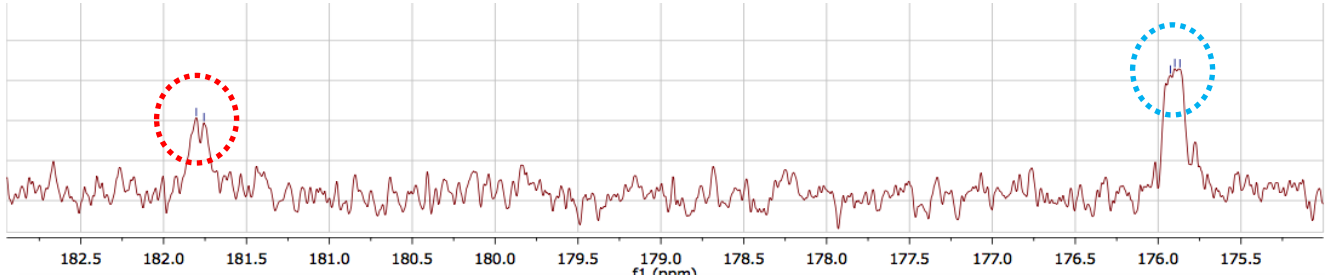
PLA/PA11



PLA/PA11 TsOH 0.5% (Batch mix)

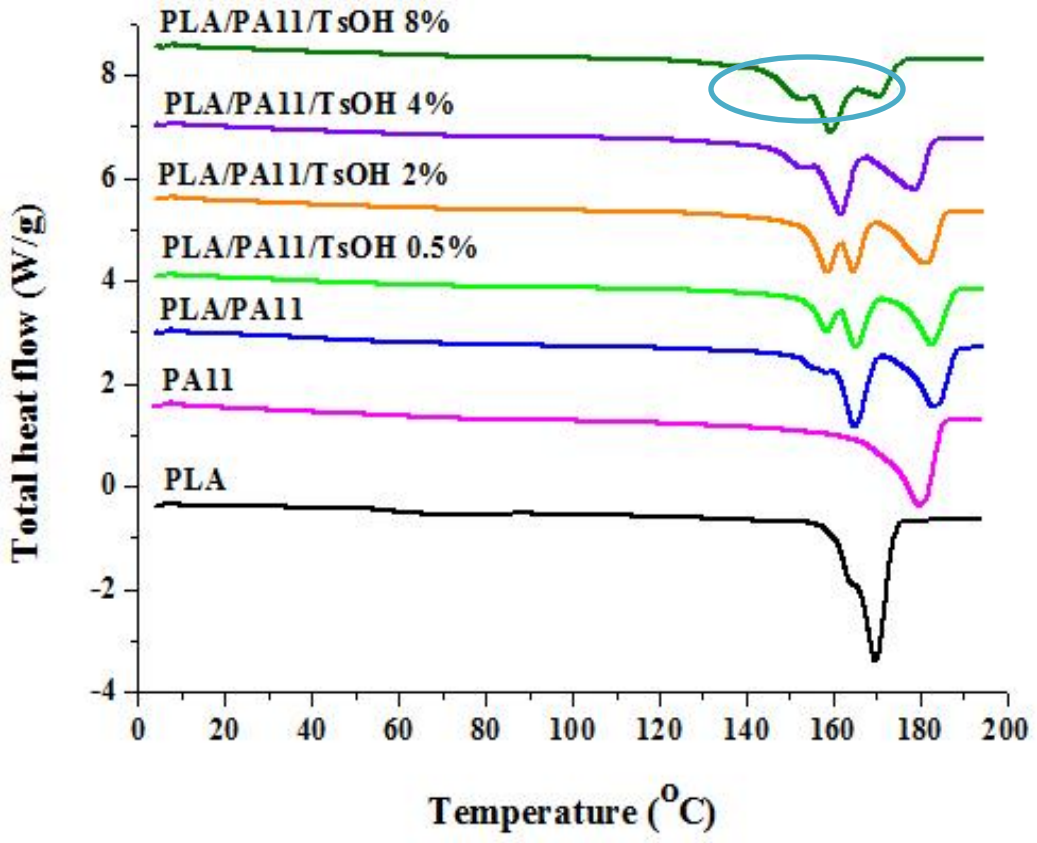


PLA/PA11 TsOH 0.5% (250 rpm, TSE)

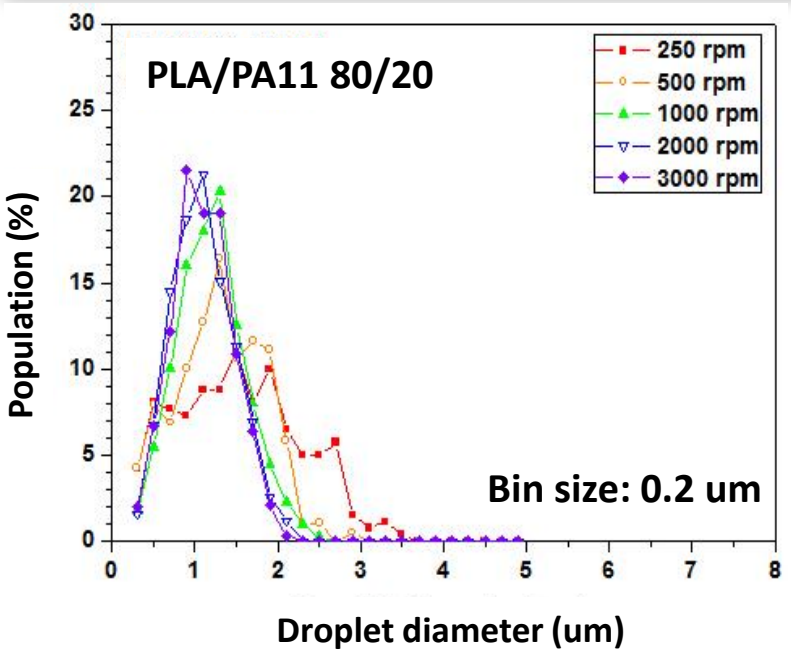


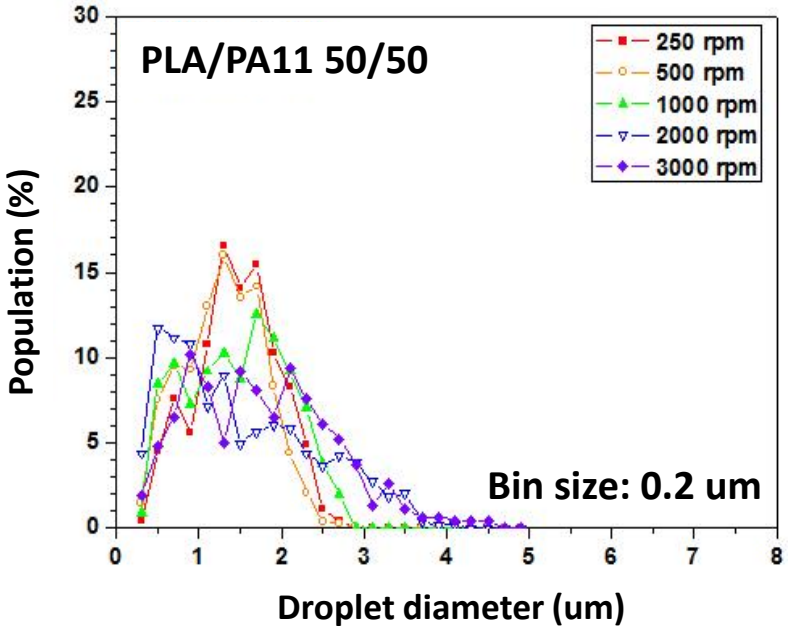
Thermal Properties of Blends

- Differential scanning calorimetry of batch mixed (low shear) blends (50:50) with different catalyst loading
- Melting peaks of both components observed in blends
- Higher amount of catalyst causes significant degradation of PLA and PA11 in the blend.



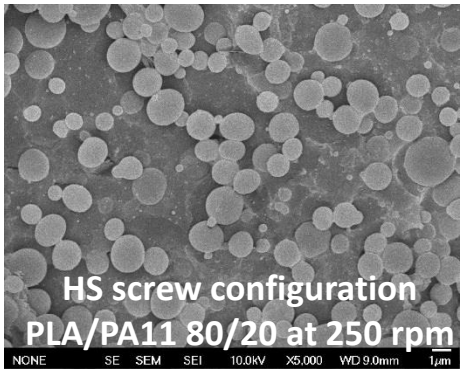
PA11 Droplet Size Distribution





→ Monodisperse (uniform) at high screw speed in 80/20

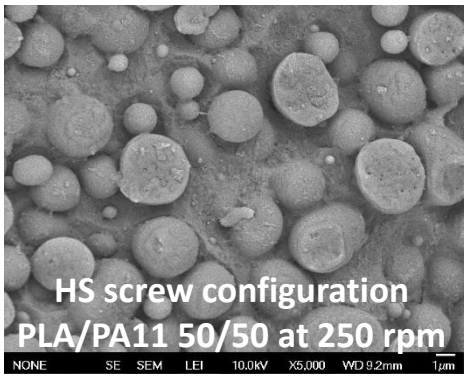
→ Polydisperse (non-uniform) at high screw speed in 50/50



