Melt and Solution Processing of the Poly(Hydroxy-Amide) Family of Polymers

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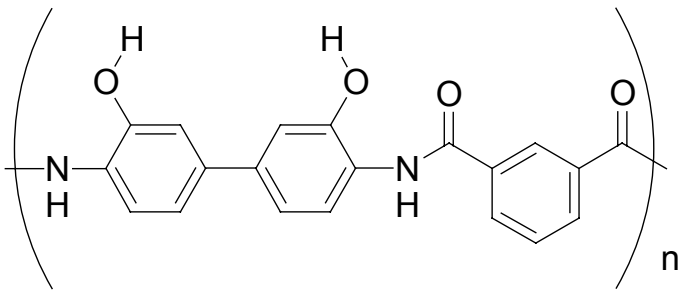
Outline

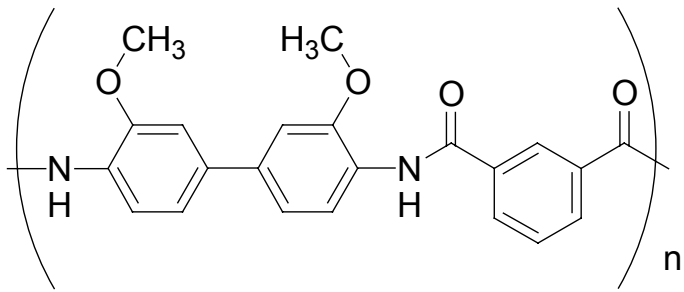
- Study of the isothermal characterization of the PHAs
- Investigation of cyclo-dehydration/demethylation behavior with respect to the applications as coatings and melt spun fibers
- The effect of film morphology on crystallization behavior

Sample Code and Structure

Sample code	PHA/PMeOA	Flexible group
PMeOA	100/0	0
50/50	50/50	0
25/75	25/75	0
25/75/F10	25/75	10



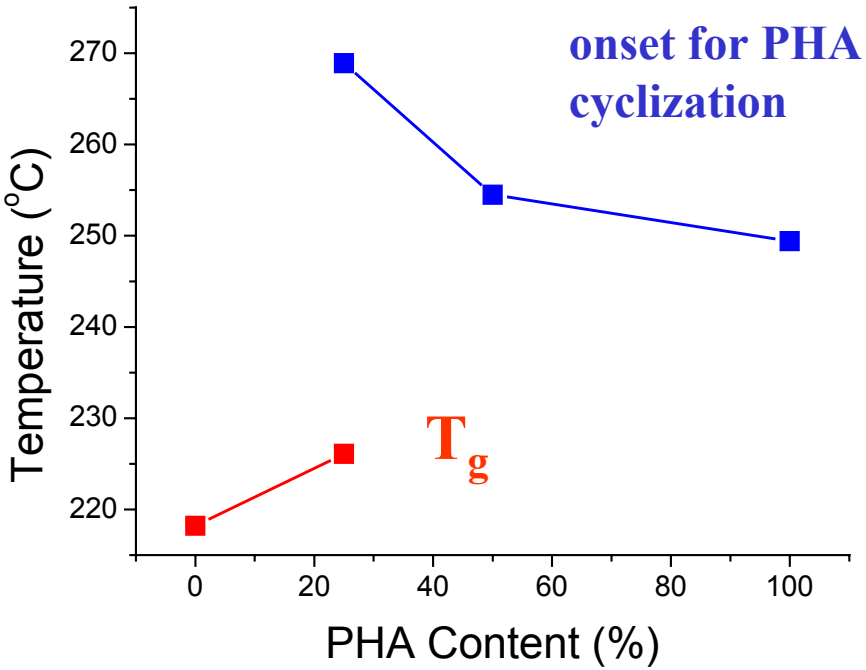
Poly(hydroxy-amide): PHA



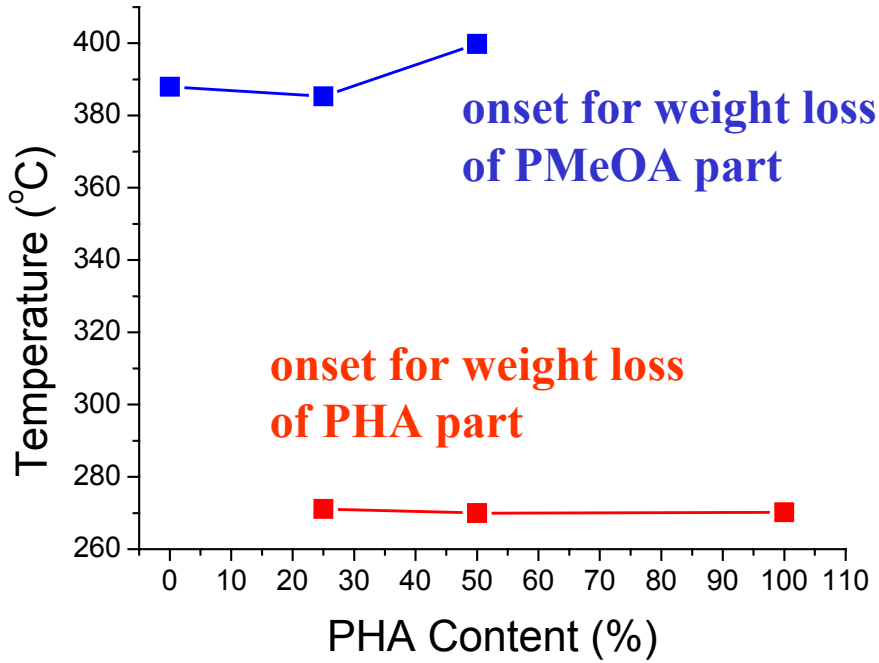
Poly(methoxy-amide): PMeOA

Thermal Characteristics of PHA/PMeOA Hybrid at different composition

Results from DSC

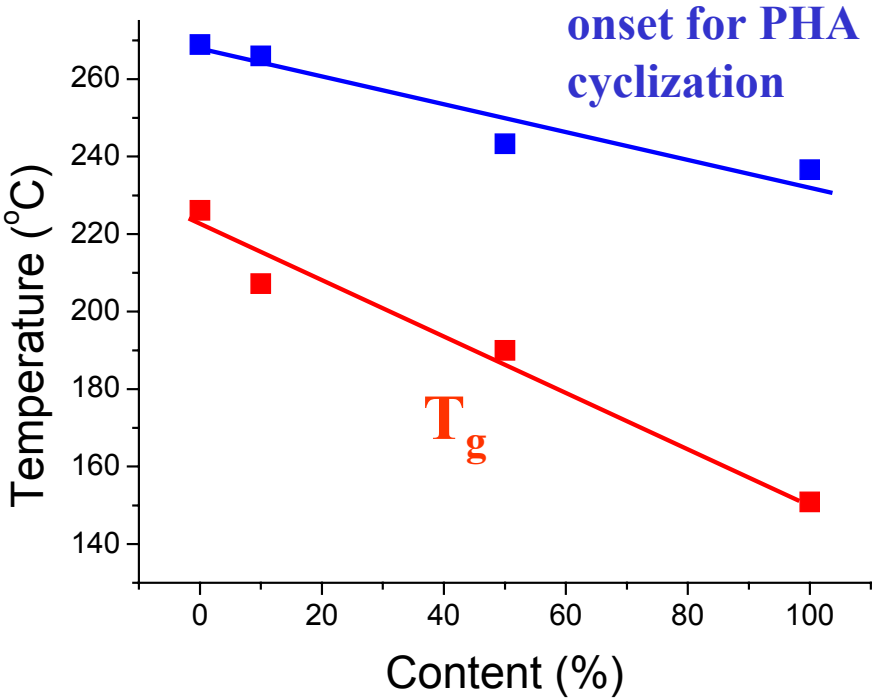


Results from TGA

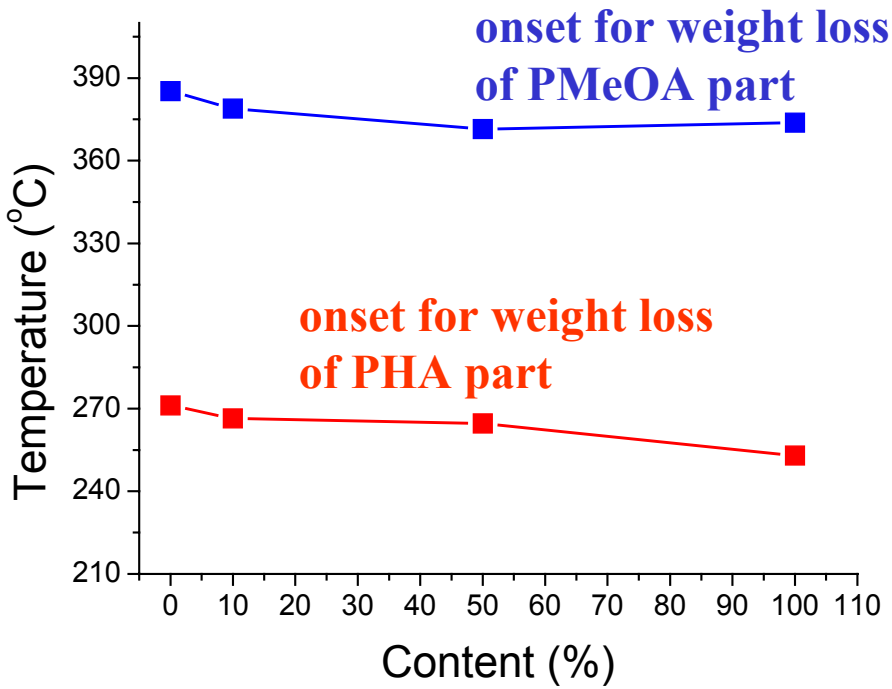


Thermal Characteristics of PHA/PMeOA/Flexible Hybrids with different Flexible part contents

