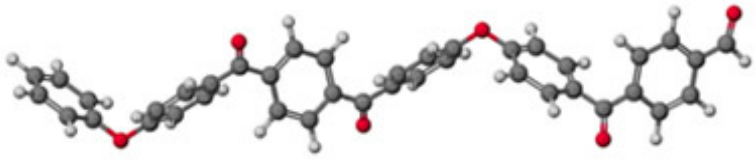


Properties of Novel PAEK Alloy System For Oil & Gas Applications

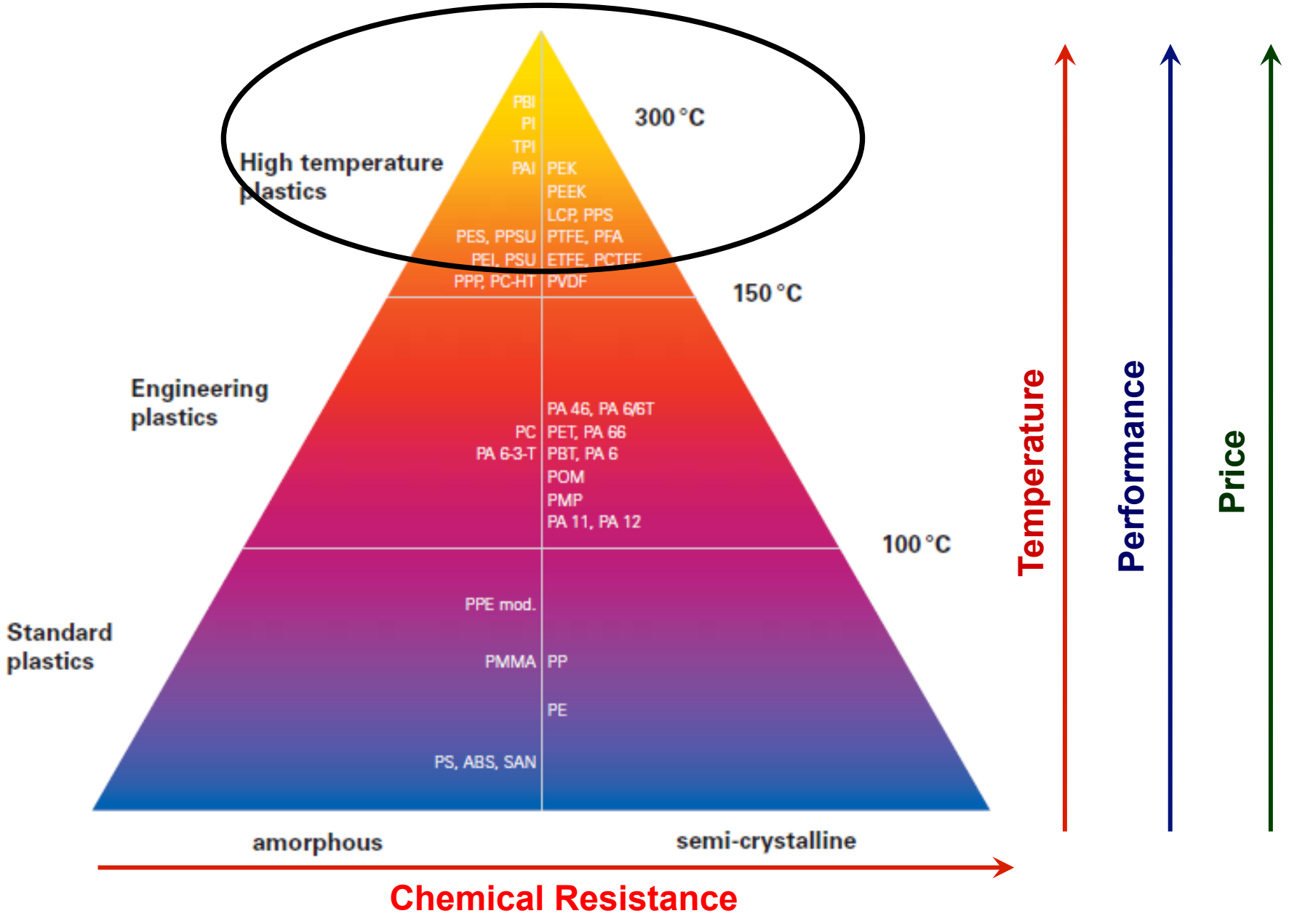
HPTC 2011

By Tim Hsu, Ph.D.

State College, PA, USA
www.polymics.com

Polymics
Concept to Solution

Polymer Pyramid



Why Use High Performance Engineering Thermoplastics ?

- Maintain strength at high temperature
- Dimensional stability at high use temperature
- Stable optical properties at elevated temperature
- Corrosion and wear resistance
- Reduce weight relative to metals
- Ease of processing compared to metals
- Complex part geometries
- Thermal conductivity
- Barrier properties
- Electrical insulation
- Coefficient of friction
- Chemical resistance
- Performance at cryogenic conditions
- Transparency
- Fire resistance

Use of HPP makes sense when their high temperature performance is combined with other desired/required properties and it provides a cost – performance and/or design advantage.