Wu model for droplet size:

$$D = \frac{4\Gamma\eta_r{}^{\pm 0.84}}{\dot{\gamma}\eta_m}$$

Γ: interfacial tension
η_r: viscosity ratio
γ: shear rate
η_m: matrix viscosity

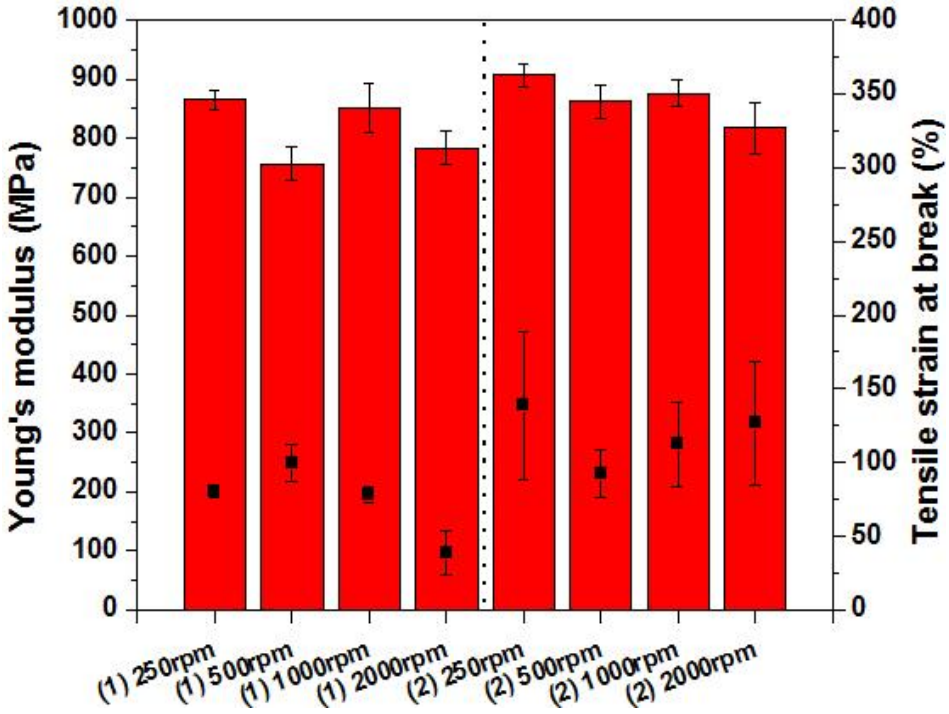


- 5 – 7 images and 300 – 1000 droplets counted per sample

Mechanical Properties PLA-PA11 Blends

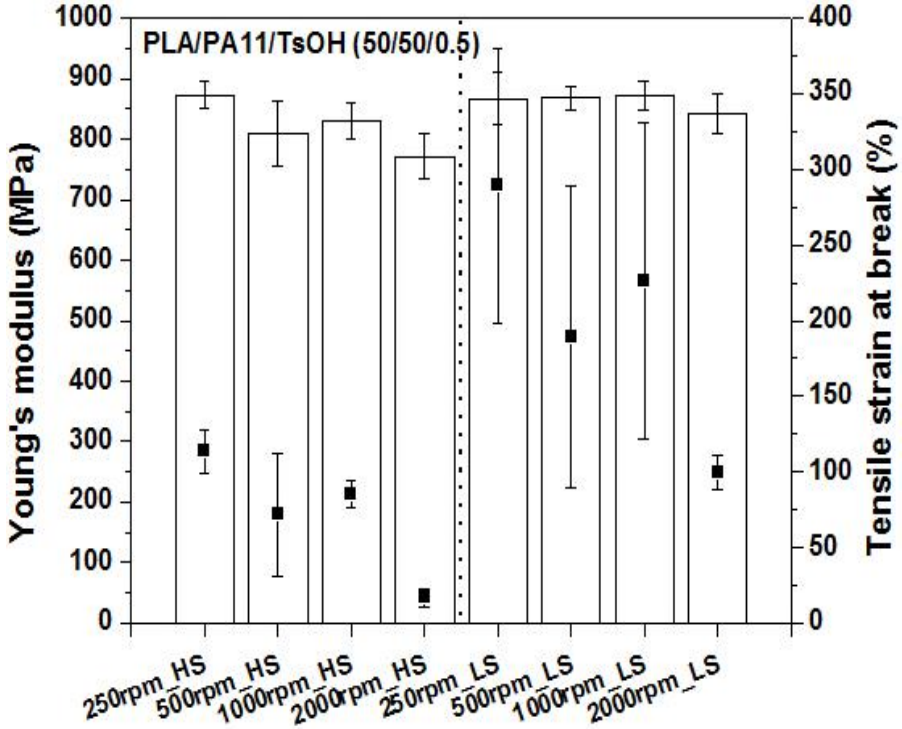
Without Catalyst

aggressive shear *low shear*



With Catalyst

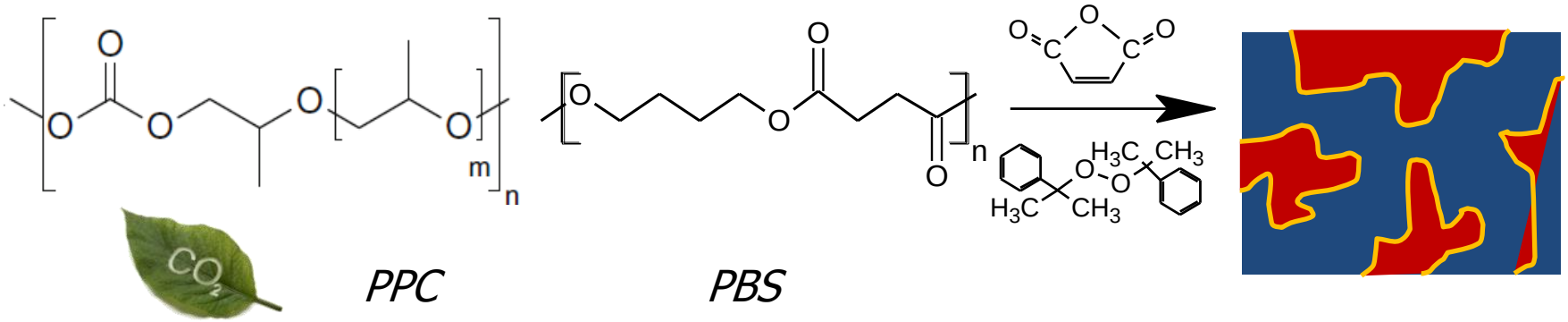
aggressive shear *low shear*



- Higher strain at break and modulus with low shear screw
- More spread in data due to broader particle size distribution

Gug J, Sobkowicz MJ; Int. Poly Process (2016)
Gug J, Sobkowicz MJ; *J. Appl Poly Sci* (2016)

PPC-PBS Blending



- PPC: low thermal stability and T_g near room temp (difficult handling)
- PBS: biopolyester with low melt strength
- Prepare compatibilizer with maleic anhydride and dicumyl peroxide initiator in different ratios
- Find optimal compatibilizer for future blend studies
- **Enhance the performance of PPC/PBS blends by tailoring interfacial chemistry and morphology**
- **Compare processing schemes with similar specific mechanical energy (SME)**

PPC-graft Compatibilizer

Grafting maleic anhydride: challenge to determine dominant reactions taking place

- Ring opening and end capping of chains
- Chain rupture vs. extension from acid end groups
- Radical vinyl grafting as pendant ring in main chain

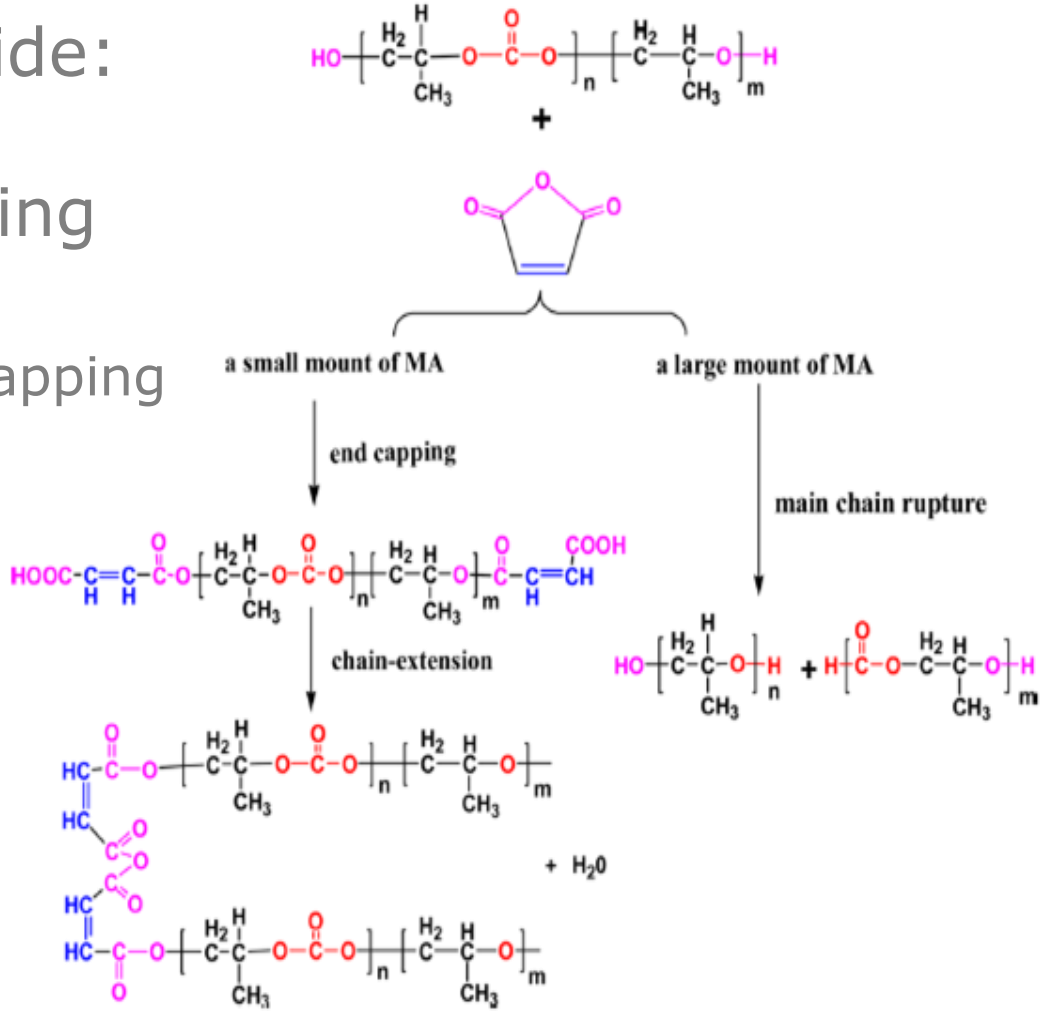


Figure 2. Proposed end-capping reaction, chain extension reaction, and main chain rupture reaction of PPC and MA.