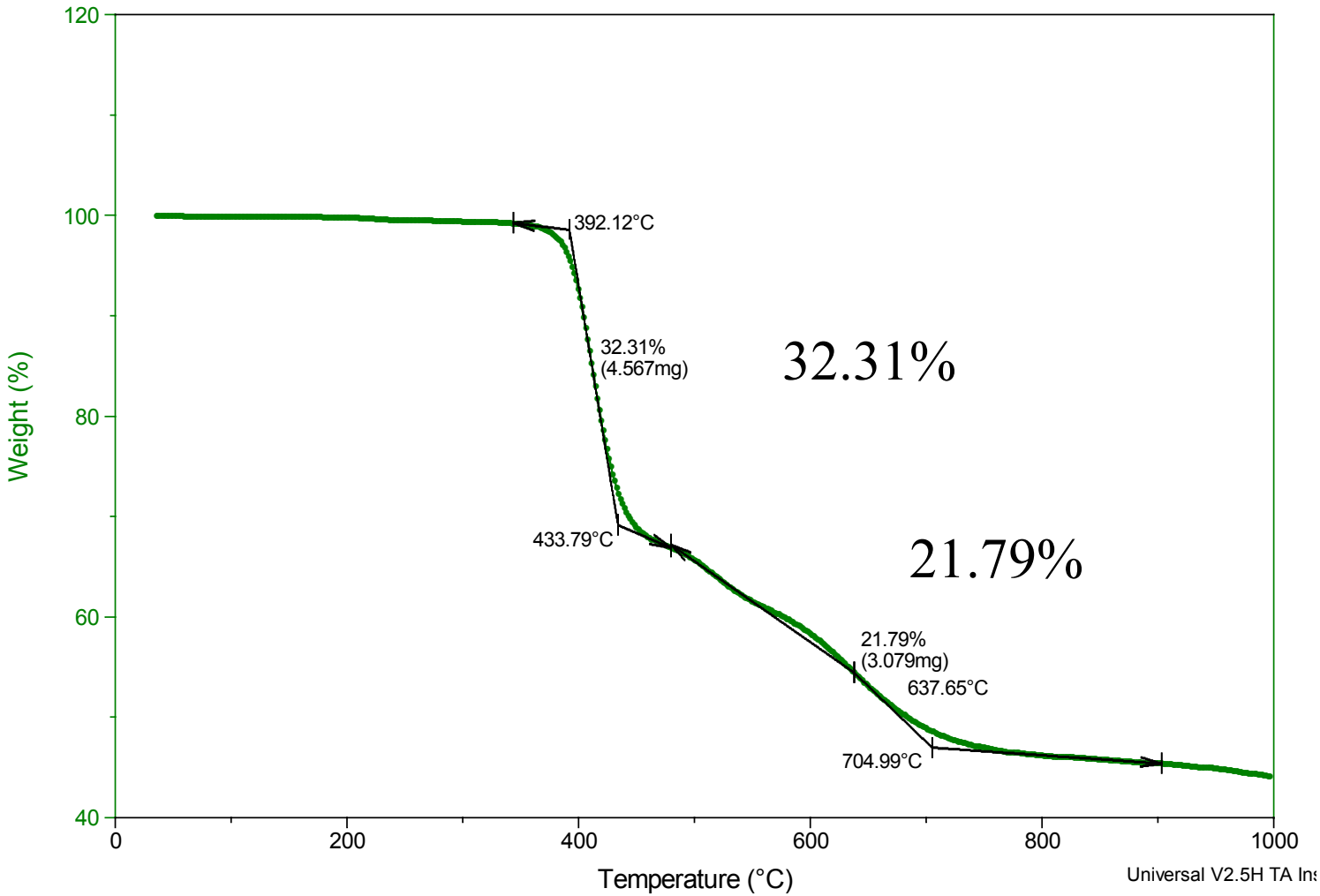
Results from DSC



Results from TGA



Typical TGA Curve of PMeOA (10°C/min.)



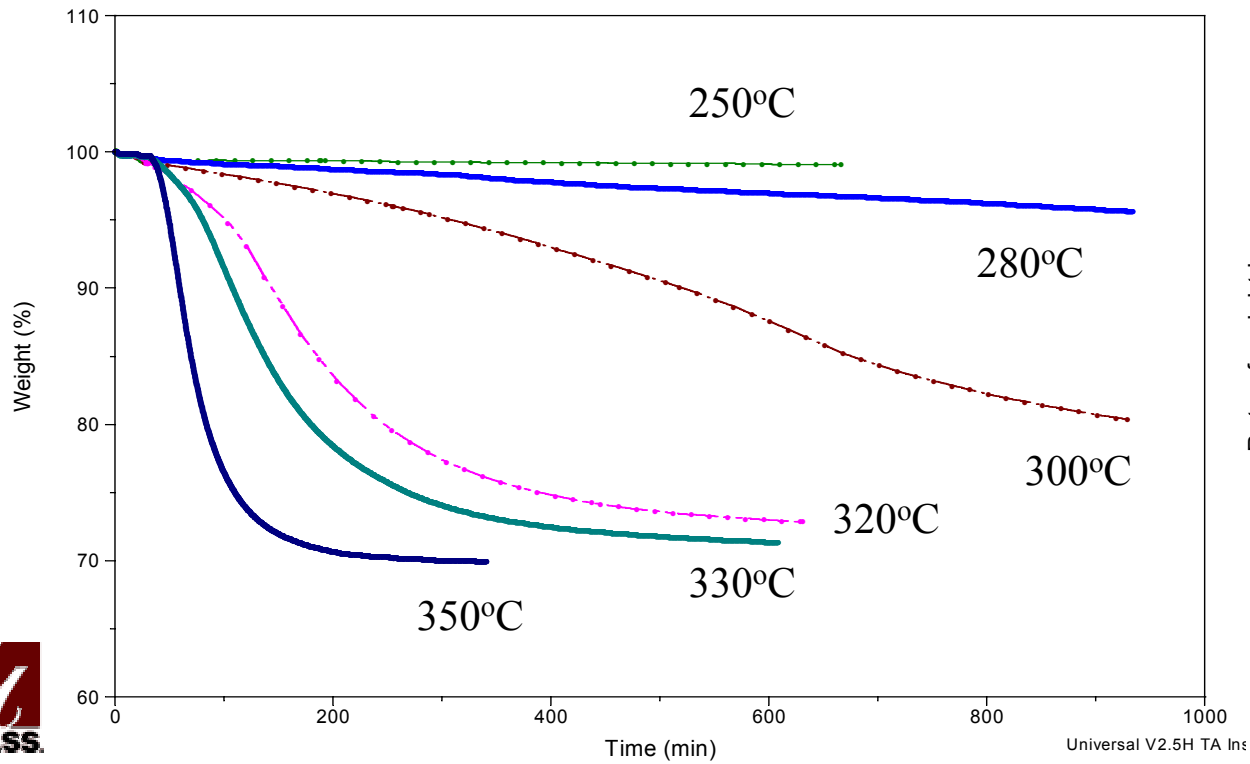
Isothermal Analysis

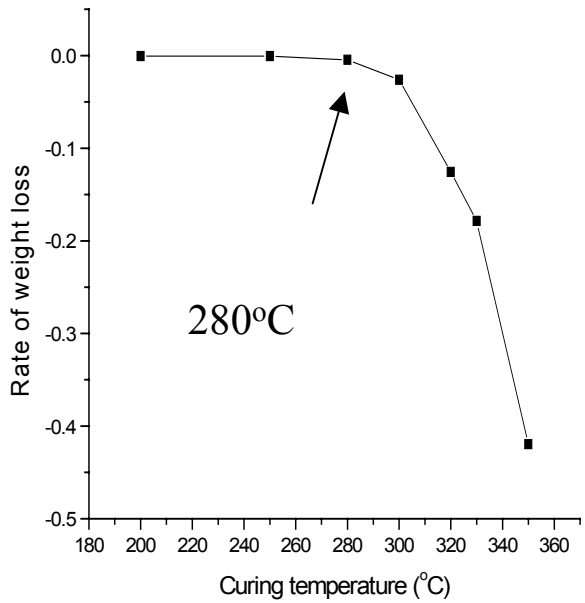
- ❑ Cyclization characteristics
- ❑ Crystallization characteristics

→

- ✓ Optimization of film preparation and curing
- ✓ Potential as a coating
- ✓ Basic data for fiber spinning from melt

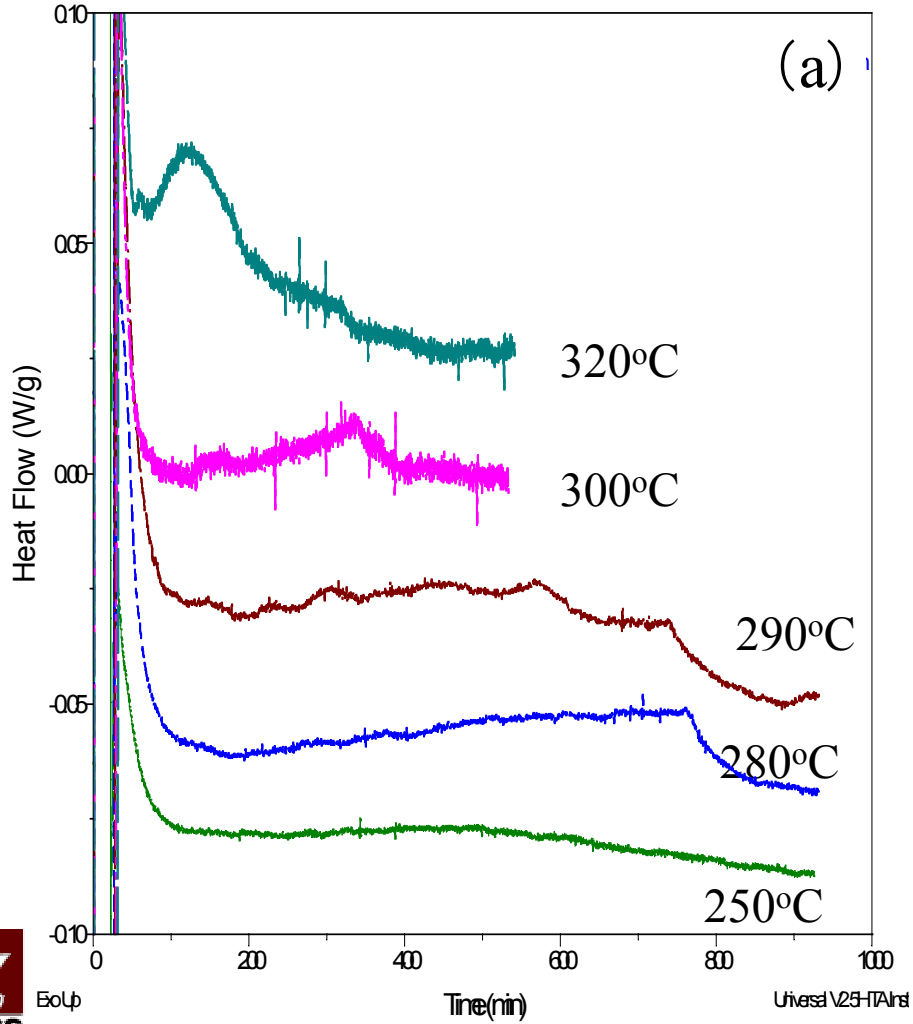
TGA results of PMeOA at isothermal condition