Commercial Semi-Crystalline High Performance Polymers

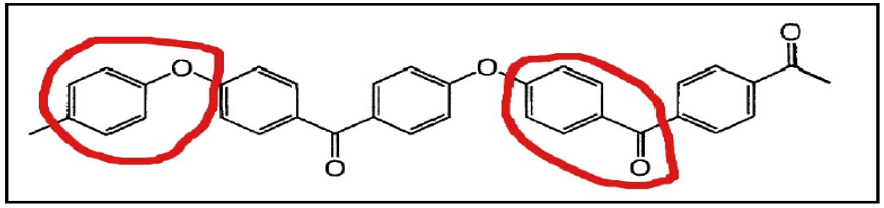
HPP	Tg/Tm (^{0}C)	Cont Use Temp (^{0}C)	Properties	Application Examples
PPS	85/285	150 - 200	• Excellent stability in organic and aqueous environment; • Less resistant to oxidants; • flame Resistant	• High Strength & good chemical resistance applications •Automotive •Consumer and industrial products •Protective coatings
PAEK	143 – 165/ 310 - 365	200 - 260	• Excellent chemical resistance; • Good creep resistance; • Good dimensional stability	• High temperature and aggressive Environment •Automotive •Aerospace •Oil/gas and chemical •Cable and insulation
LCP	120/335	225	• Good processability; • Good weathering properties; • Low moisture absorption; • Dimensionally stable	• Thin-walled and high strength components •Aerospace •Electronics •Medical

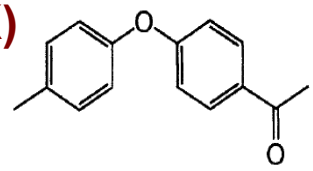
PAEK (PolyArylEtherKetone) Family

Commercial Polyketone Family

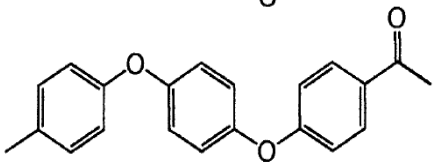
- **Thermoplastic Poly Aryl Ether Ketone (PAEK)**
  - **Semi-Crystalline Polymer**

Keto Ratio: Aromatic Ketone to Ether Linkage





polyEtherKetone (PEK)



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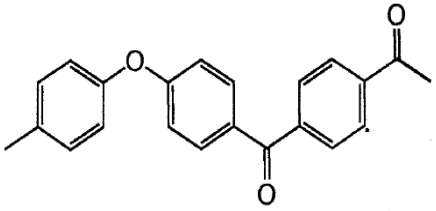
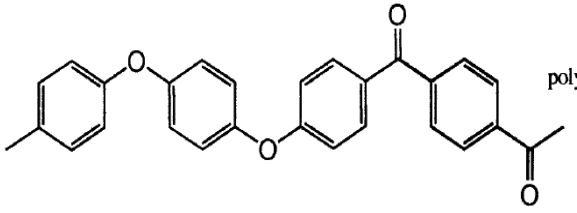
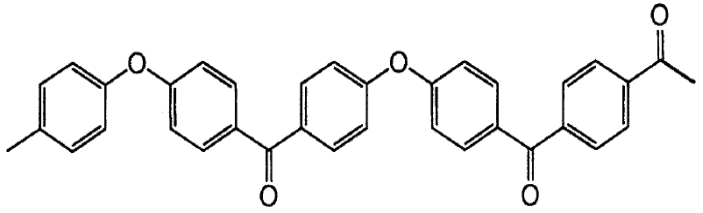


polyEtherKetoneKetone (PEKK)



polyEtherEtherKetoneKetone (PEEKK)



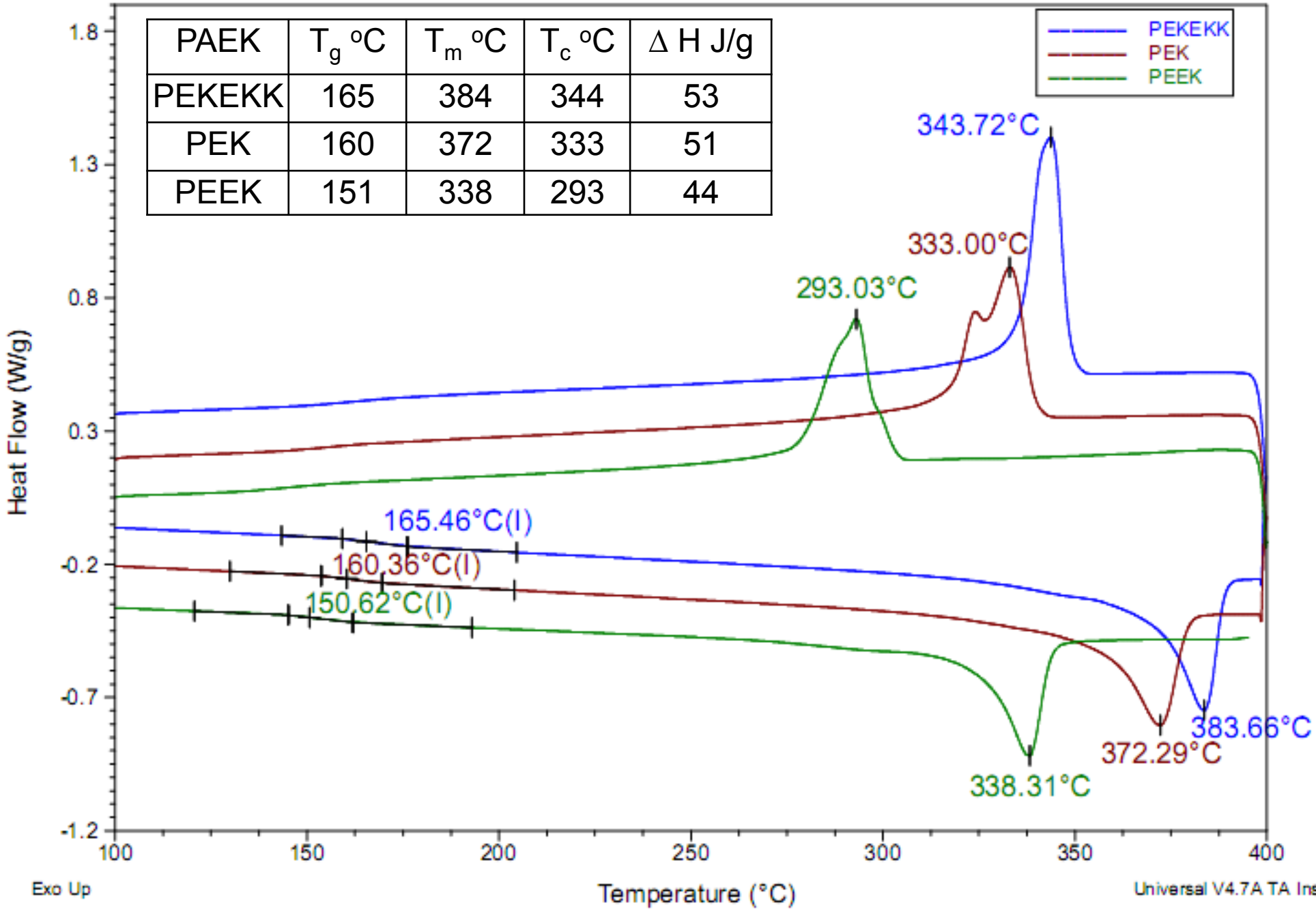
polyEtherKetoneEtherKetoneKetone (PEKEKK)