EXPERIMENTAL APPROACH

Reactive extrusion of PPC and PBS blends

Materials

Poly(butylene succinate)
Tg: -32 °C
Processing T: 120 to 190 °C

Poly(propylene carbonate)
Tg: 26 °C
Processing T: 140 to 190 °C

Synthesis of biocompatibilizer

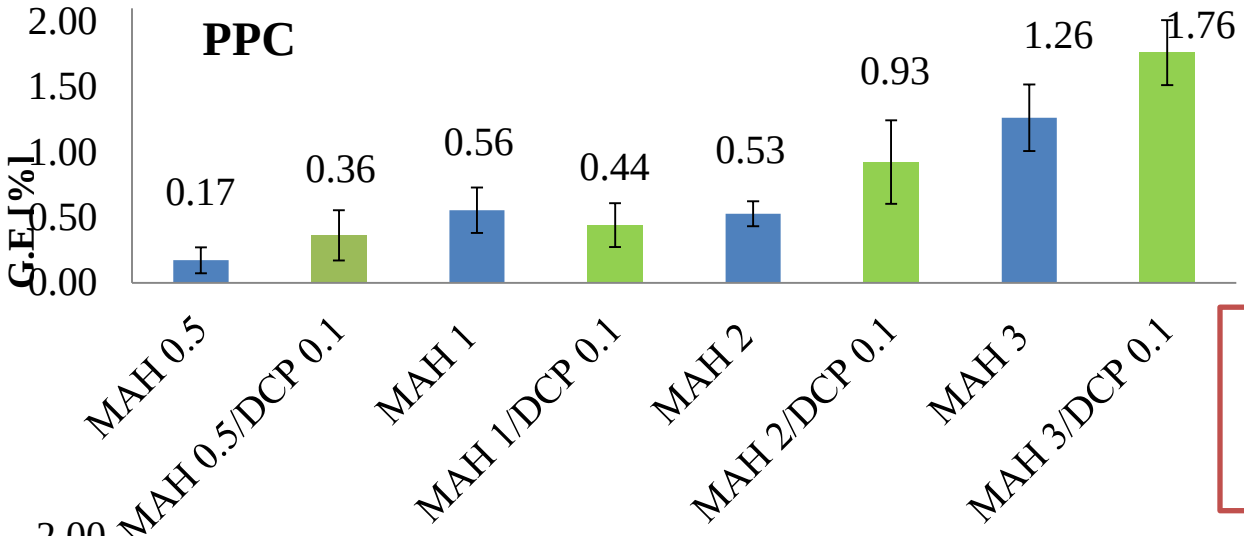
Sample	MAH (wt%)	DCP (wt%)
PPC 0.5	0.5	-
PPC 0.5/0.1	0.5	0.1
PPC 1	1	-
PPC 1/0.1	1	0.1
PPC 2	2	-
PPC 2/0.1	2	0.1
PPC 3	3	-
PPC 3/0.1	3	0.1
PPC 5	5	-
PPC 5/0.1	5	0.01

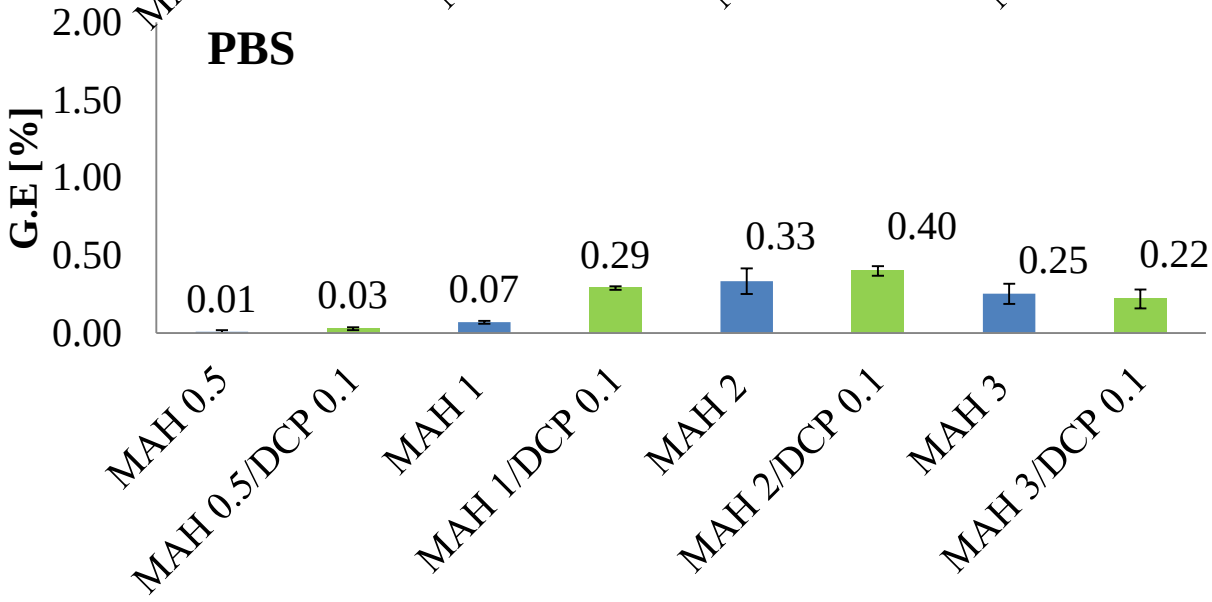
Characterization

- Titration
- TGA
- GPC
- NMR
- FTIR
- Rheology

Calderon B, Sobkowicz MJ; under review

Acid Group Titration



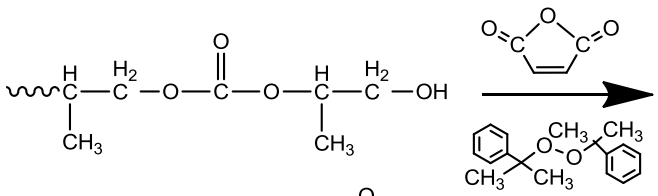


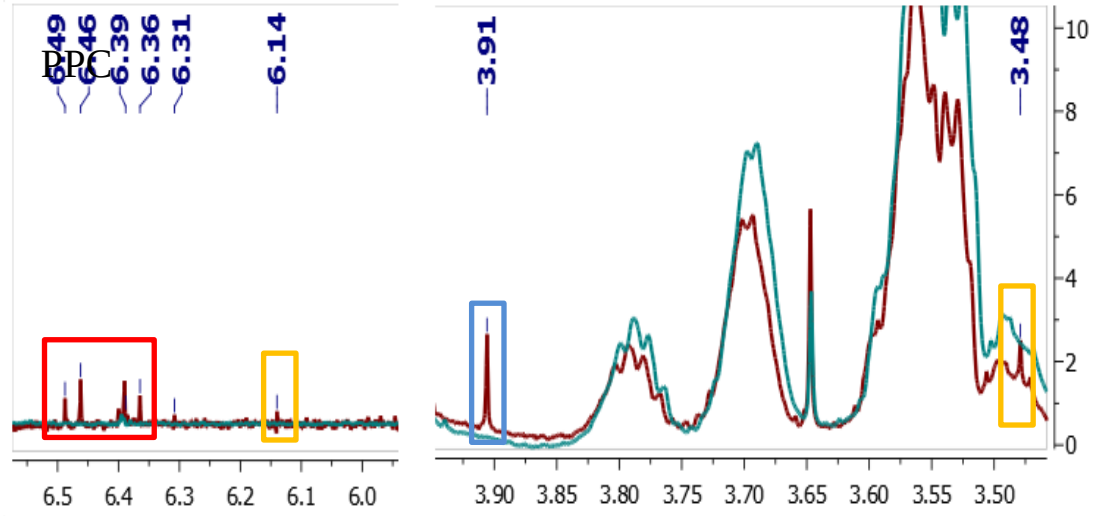
$$GE\ [\%] = \frac{V_{KOH} N_{KOH} Mw_{MAH}}{2W} \cdot 100$$

N_{KOH} = *Volume titrant*
N_{KOH} = *Normality titrant*
Mw_{MAH} = *MAH Mol. weight*
W = *Sample weight*

Spectroscopic Analysis of gPPC

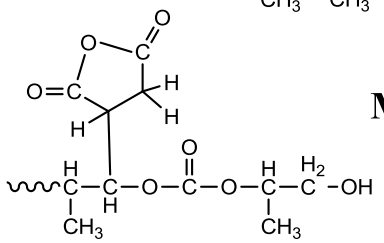
- PPC+MAH2%+DCP 0.1% highest amount of peaks



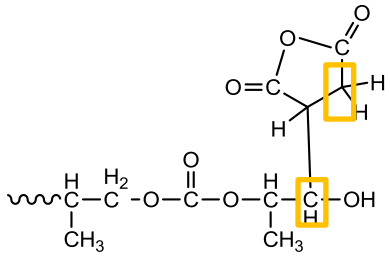


Neat PPC

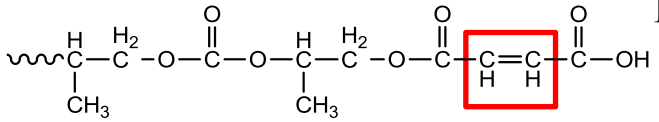
PPC with 2% MAH DCP



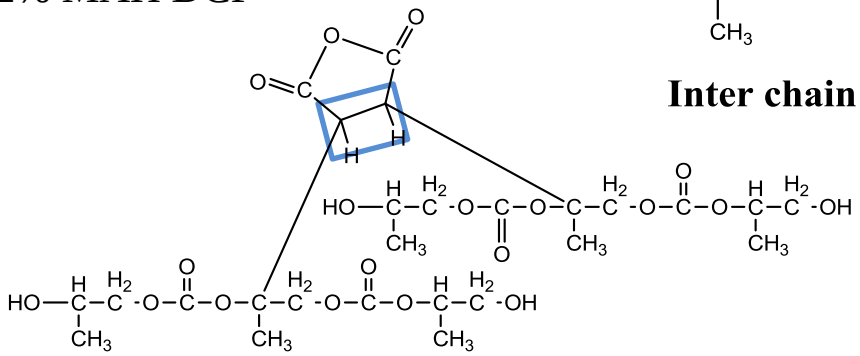
Middle pendant ring



End pendant ring



Ring opening



Inter chain grafting

Selection of Ideal Compatibilizer

- PPC MAH2% DCP 0.1% proved to be the most reactive and stable of all the formulations
- **PPC grafted with MAH: "gPPC"**