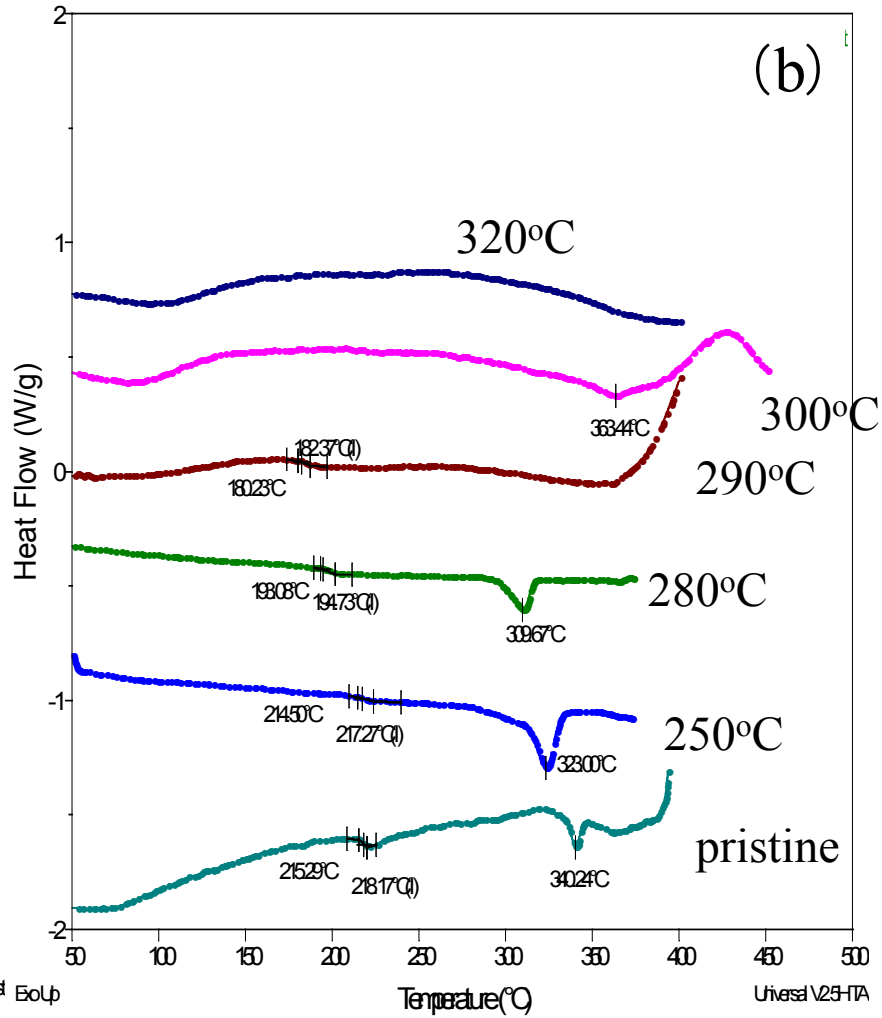


DSC Isothermal Curves of PMeOA

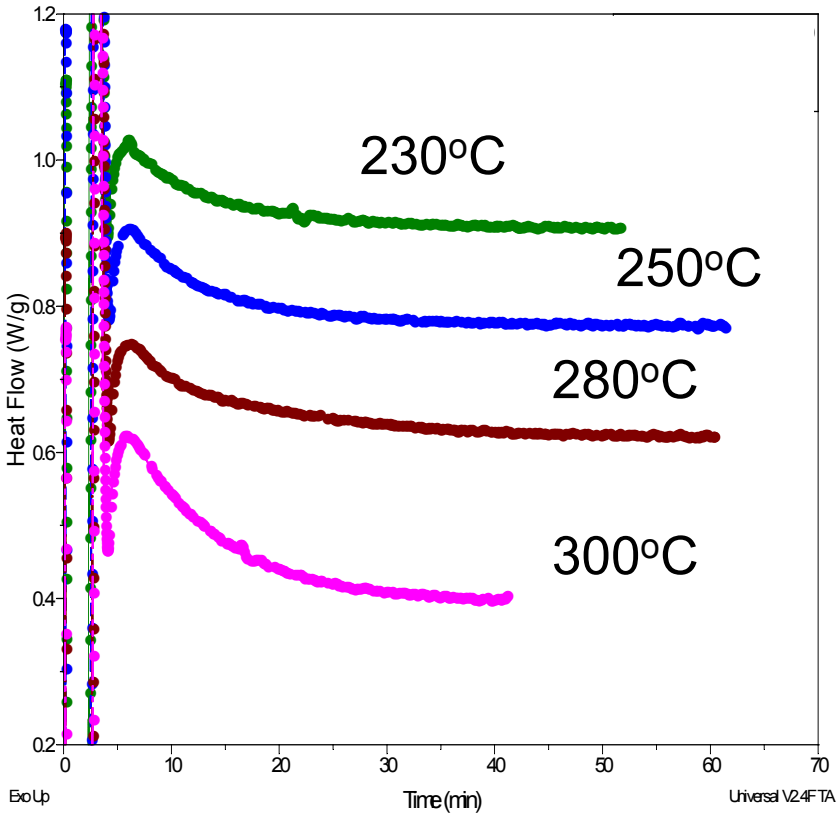
different temperatures

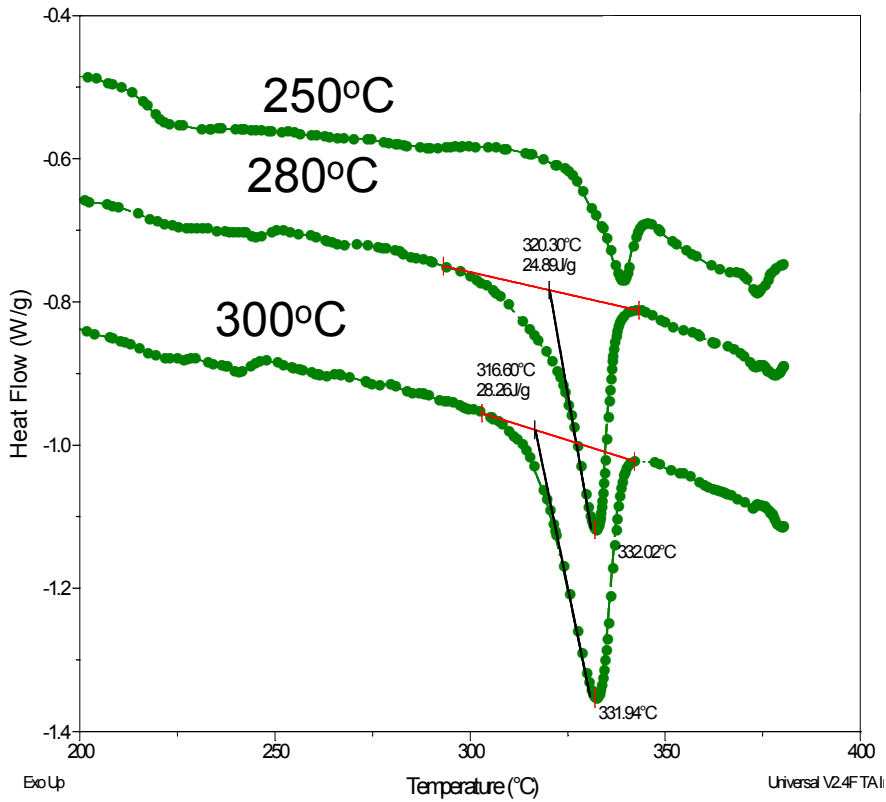


heating scan after curing

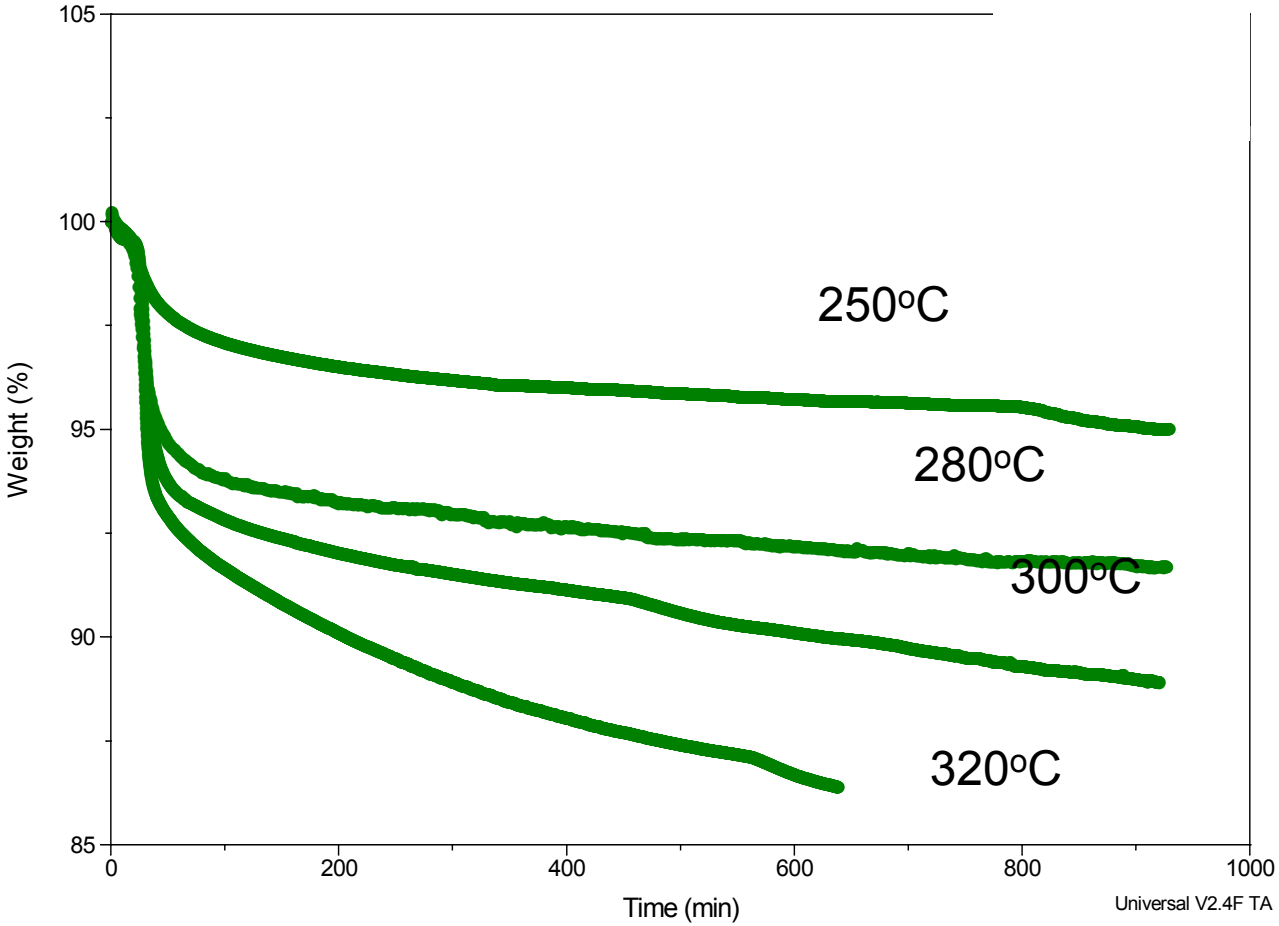


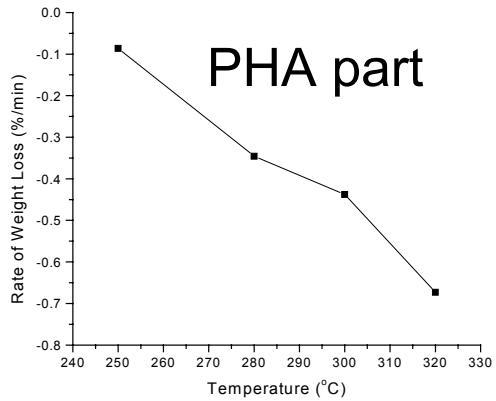
Isothermal Crytallization of PMeOA