Commercial Grades:

	Manufacturer	Keto Ratio
PEEK	Victrex/Generic	33 %
PEK	Victrex	50 %
PEEKK	Generic	50 %
PEKEKK	BASF	60 %
PEKK	Generic	67 %

Thermal Transitions of Commercial PAEK's

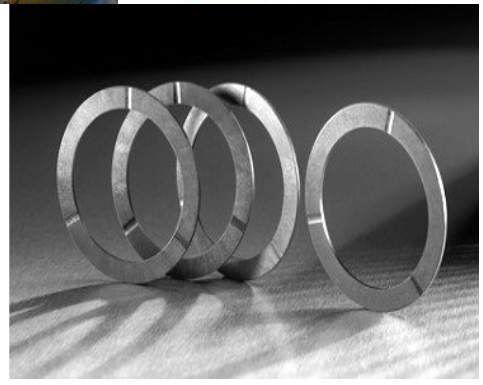
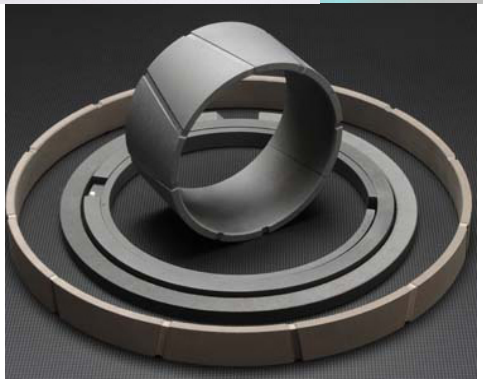
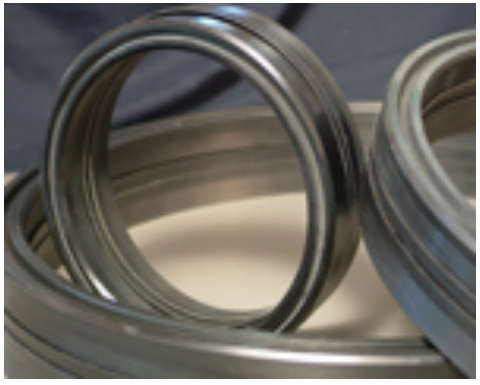
PAEK	T_g °C	T_m °C	T_c °C	Δ H J/g
PEKEKK	165	384	344	53
PEK	160	372	333	51
PEEK	151	338	293	44

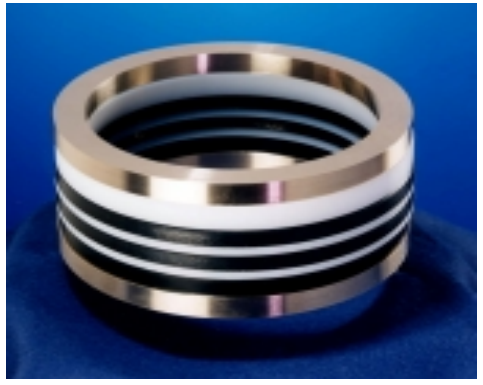


Typical PEEK Components in Oil/Gas Applications







Benefit & Value of PEEK in Oil/Gas Applications

- High mechanical strength to withstand high pressures and loads.
- High continuous operating temperature –
  Long life at elevated temperatures up to 150°C in critical environment.
- Resistant to chemical attack – provides corrosion resistance.
- Can be compounded with fillers to provide improved properties.