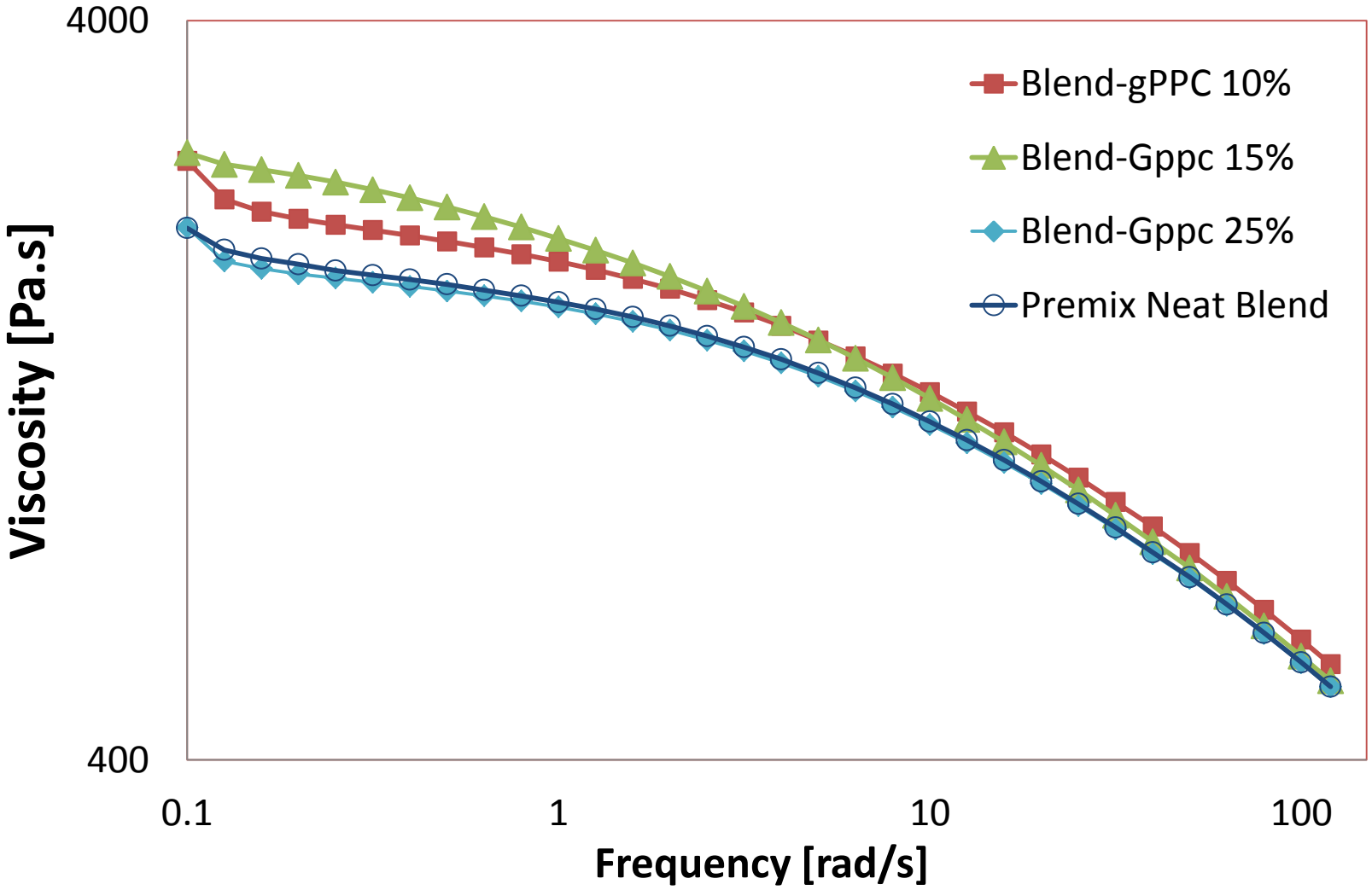
Samples	PPC	PBS
	Viscosity ratio	
MAH 1%	1.43	0.82
MAH 1% DCP	0.97	1.70
MAH 2 %	1.11	0.40
MAH 2% DCP	1.39	1.15
MAH 3%	0.68	0.42
MAH 3% DCP	0.63	1.47

$$\eta_r = \frac{\eta_{formulation}}{\eta_{neat\ processed\ poly}}$$



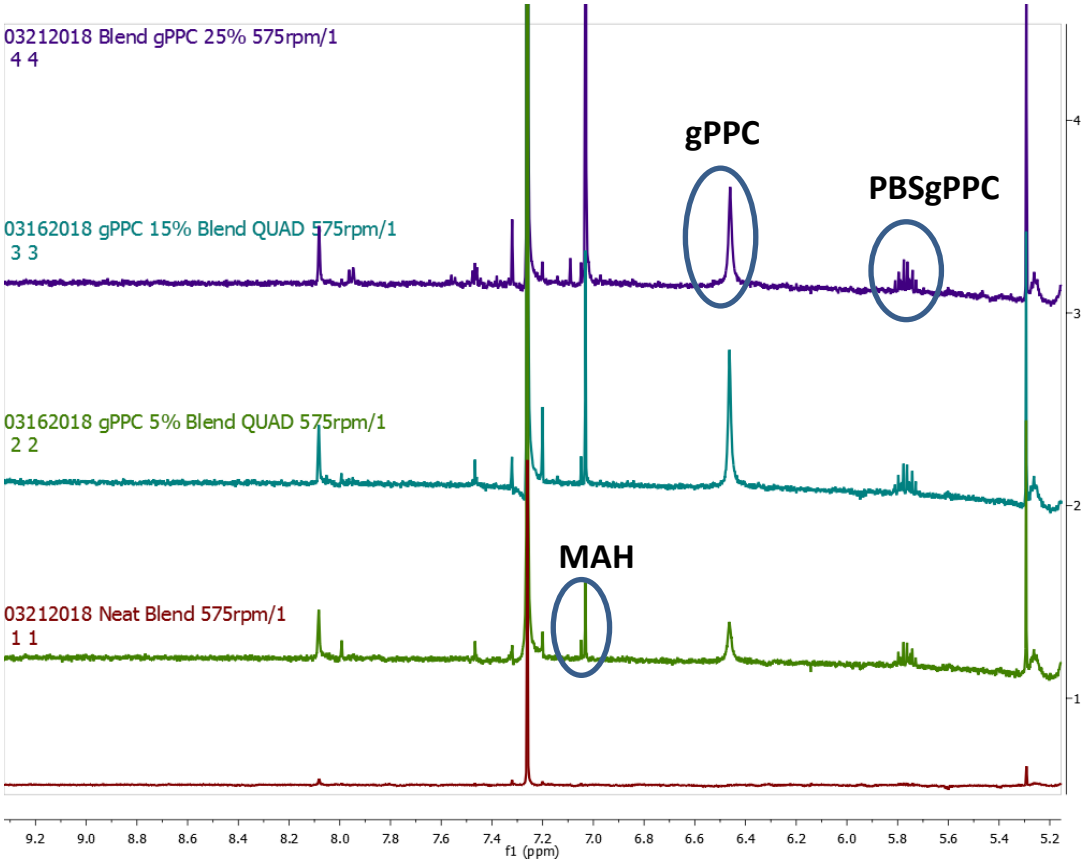
Melt Rheology: Compatibilized Blends

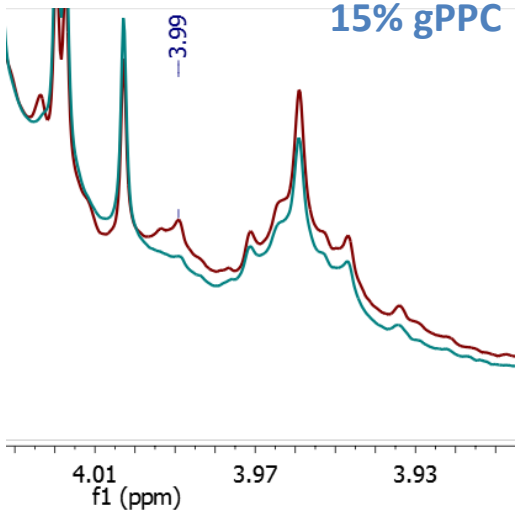
75% PBS 25% PPC with various gPPC contents