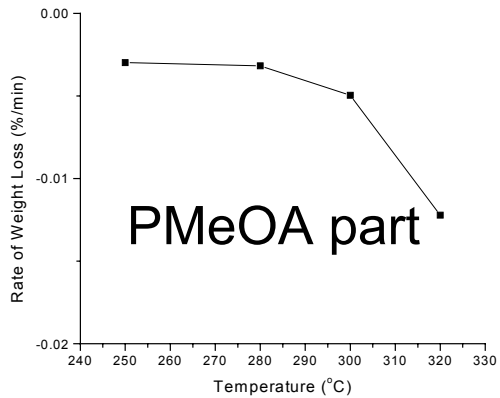




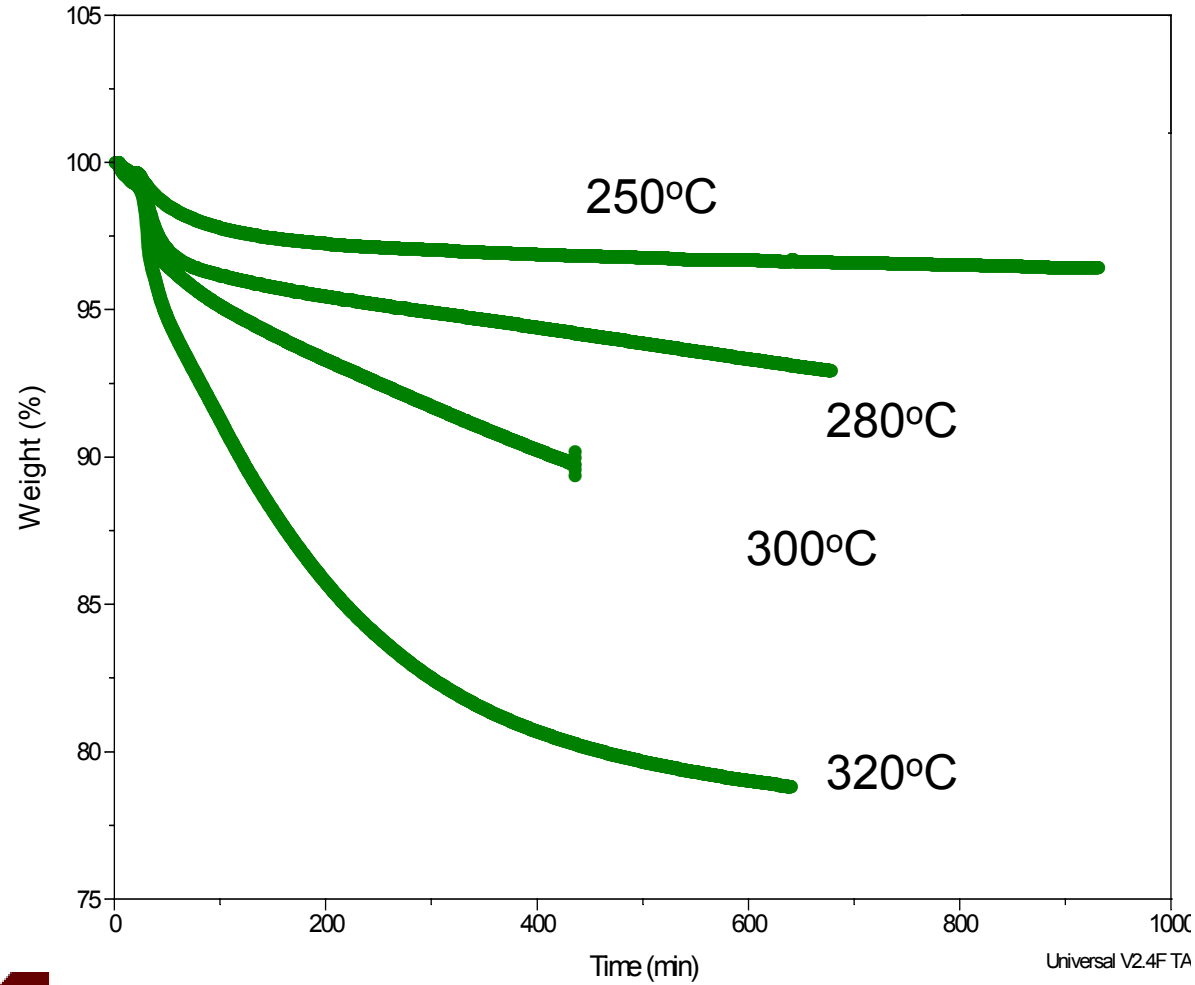
TGA Results of 50/50 Under Isothermal Conditions

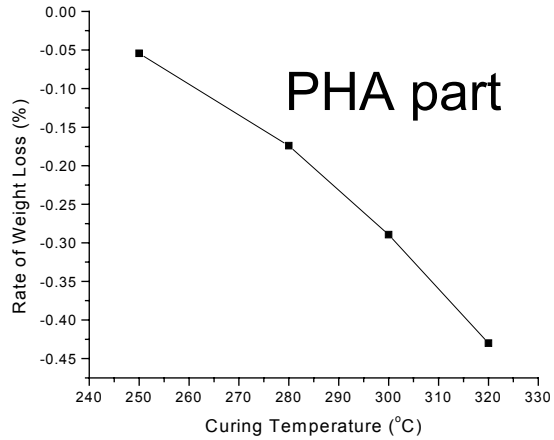


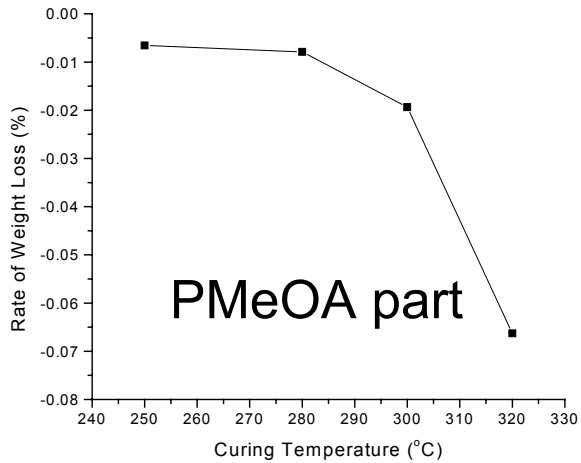




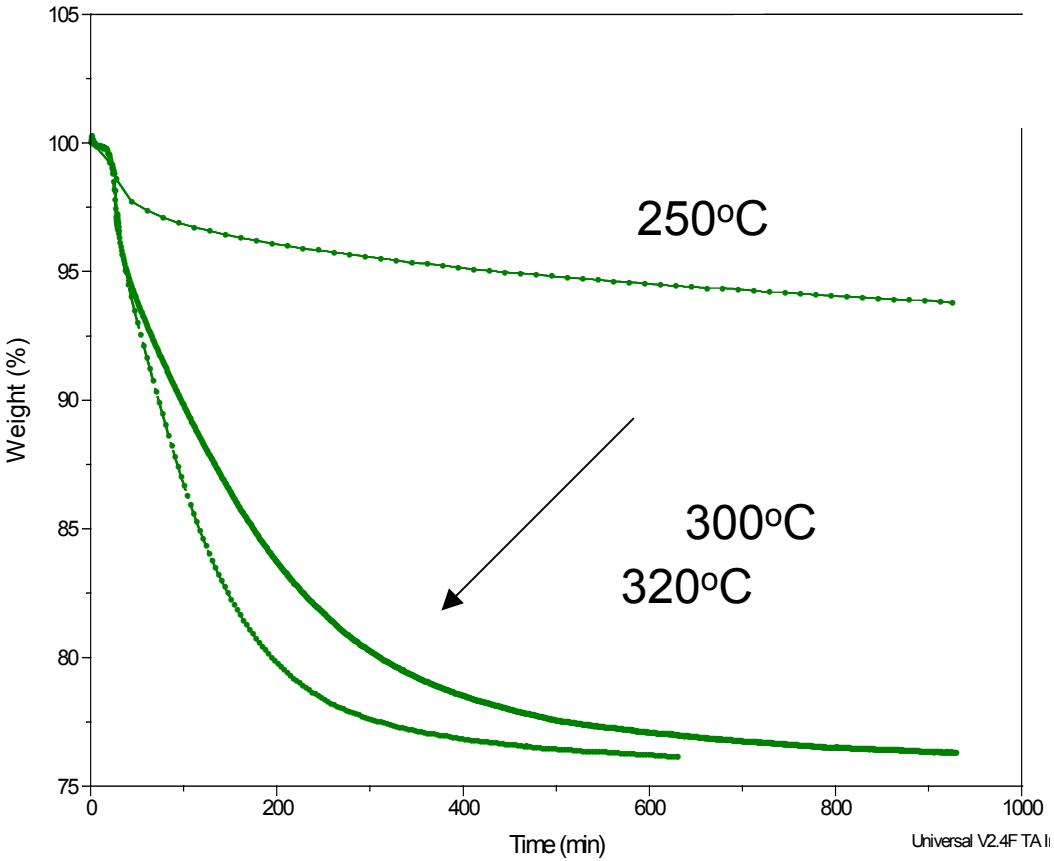
TGA Results of 25/75 Under Isothermal Conditions