Limitation of Existing PAEK in Oil/Gas Applications

- Limited use in high pressure environment above 180 °C due to reduced creep resistance, even with reinforced grades.
- Existing higher Tg PAEK is cost prohibitive and has various processing concerns and still limited to 200 °C under high pressure environment.
- Many high Tg PAEK lacks PEEK ductility with limited process option.

Industry Requirements:

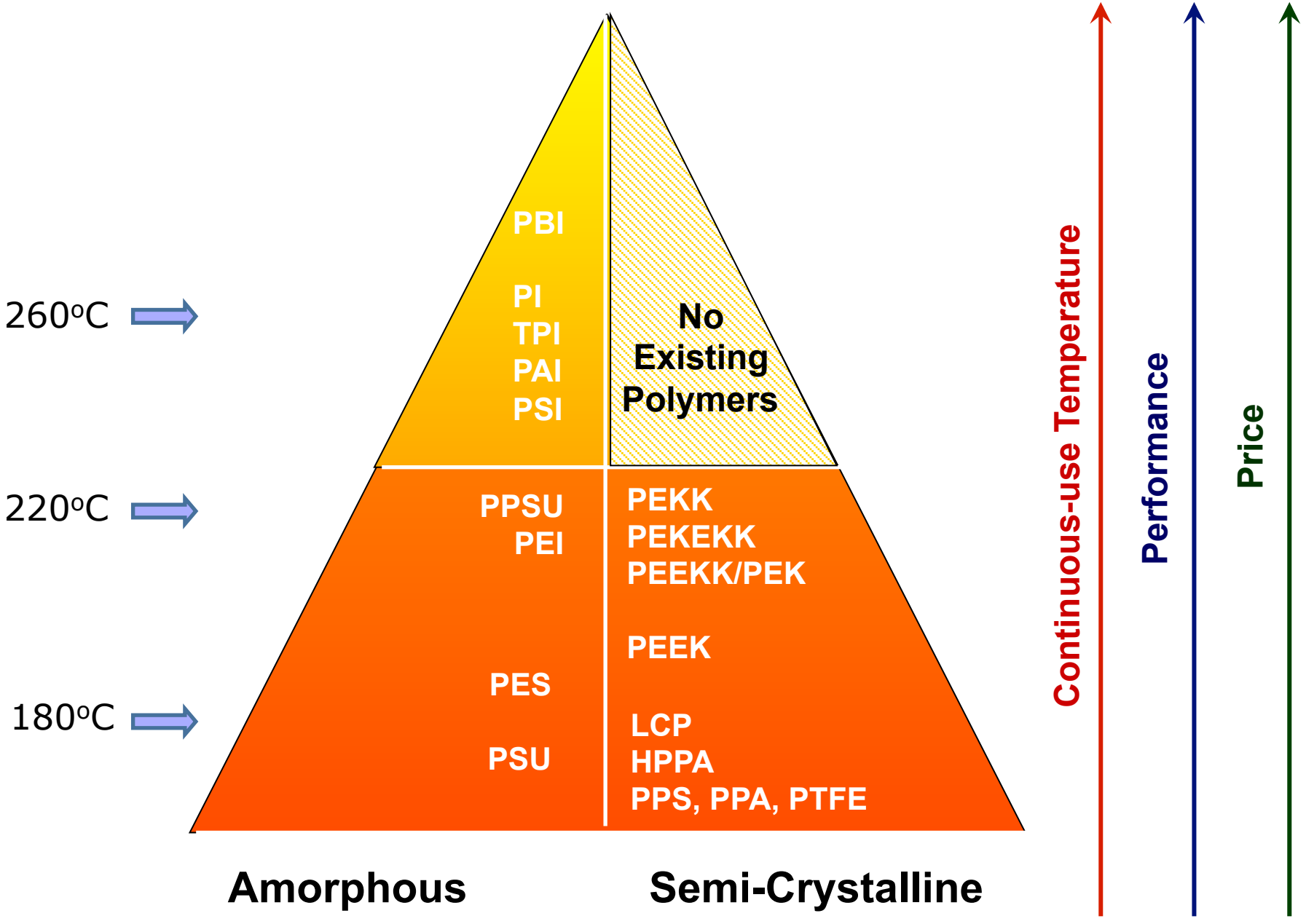
- High Tg PAEK that maintains high mechanical strength above 200 °C.
- Maintain ease of processing similar to PEEK.
- Maintain chemical resistance at high temperatures.
- Cost Effective.

Potential Solution(s):