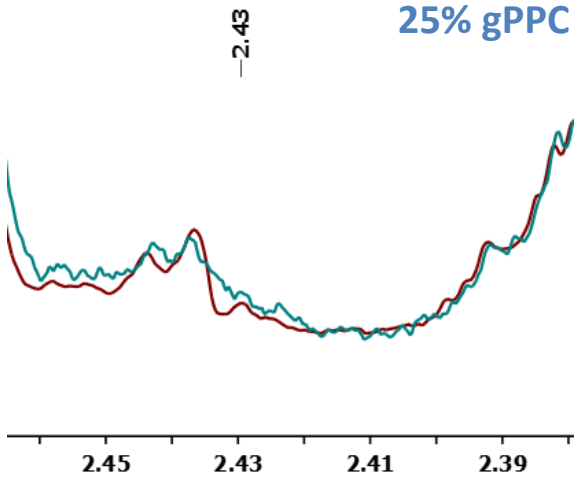


NMR of graft-Blends

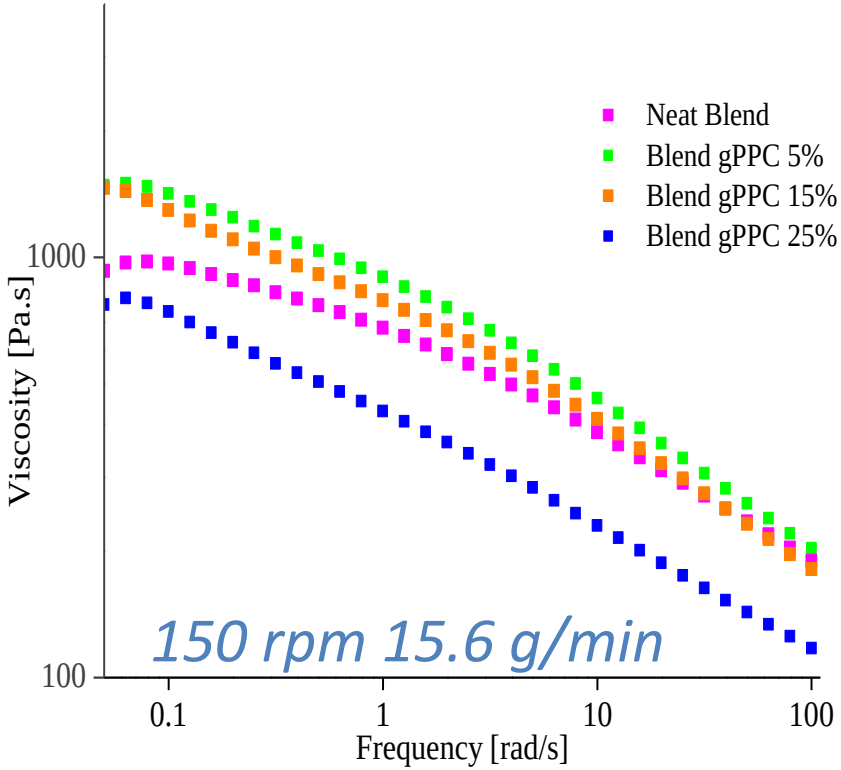
@ 575 rpm 64g/min

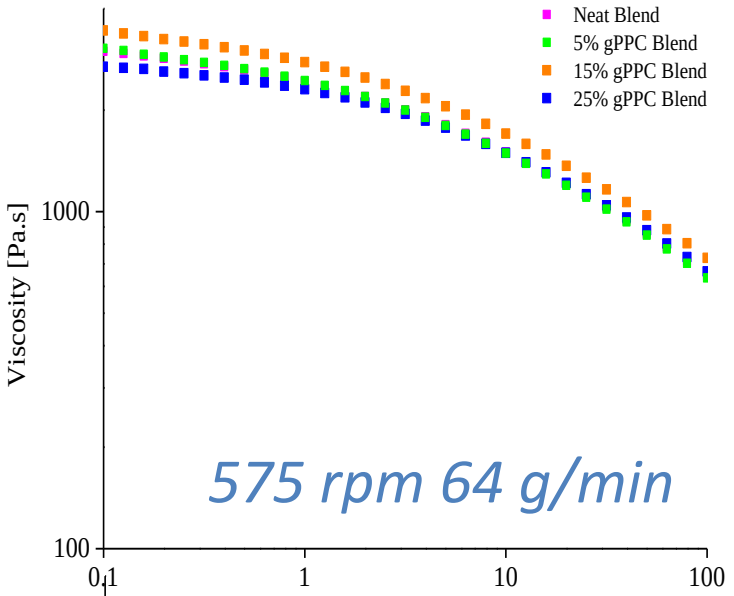


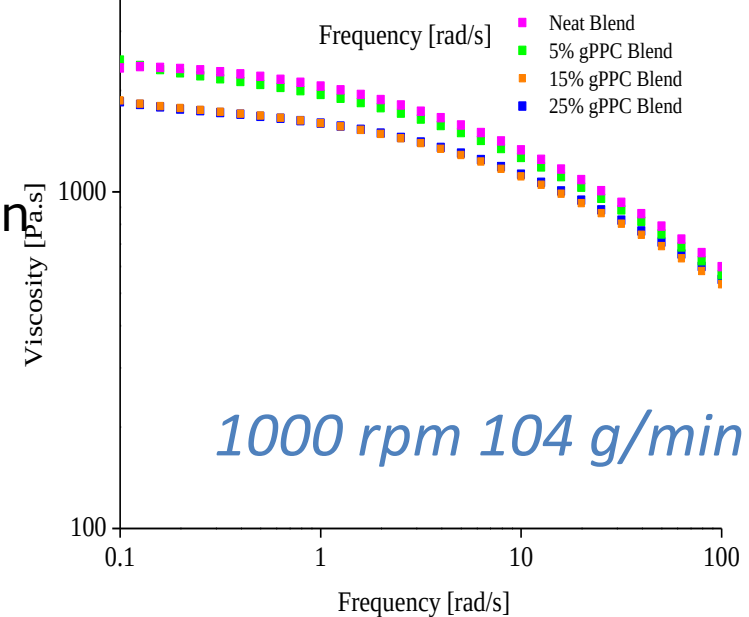




Blend Rheology: Constant SME





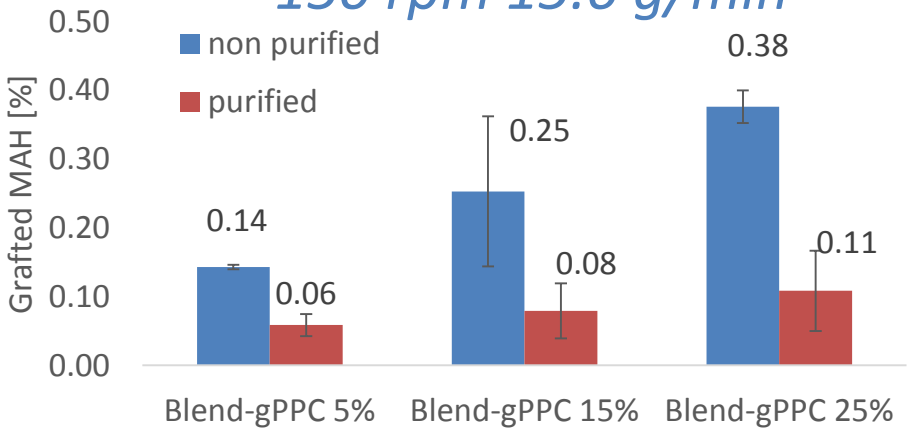


- Longer residence time→ more degradation & shear thinning indicates branching
- Higher shear and shorter times→ Less effect on viscosity
- 5 and 15% closer in viscosity to neat blend (due to interfacial interaction)
- 25% usually lower (degradation effects)

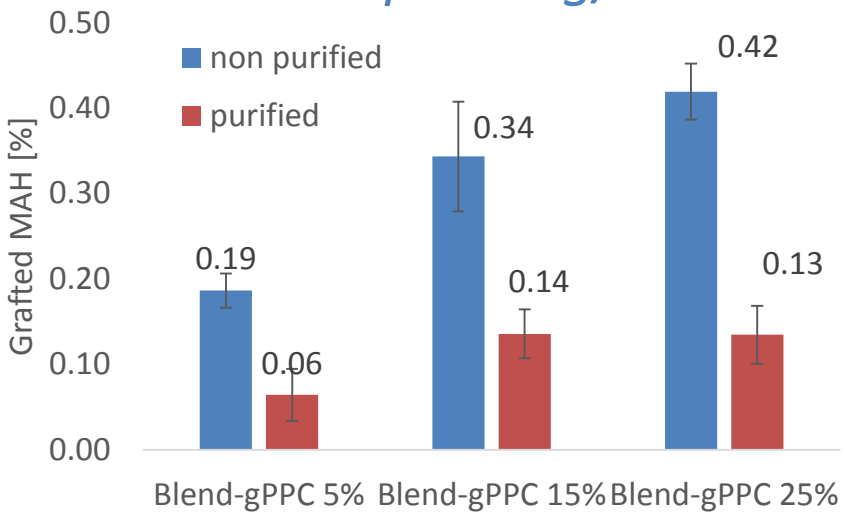
Acid Titration: Constant SME

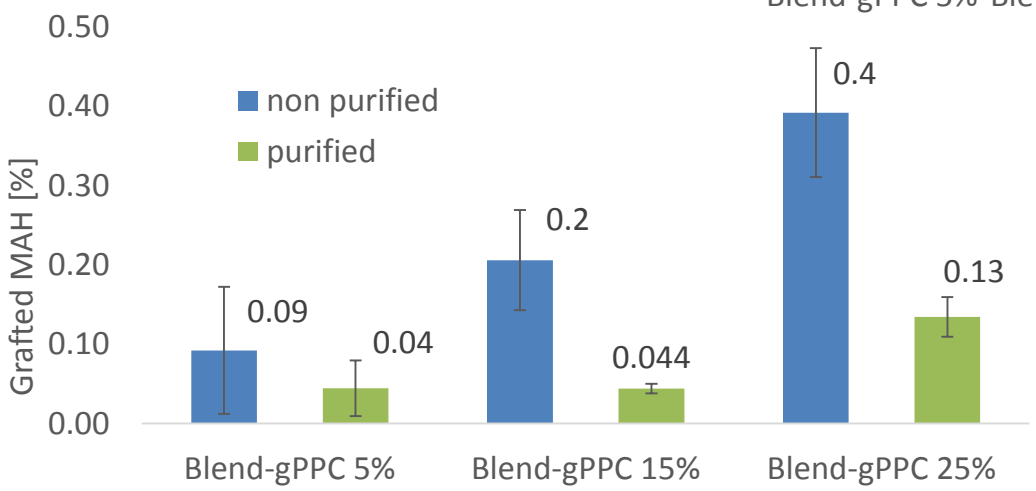
- All purified samples showed similar acid concentration with increasing fraction gPPC