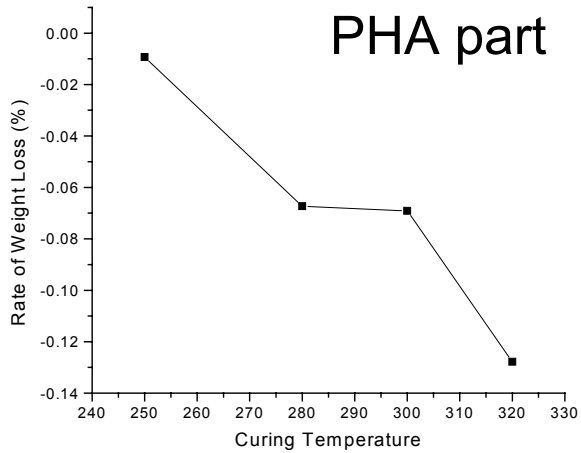


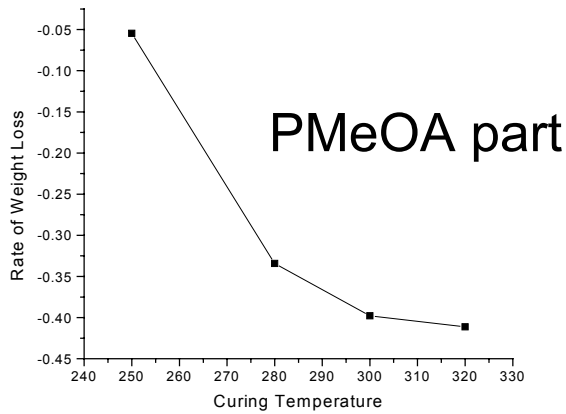




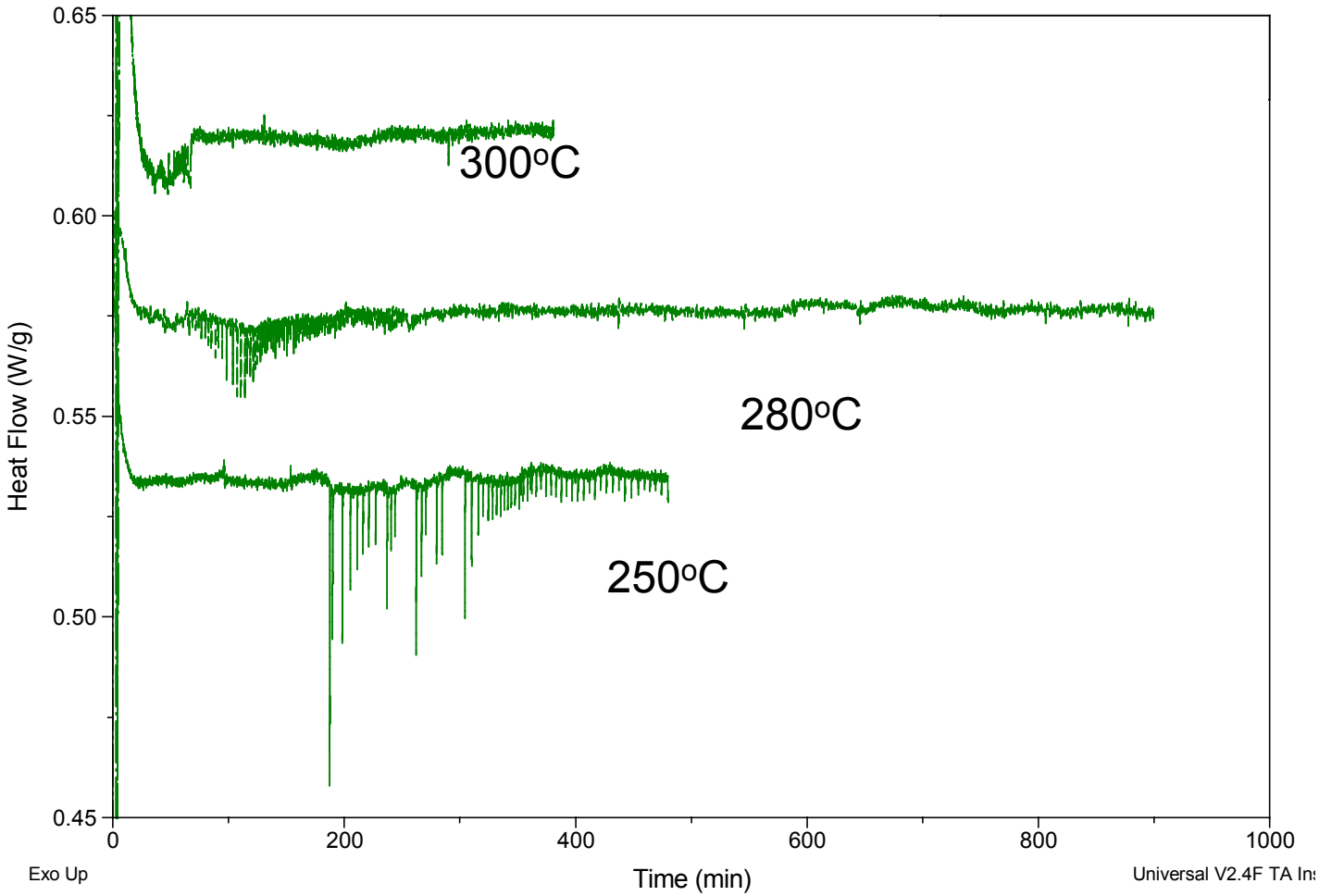
TGA Results of 25/75F10 Under Isothermal Conditions







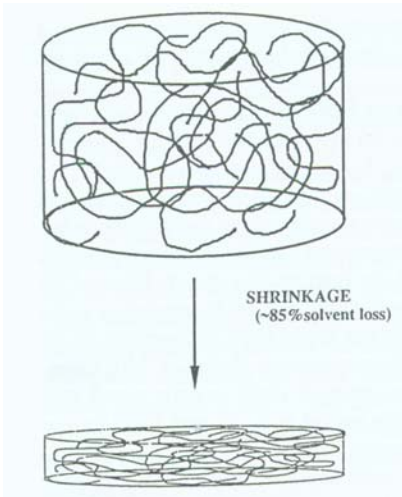
DSC Thermograms of 25/75F10 Under Isothermal Conditions

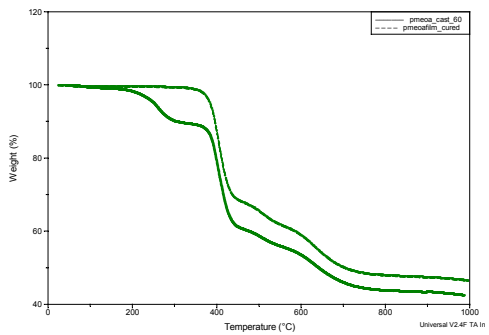


Film and Fiber Preparation and Analysis

- Solvent cast films (70 – 100 μm) were used for thermal analysis, tensile testing, and x-ray diffraction studies. (solvent is DMSO)
- Spin coated films (< 10 μm) were used for IR spectroscopy. (solvent is DMSO)
- Fiber was spun from the melt state using a DACA Micro compounder at 320 ~ 330°C.

Film preparation





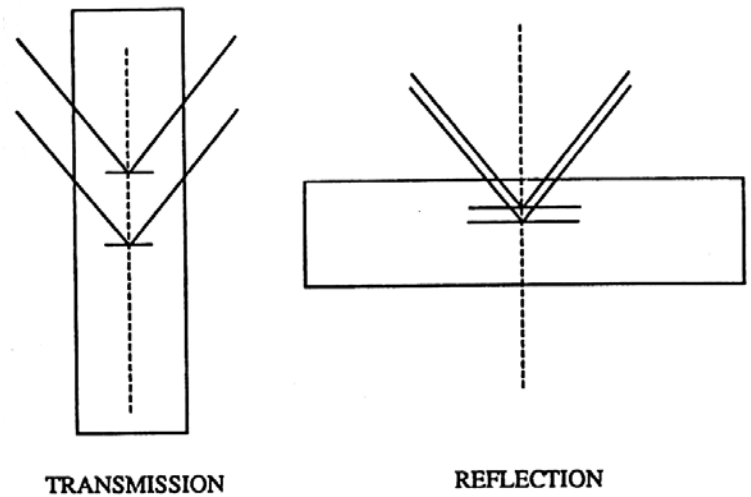
- Poor solvent yields denser molecular packing
- PMeOA shows different colors when dissolved in DMSO, NMP and DMAc.
- Gelation behaviors differs in each solvent.
- Usually, about 12% DMSO remains in the film after drying at 60°C in a vacuum.

Morphology of Films

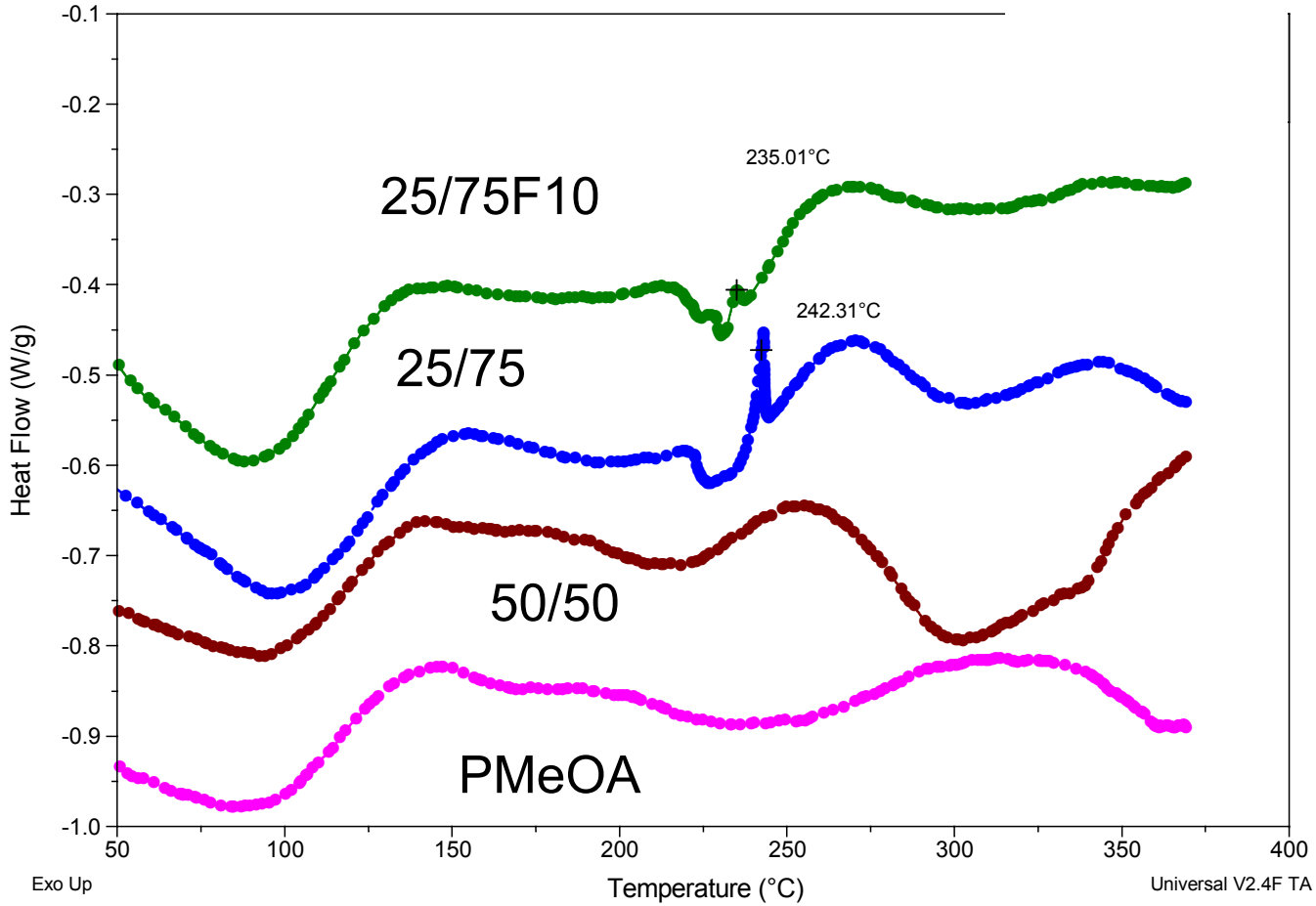
- Spin coating : some in-plane orientation
- Solvent casting : little in-plane orientation
- Thinner film shows higher in-plane orientation
- Substrate induces higher in-plane orientation