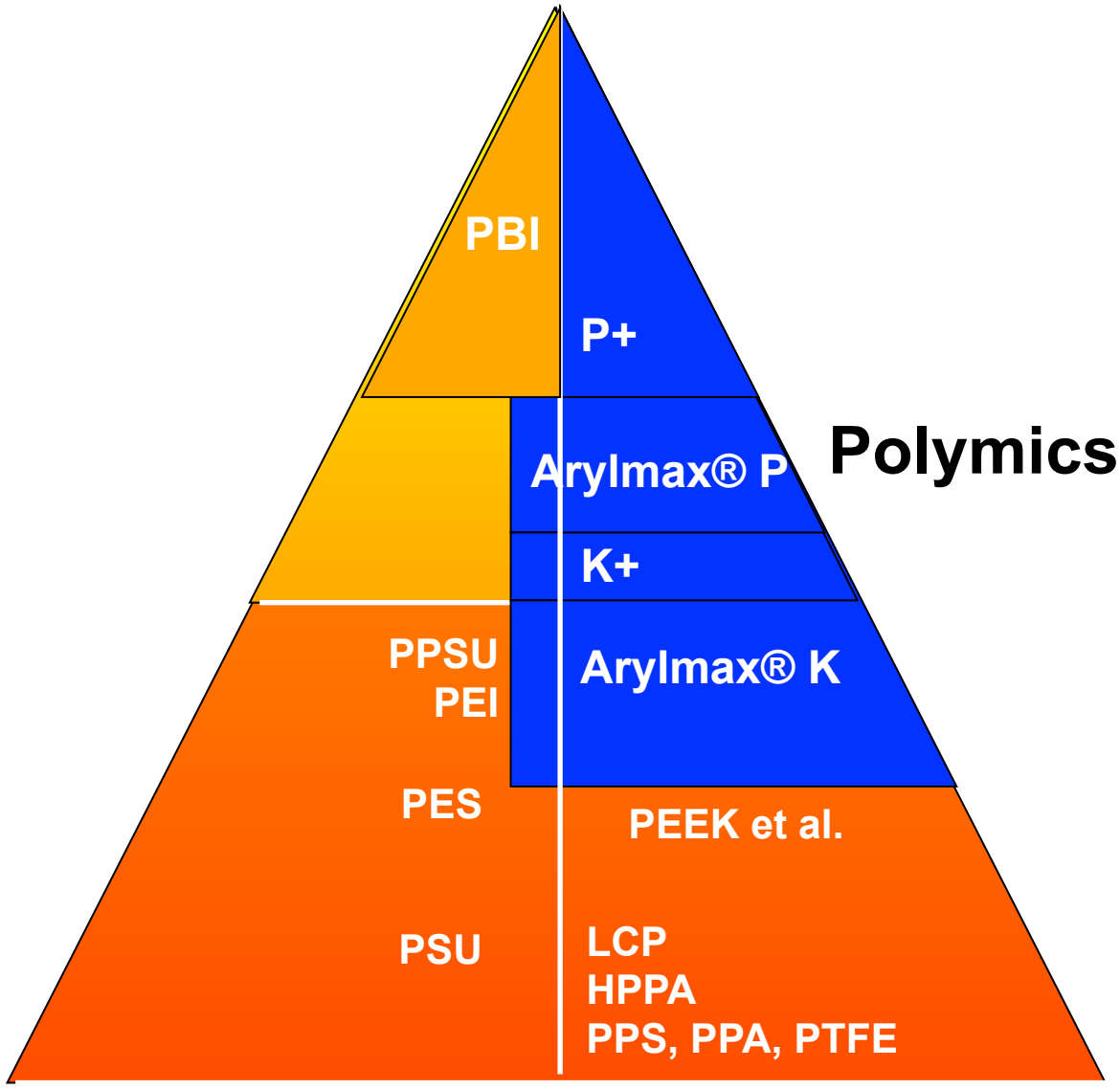
- Alternative high temperature polymer family.
- Copolymers of PAEK.
- PAEK Alloy & Blends.
- PAEK Nano-composites.
- Crosslinked PAEK system.