150 rpm 15.6 g/min



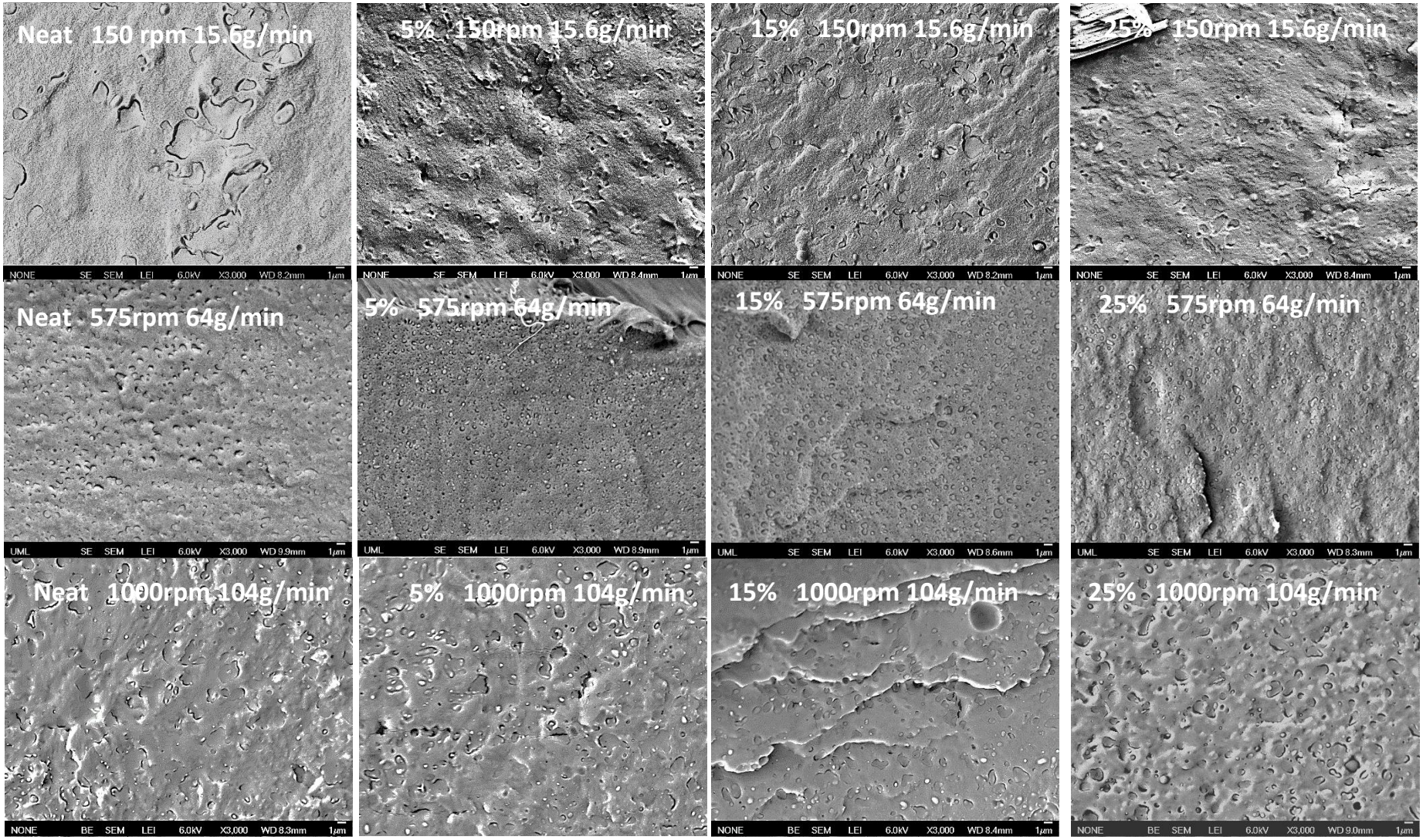
575 rpm 64 g/min



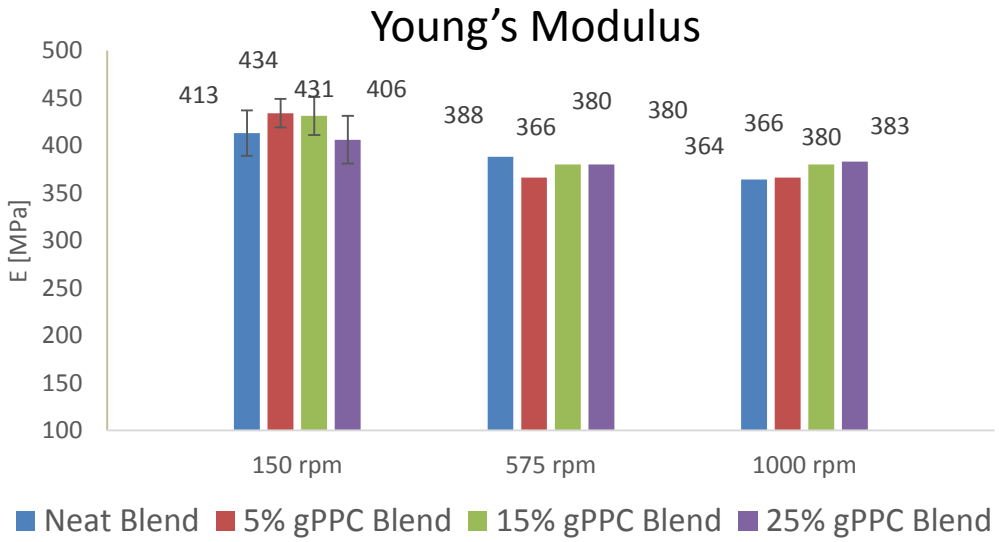


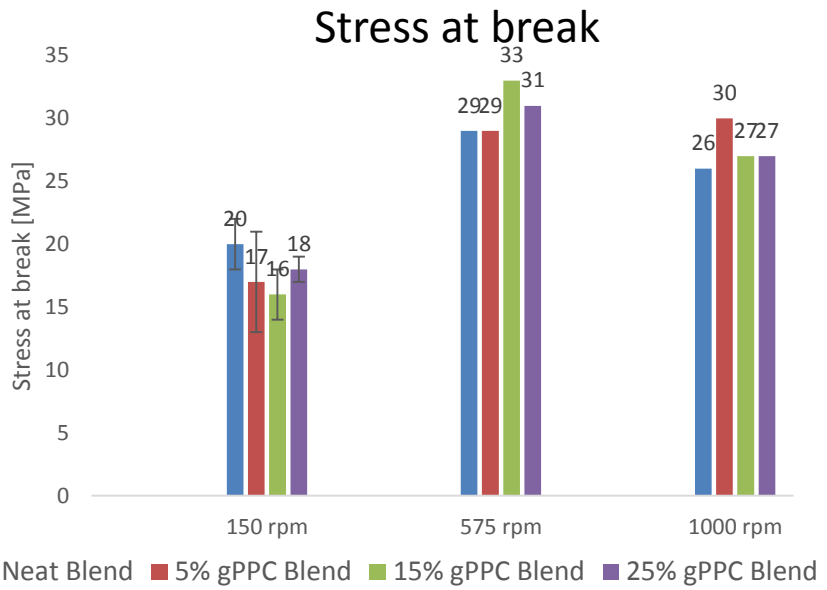
1000 rpm
104 g/min

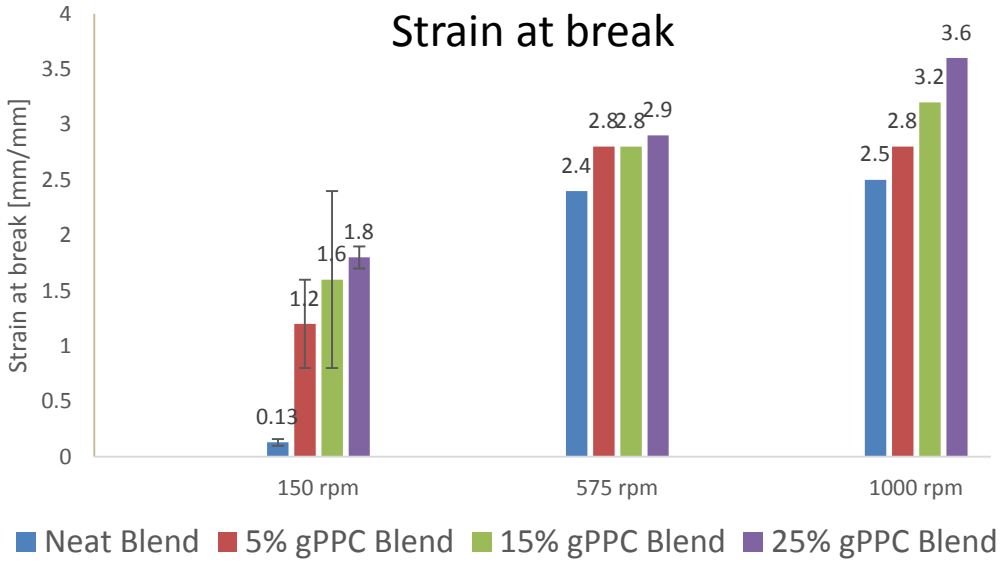
Blend Morphology: Constant SME



Mechanical Properties



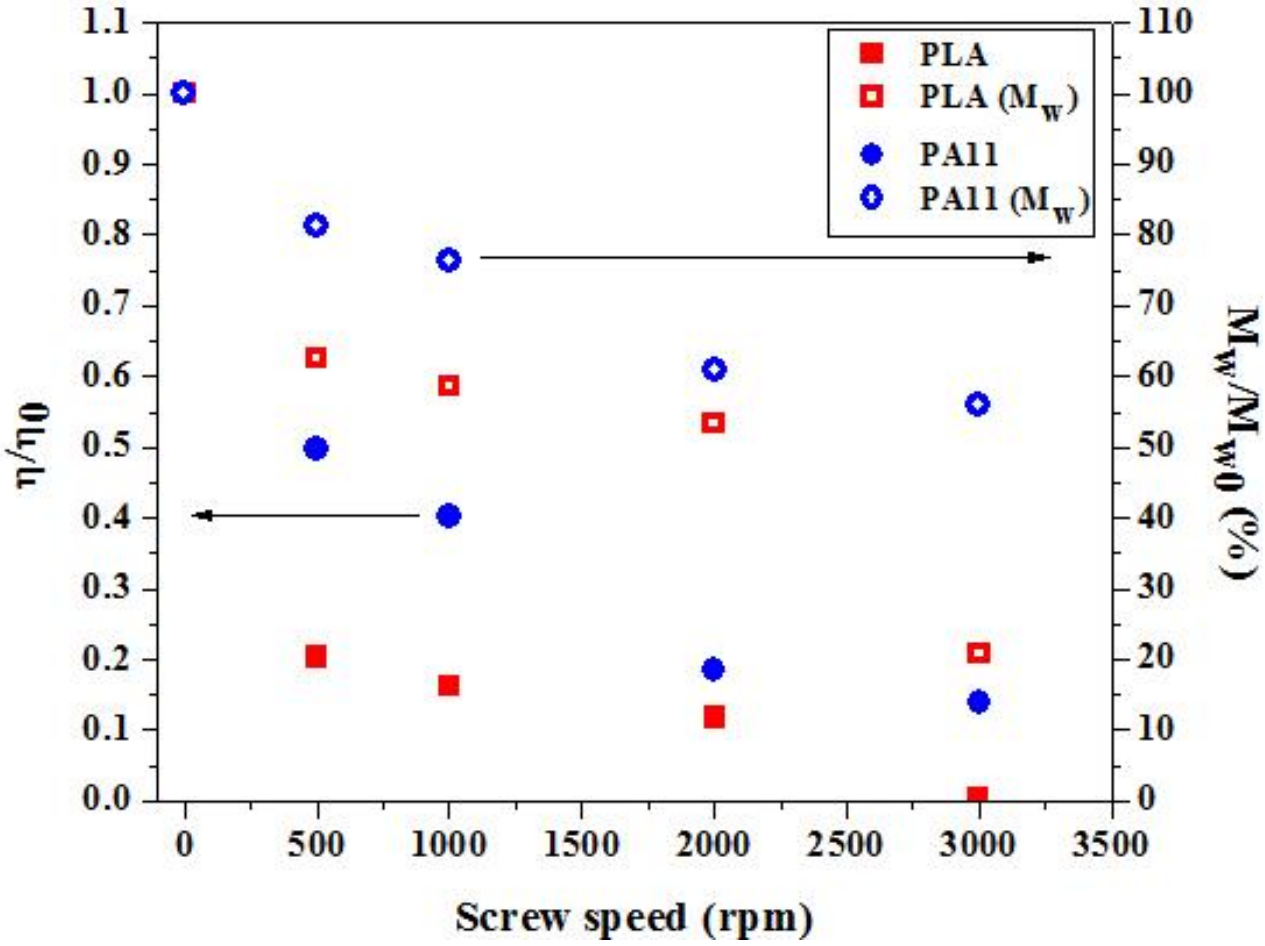




- Effects of shear, residence time, compatibilizer on reaction and mixing
- Shorter res times → less thermal and mech stress → less degradation & higher stability