➢ WAXD : in-plane and out of plane diffraction measurement

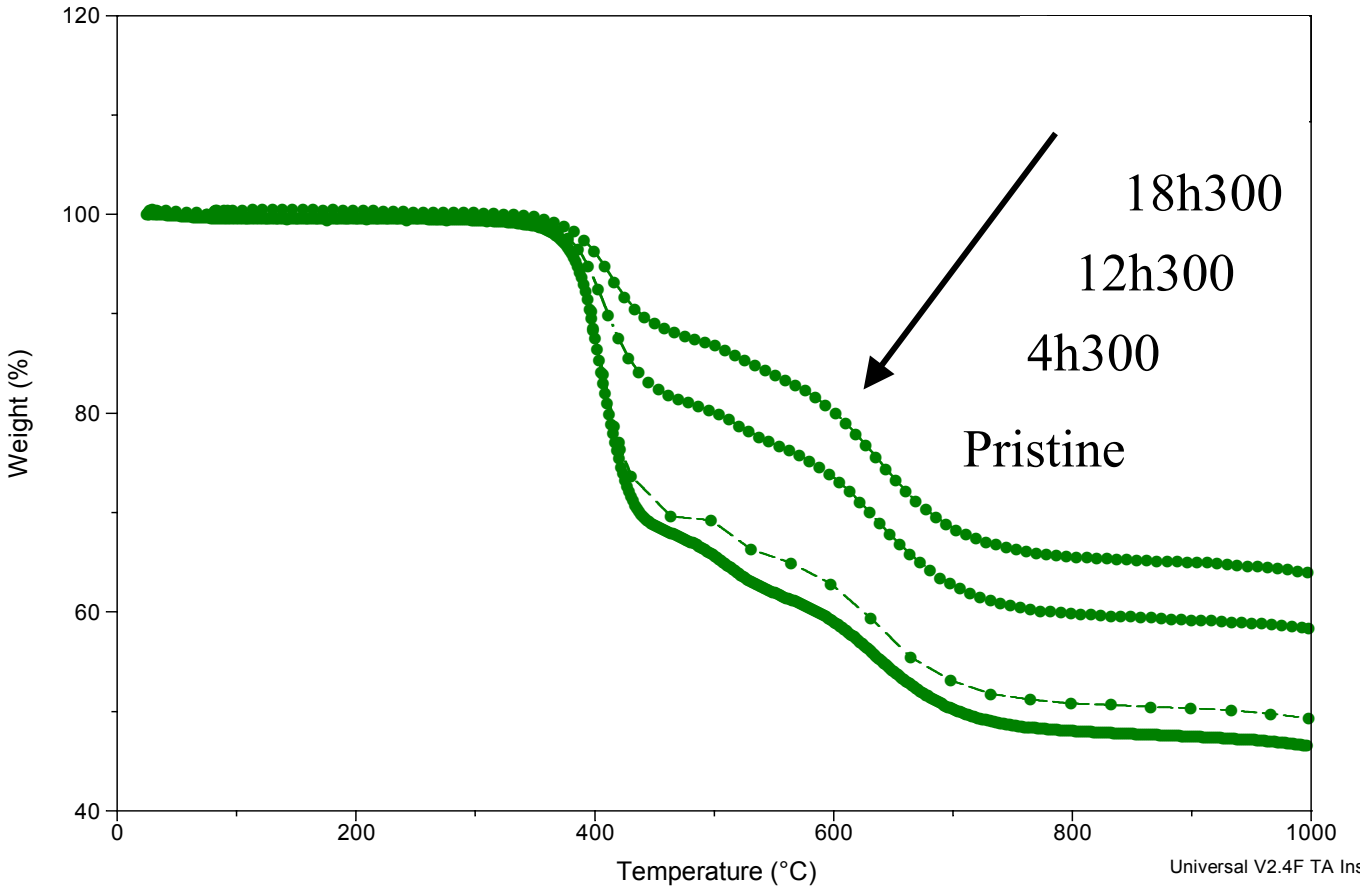
- In-plane (transmission) : information about intra-molecular ordering
- Our of plane (reflection) : information about inter-molecular ordering



DSC Heating Scans of Films Containing Solvent (DMSO)

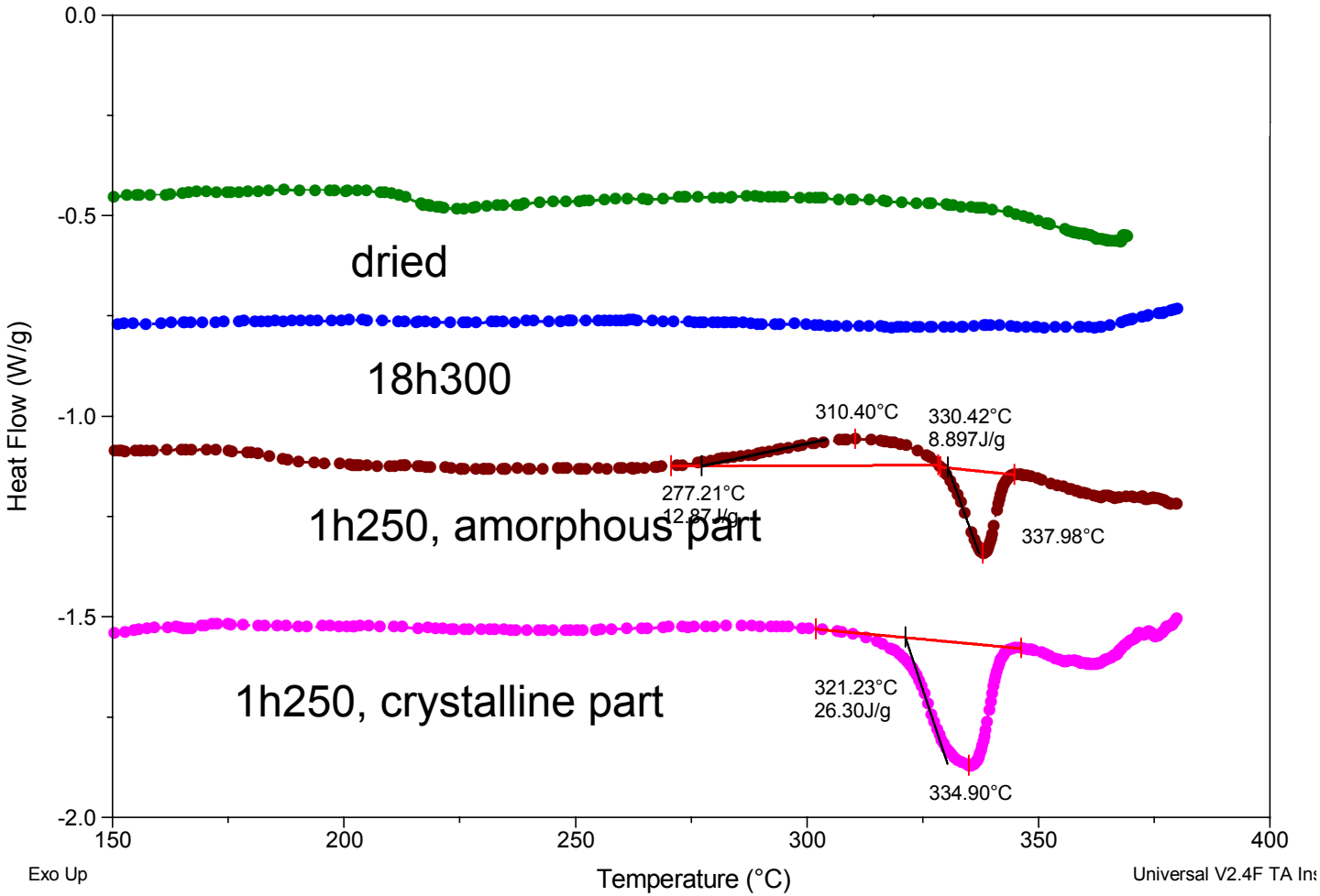


TGA Results of PMeOA Films Cured Isothermally



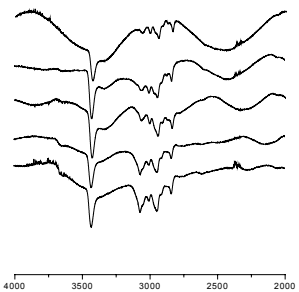
- Code of 6h300 means a film cured at 300°C for 6 hours.