New High Temperature PAEK's by Polymics

High Temp/High Performance Polymers



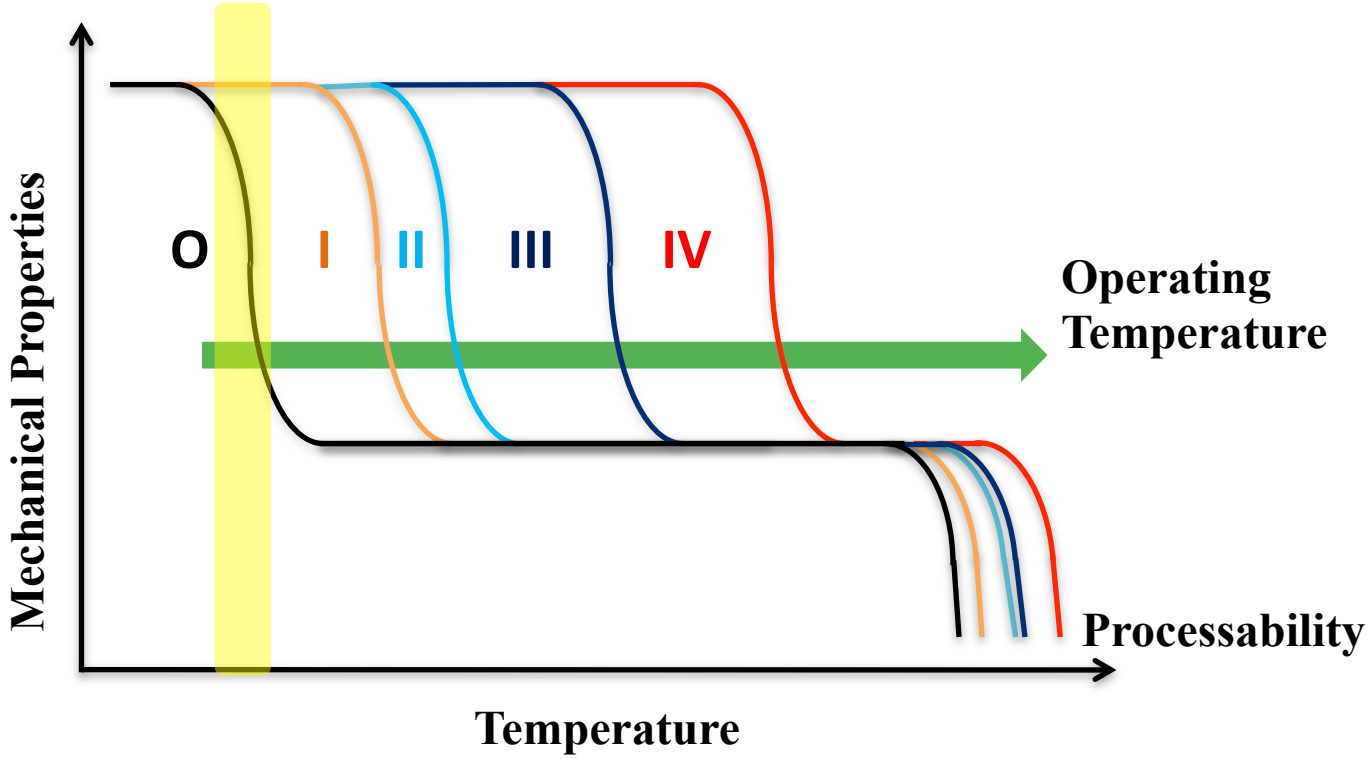
New High Temp PAEK by Polymics



Polymics, Ltd.

Arylmax® Polymers – New High Tg PAEK System

- Increases operating temperatures
- Maintains processing temperatures



Semi-Crystalline Arylmax® Polymers

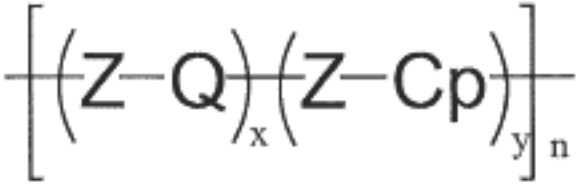
Application Zones	Tg, ºC	Tm , ºC	Polymer	Status
0	145	343	PEEK	Industry Std
I	165 - 175	305 - 365	Arylmax®-K	Commercial
II	170 - 200	320 - 360	Arylloy K	Commercial
III	190 - 250	330 - 350	Arylmax®-P	2011
IV	240 - 300	330 - 350	Arylloy P	2012

Arylmax® P Polymers

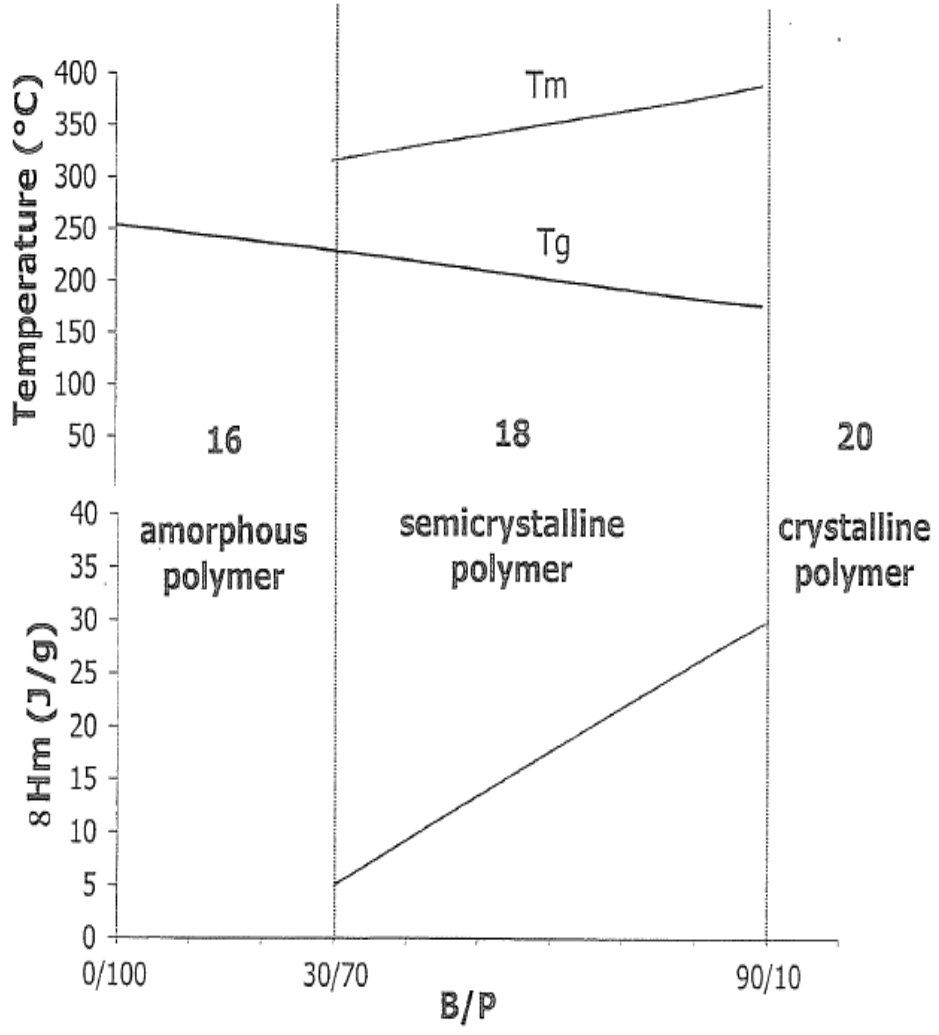
Arylmax™ P Polymers

- **Arylmax® P is a new family of copolymers**
- **Generically named PAEKP copolymers**
- **Each copolymer property is determined by x : y ratio, or**