Extrusion Reduces Molecular Weight

- Capillary rheology tracks decrease in zero shear viscosity
- PA11 lost ~20%, while PLA lost ~40% when processed at 500 rpm and 205 °C

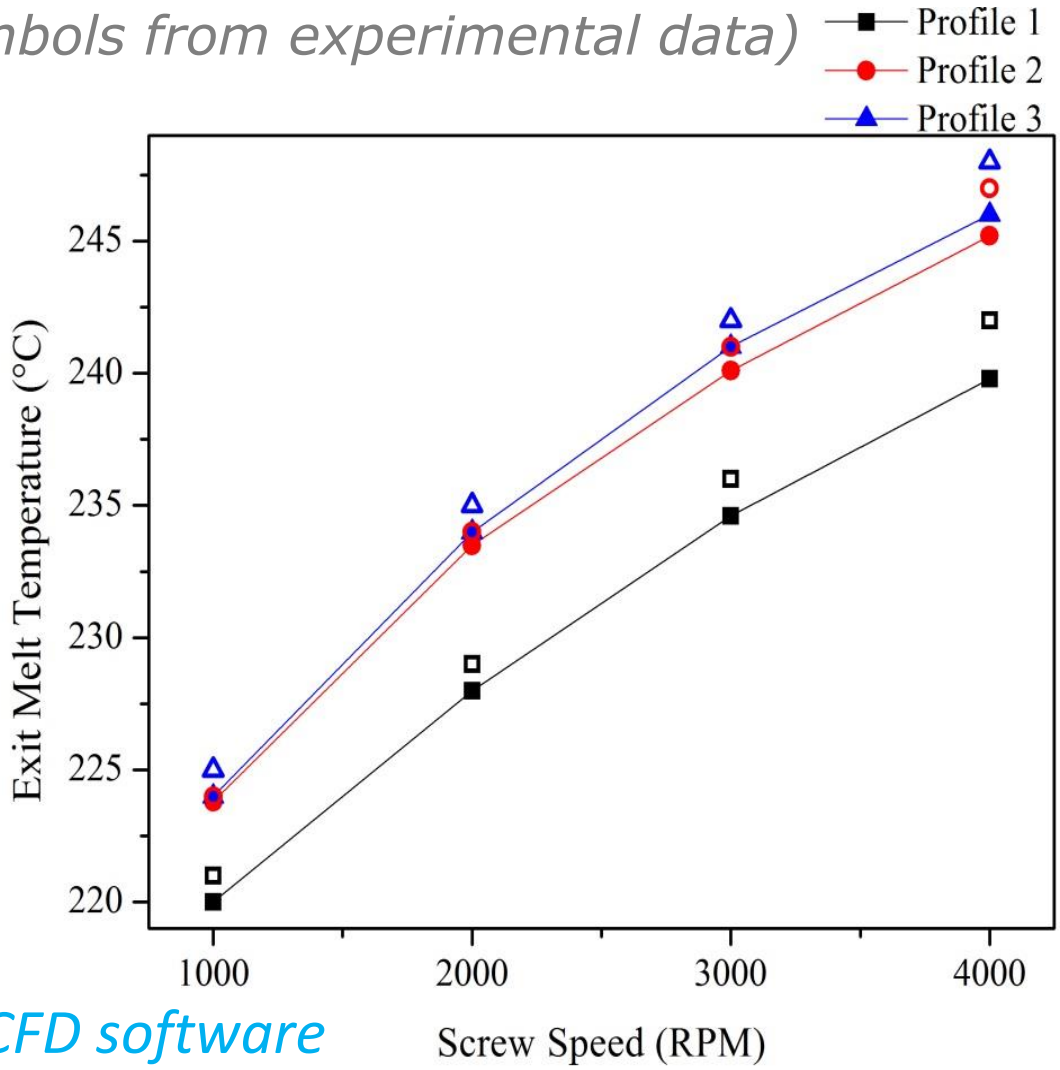


$\eta_0 \approx M_w^{3.4}$

Extrusion Melt Temperature Rise

Polystyrene extruded in different screws, different speeds

(Open symbols from experimental data)

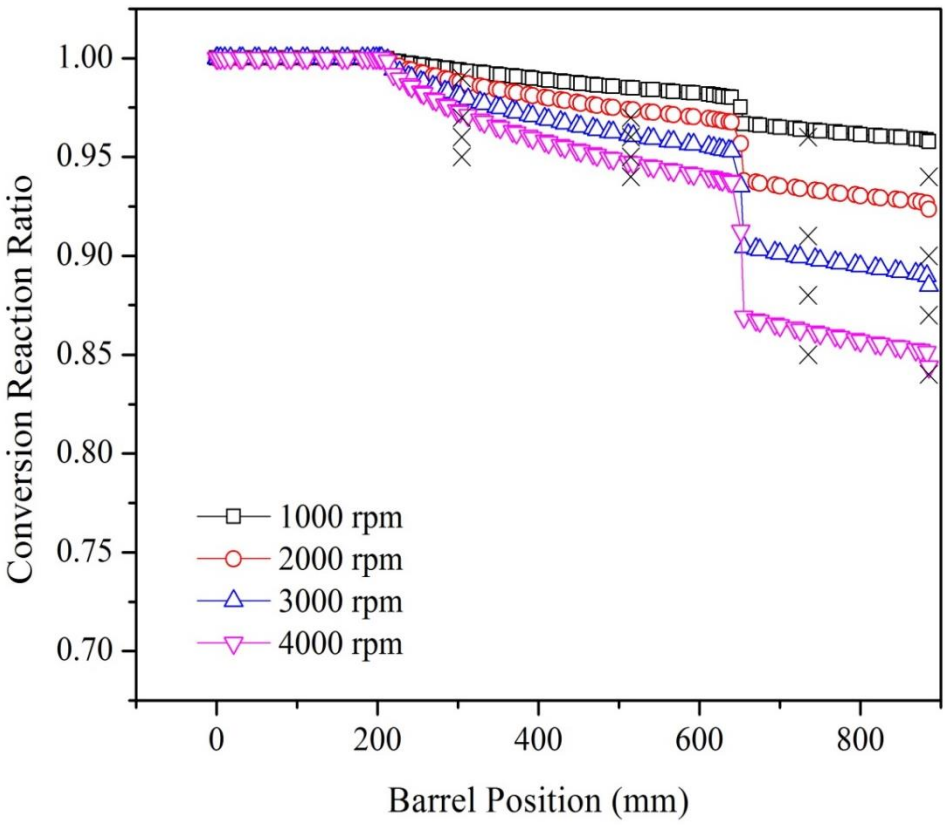


Ludovic TSE-CFD software

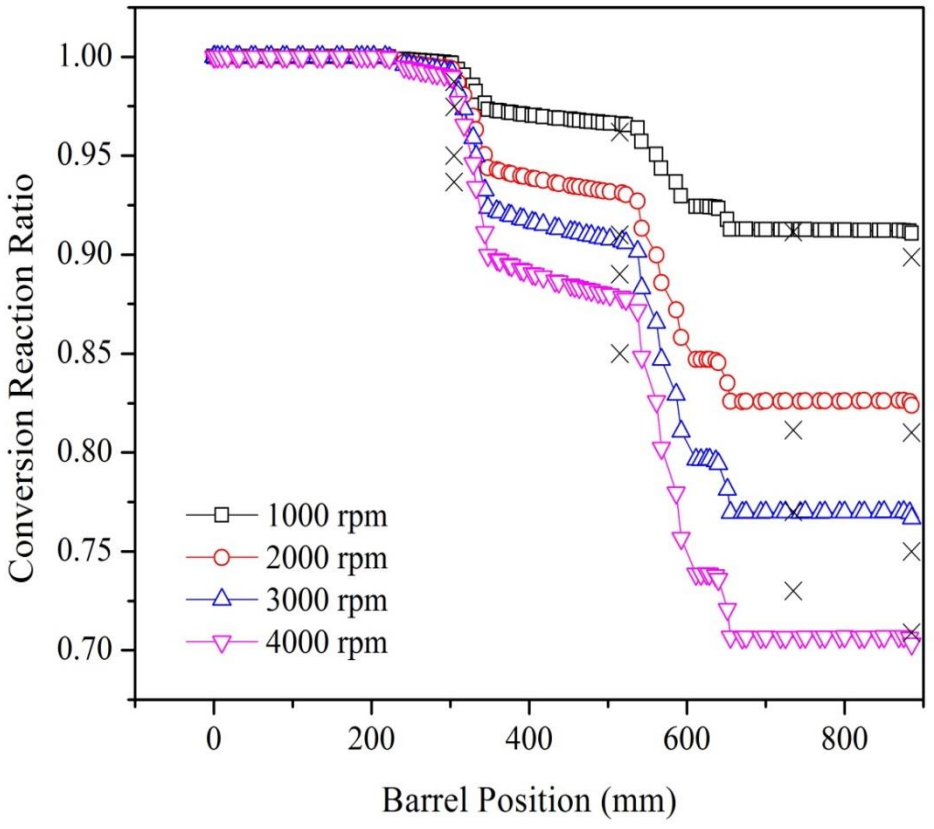
Modeling Depolymerization

- Samples (X) from locations down screw from screw pull
- Simulation of simple depolymerization kinetics agrees well with GPC data

Low shear profile



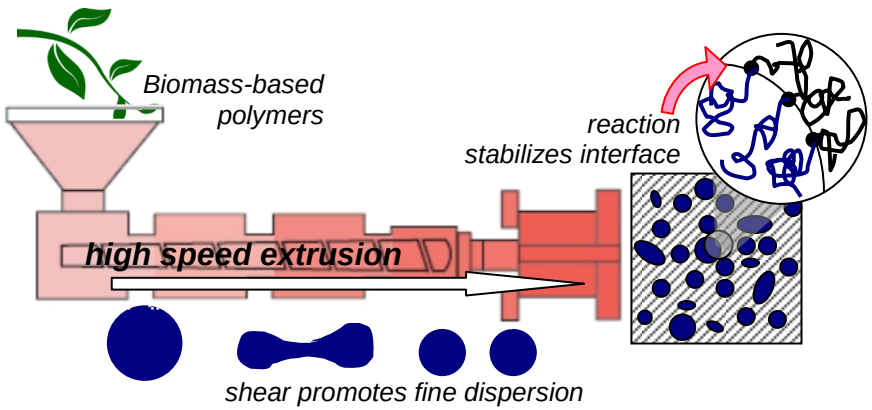
High shear profile



Farahanchi, Malloy, Sobkowicz, Poly Eng Sci (2016)

Summary and Outlook

- Polymer degradation becomes severe at highest screw speeds, evidence it is decoupled from temperature
- Depolymerization reaction tracked using process simulation
- Catalyzed blending results in copolymer formation, enhanced degradation
- Droplet size analysis shows broader distribution with low shear screw
- Ongoing work to control degradation at high screw speed condition via stabilizer, kinetic analysis of interchange reaction





We are proud to announce that the Polymer Processing Society Americas Regional Conference 2018 will be held in Boston, MA!