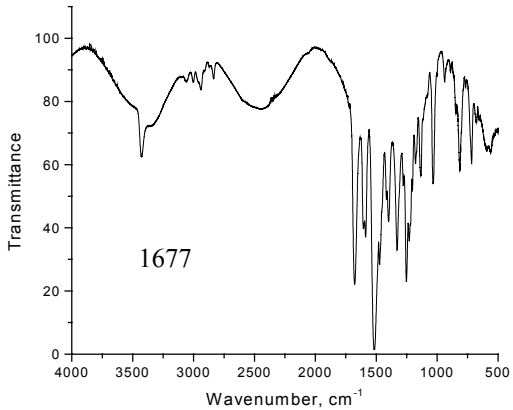
DSC Heating Scans of Isothermally Cured PMeOA Films



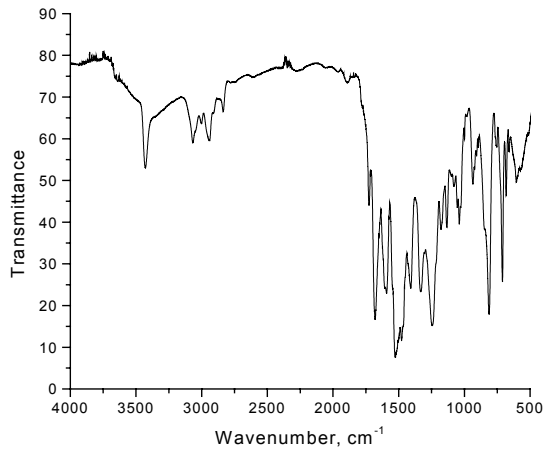
18h300 : heat treated for 18 hours at 300°C

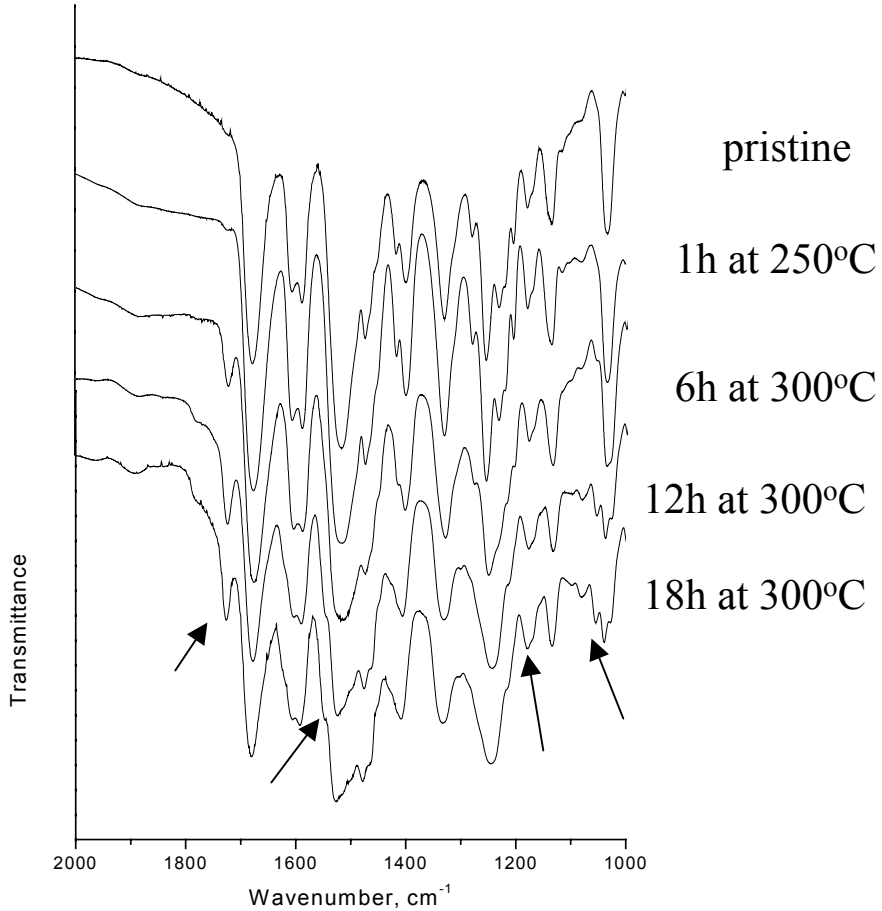
FTIR Spectra of Isothermally Cured PMeOA Thin Films





Pristine sample

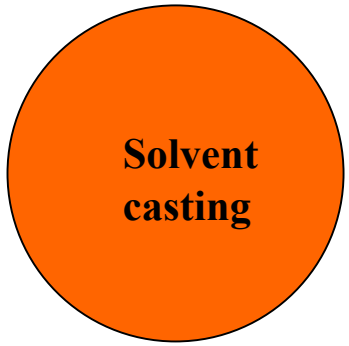


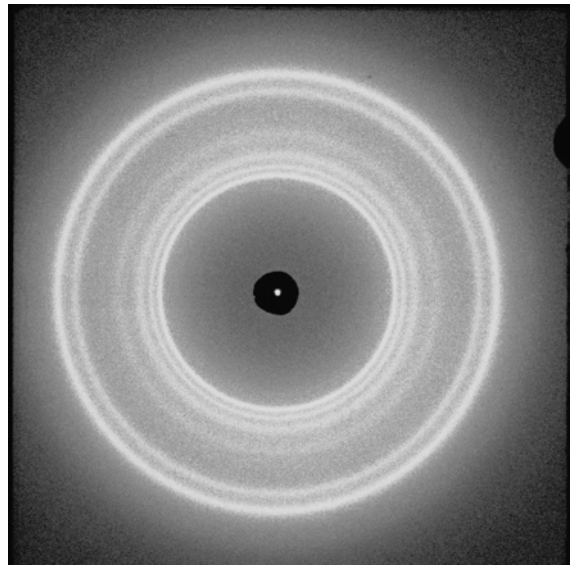


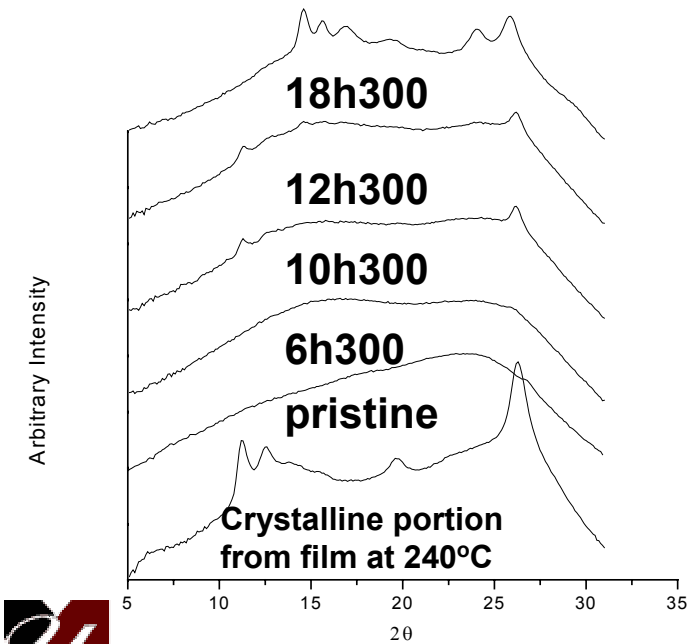
PMeOA film after curing at 300°C for 18 h

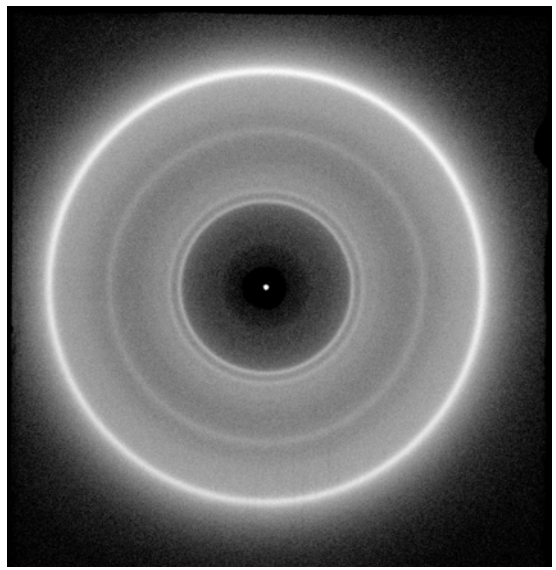
Change of Crystal Structure During Curing at 300°C

Crystals grow inward from the edge to the center due to the in-plane orientation at the edge.