B/P Ratio

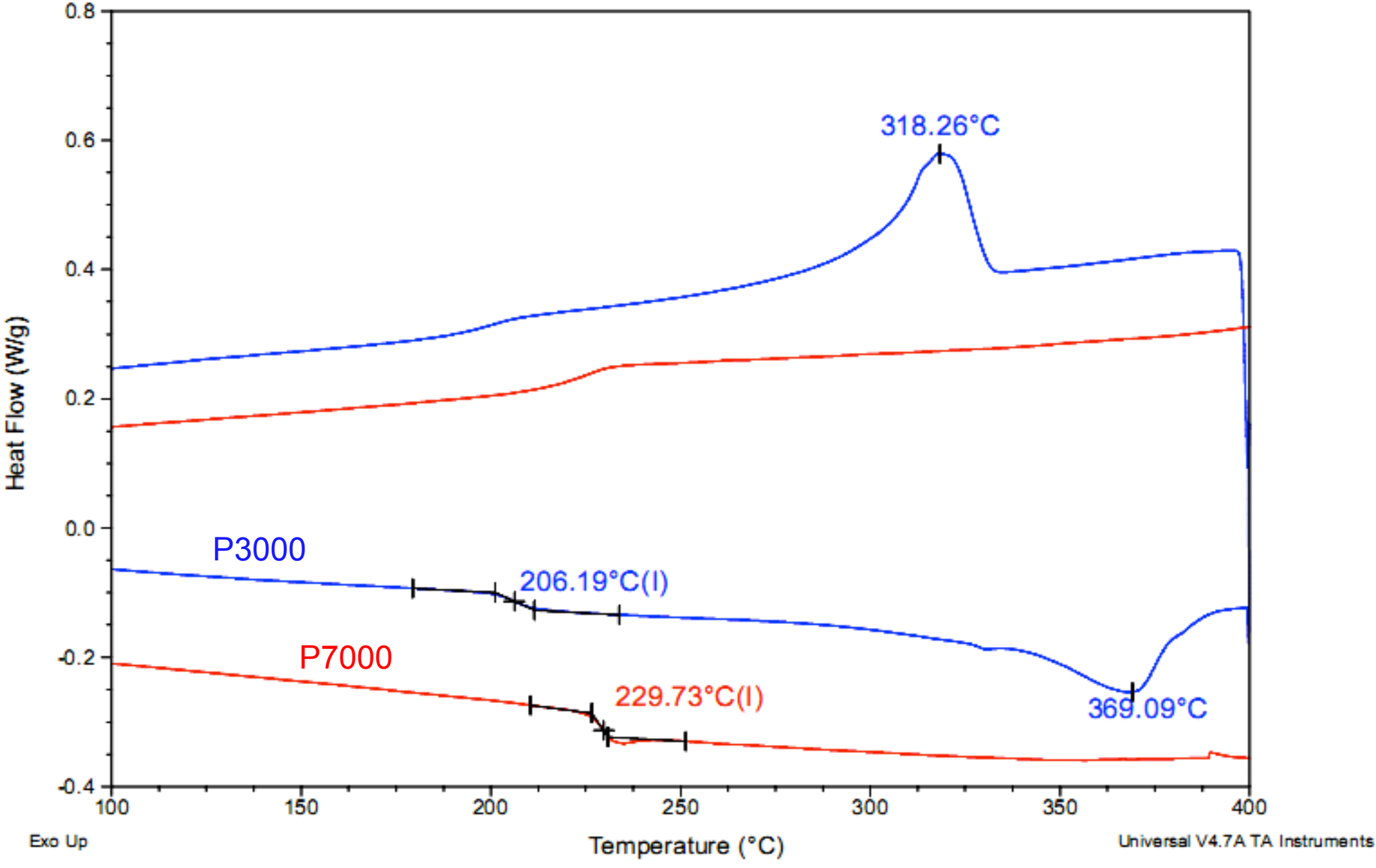


- Z = bisphenyl(di)ketone radical
- Q = bisphenol radical
- Cp = proprietary aromatic radical