Symposium Topics to Include:

- Polymeric Nanocomposites and Nanomanufacturing
- Rheology of polymers
- Processing: injection molding, extrusion, blow molding, thermoforming
- Polymers and Sustainability
- Blends, compounding and mixing
- Bio-medical polymers
- Smart and multi-functional polymers
- Colloidal Materials and Advanced Coatings
- Elastomers and Foams
- Simulation and Design
- 3D Printing
- Fibers and films

For more information, contact us at
PPS2018@uml.edu

Acknowledgements

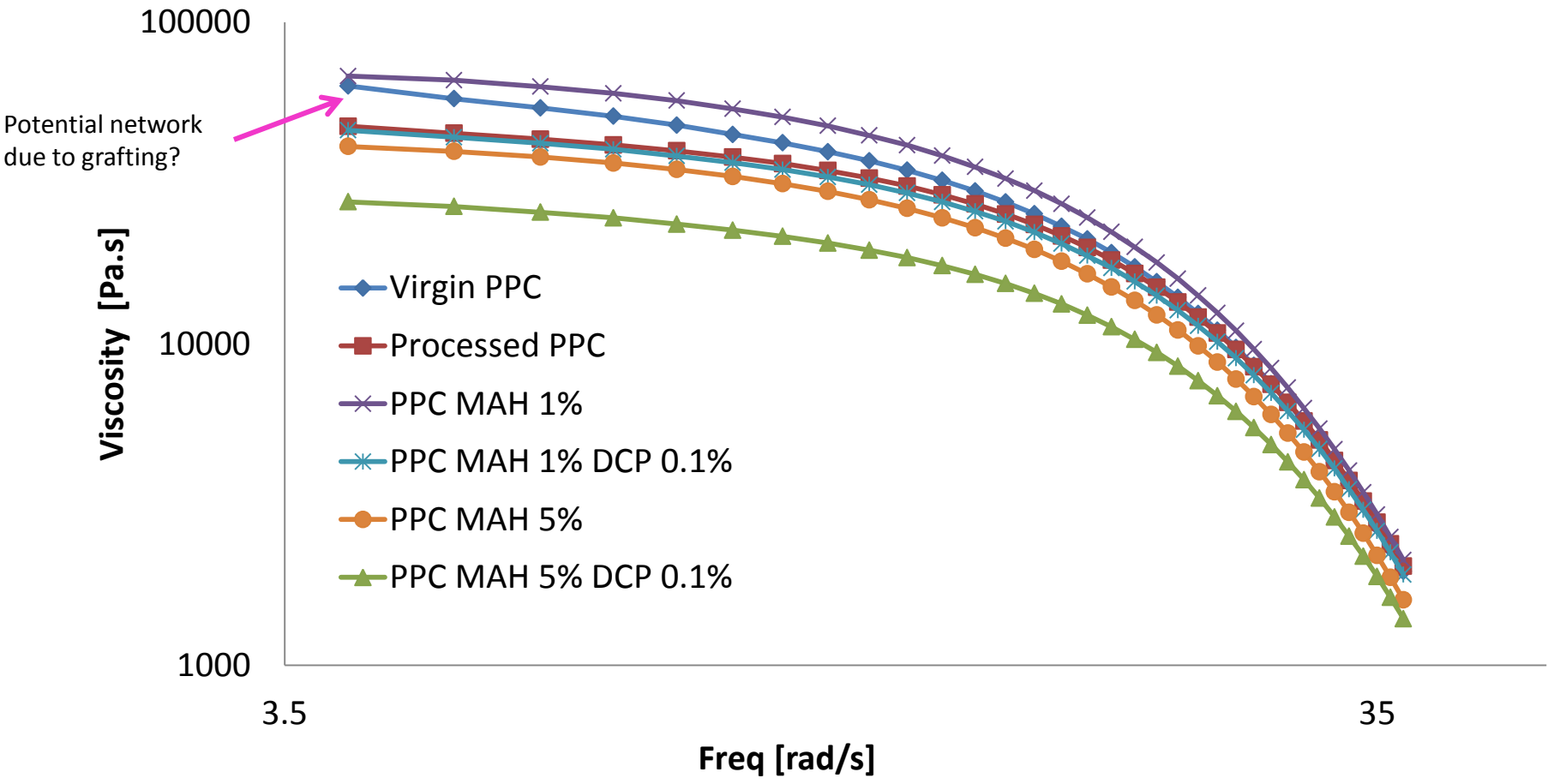
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- Sobkowicz-Kline research group: JeongIn Gug, Azadeh Farahanchi, Bárbará Calderon, Bin Tan, Hao Pan, James Soule,



- Thanks to Prof. Bob Malloy, Plastics Engineering Department, Technovel for equipment assistance and helpful discussions

Parallel Plate



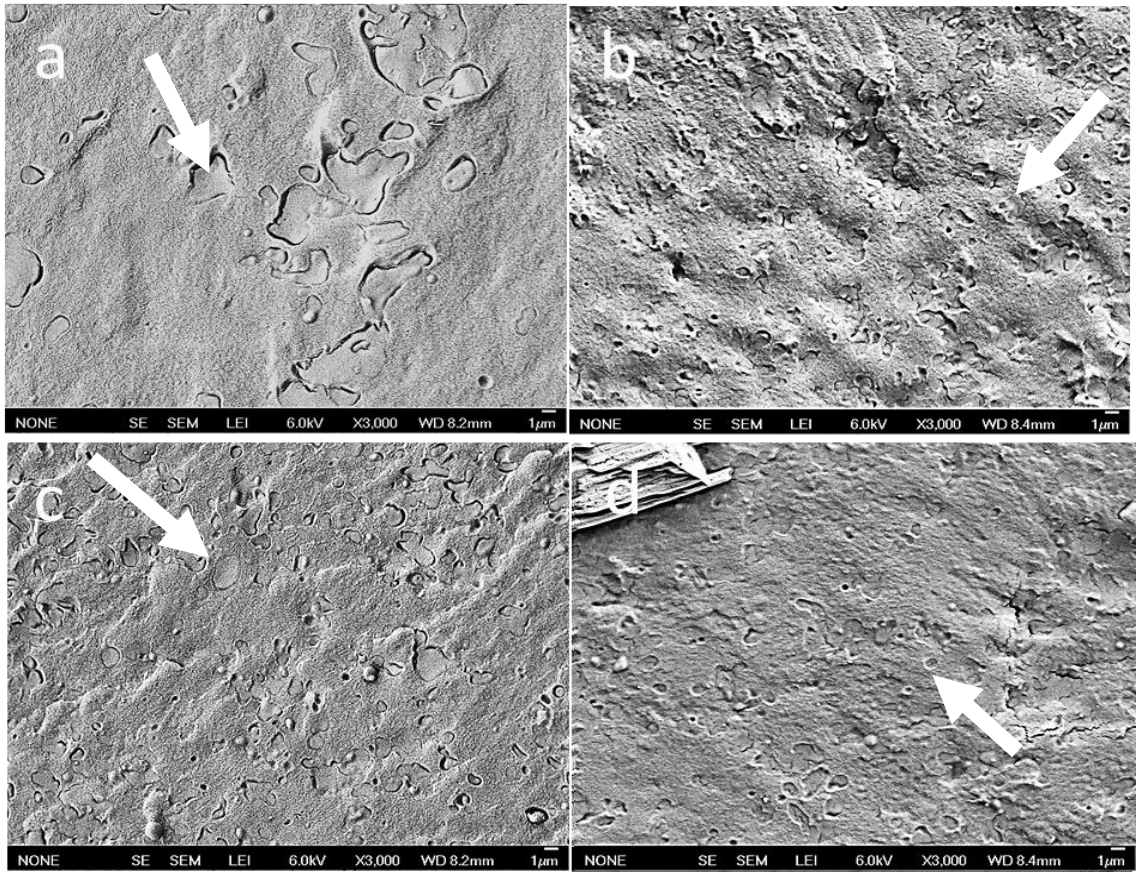
Mechanical Properties

Samples	Modulus [MPa]	Strain at break	Stress at break [Mpa]
Neat Blend	413±36	0.13±0.03	20±3
5% gPPC Blend	434±50	1.2±0.4	17±3
15% gPPC Blend	431±60	1.6±0.8	15±3
25% gPPC Blend	406±30	1.7±0.1	18±2

Samples 575 rpm	Modulus [MPa]	Strain at break	Stress at break [Mpa]
Virgin PBS	418±27	2±1	25±2
Neat Blend	388±24	2.4±0.5	29±2
5% gPPC Blend	366±15	2.8±0.2	29±4
15% gPPC Blend	382±20	2.8±0.2	33±2
25% gPPC Blend	380±25	2.9±0.5	31±1

Samples 1000 rpm	Modulus [MPa]	Strain at break	Stress at break [Mpa]
Virgin PBS	418±27	2±1	25±2
Neat Blend	364±9	2.5±0.6	26±11
5% gPPC Blend	366±15	2.8±0.2	30±5
15% gPPC Blend	380±20	**3.2±0.4**	27±2
25% gPPC Blend	383±13	**3.6±0.3**	27±3

Morphology of Reactive Blends



(a) Neat Blend
(b) 5% gPPC Blend
(c) 15% gPPC Blend
(d) 25% gPPC Blend

Functionalized blends:

- Smaller droplet size→ Compatibilizer at the interface suppress coalescence
- Smoother edges→ Improved interfacial interaction
- Broader particle size distribution