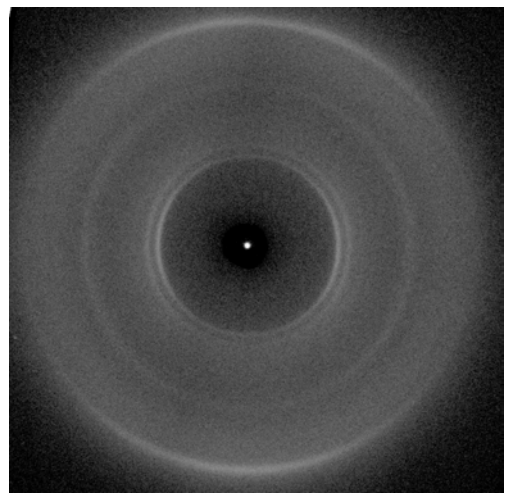




PMeOA crystalline part

In-plane diffraction

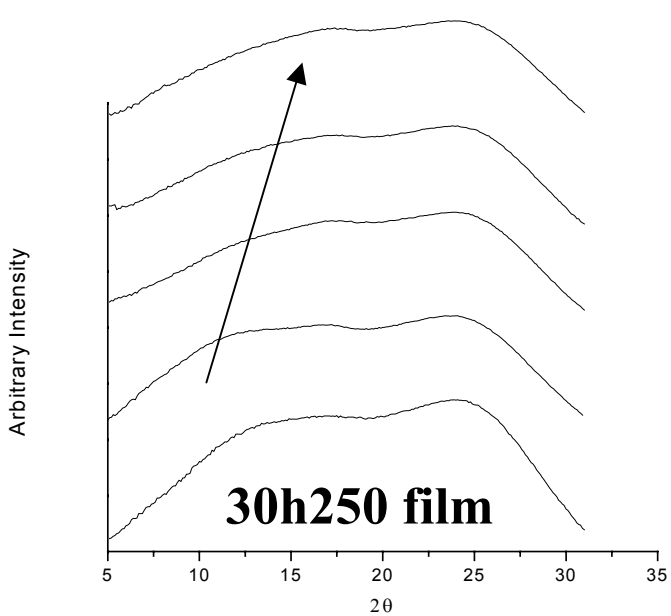
18h300



PMeOA crystalline part

Out of plane diffraction

WAXD Patterns of Powder and Solvent Cast Films of Hybrid

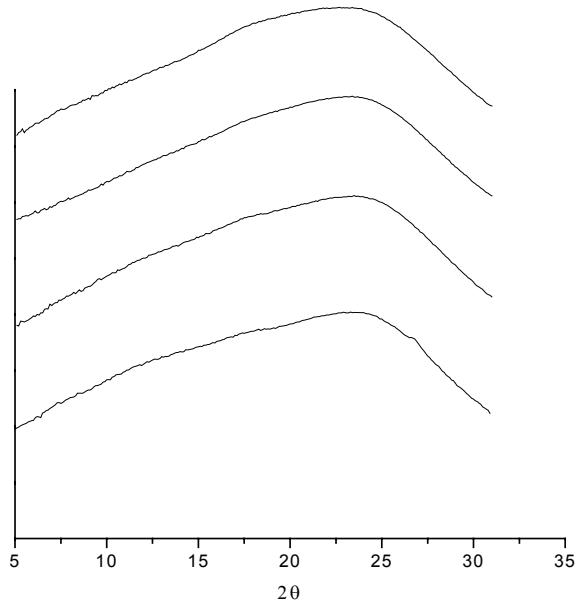


50/50

25/75/F10

25/75

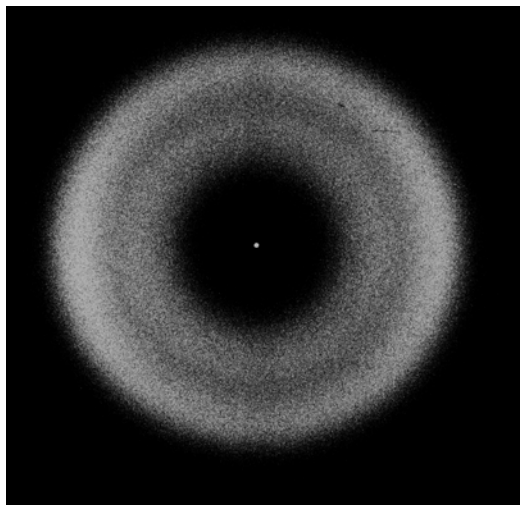
PMeOA



Powder form of hybrid

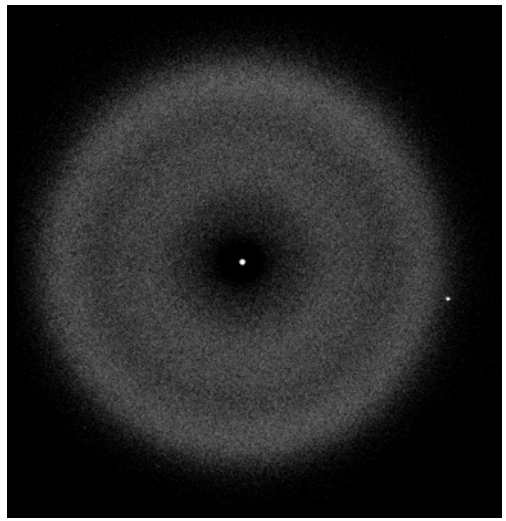
Solvent casted film of hybrid

WAXD Patterns of PMeOA Fiber and Spin-coated Thin Film

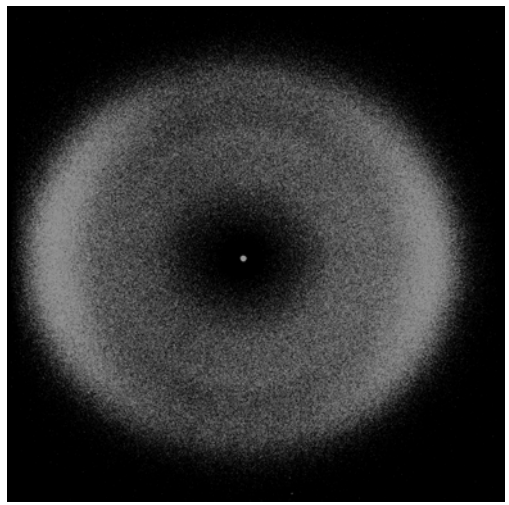


Fiber axis direction

Fiber

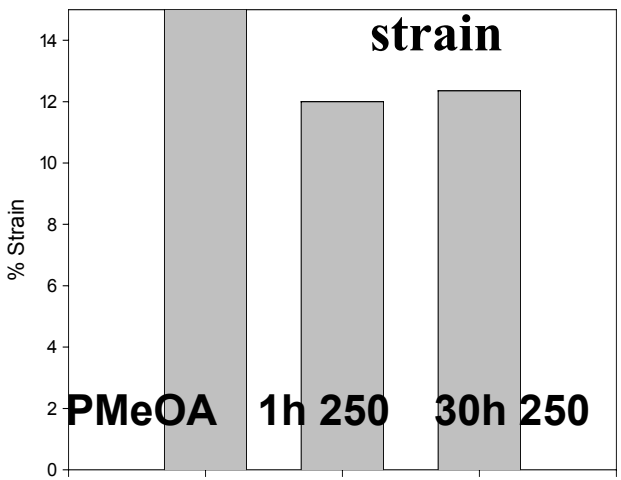


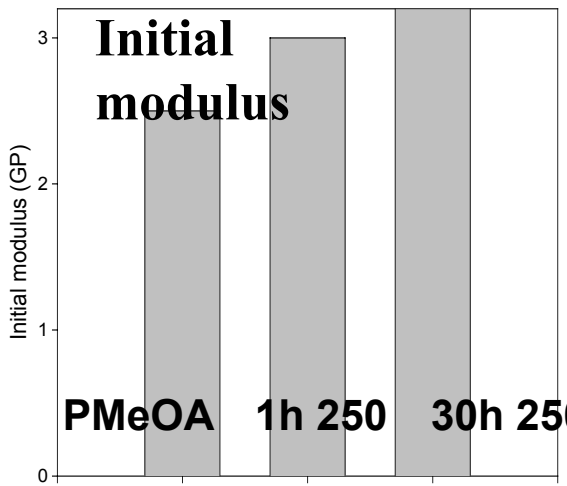
Thin film, in-plane diffraction

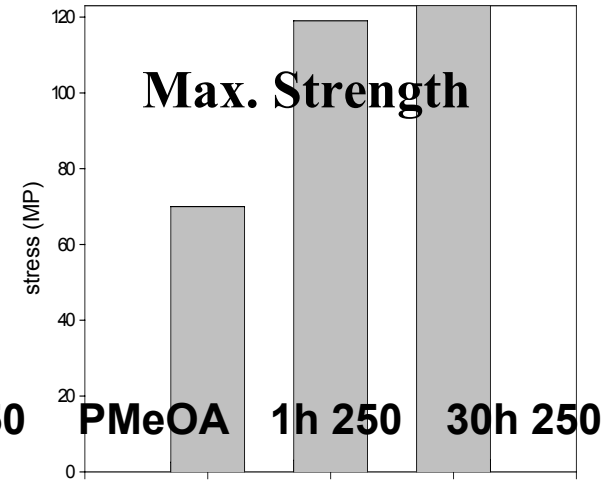


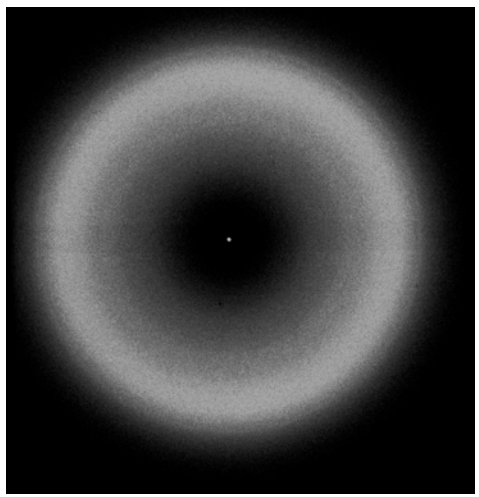
Thin film, out of plane diffraction

Tensile Properties of PMeOA After Curing

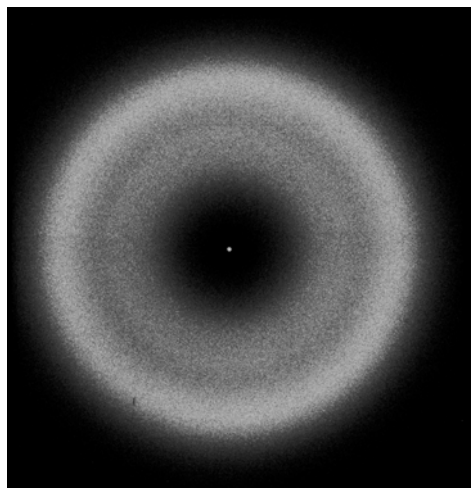




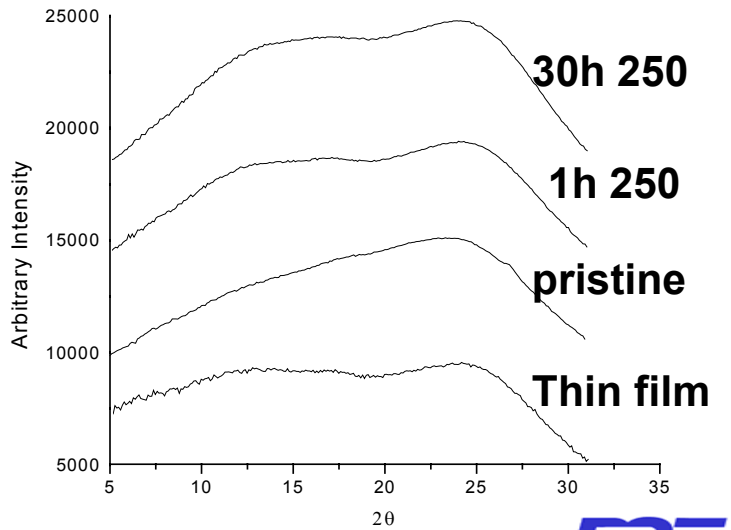




Solvent cast film



30h 250



Summary

- PMeOA and PMeOA/PHA copolymers can be crystallized above their glass transition temperatures.
- Crystallization of spin coated films starts from the edge and grows toward the center. In-plane orientation at the edge induces crystal formation.
- Chain scission may occur during cyclization. Cyclization, crystallization and degradation phenomena occur competitively at the same time.
- Flexible groups increase the rate of weight loss during isothermal TGA analysis.
- Heat treated PMeOA film at 300^{o}C for 18 hours showed another crystal structure. It is thought to be a PBO crystal structure.

Future Work and Acknowledgments

- Fiber spinning of hybrids
- Determine the effect of orientation on cyclization
- Determine the solution spinning parameters for these polymers

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- Schneller Inc.
- Eikos
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- National Institute of Standards and Technology