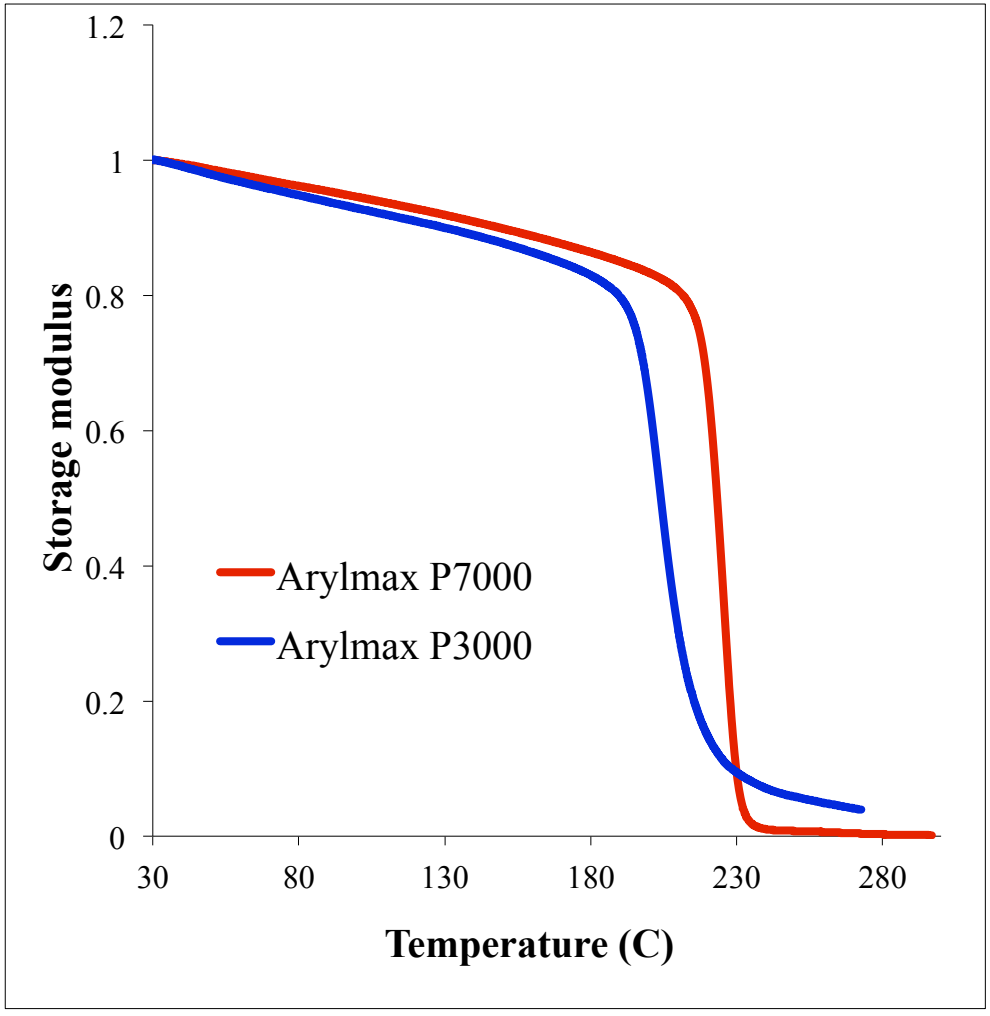


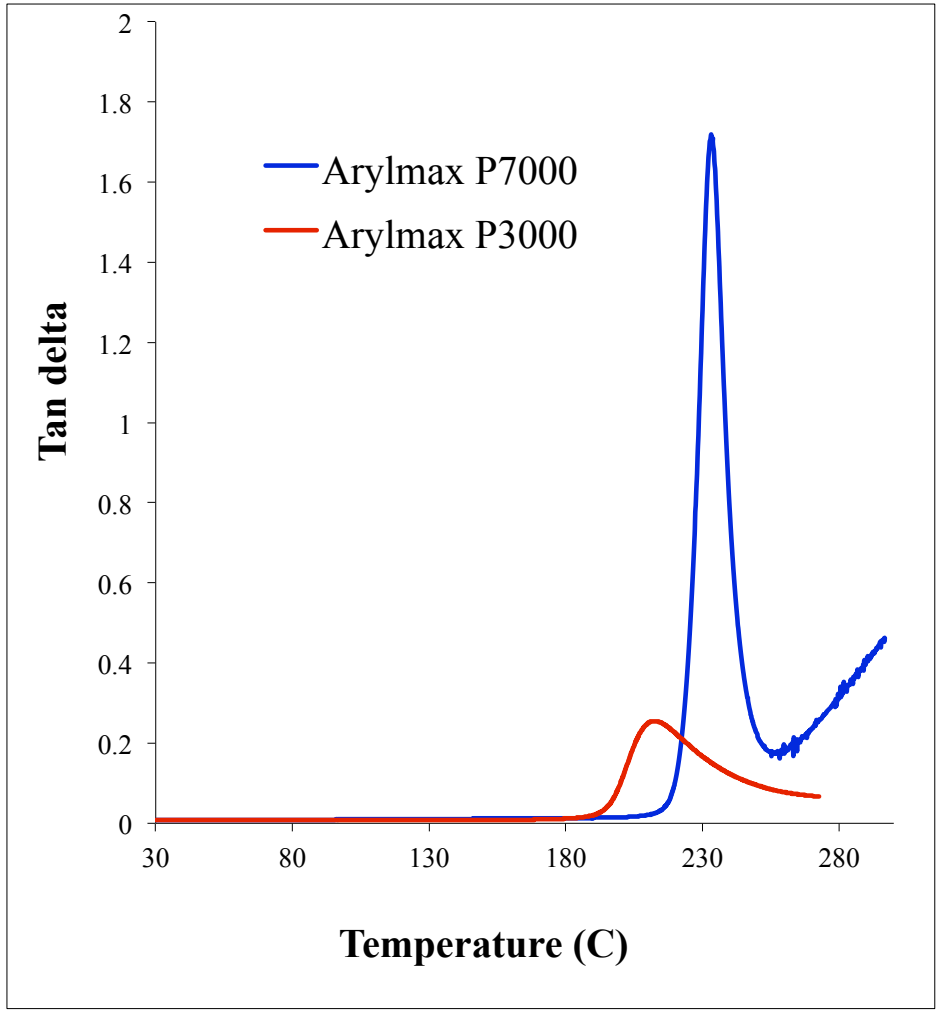
16: AMORPHOUS POLYMER
18: SEMICRYSTALLINE POLYMER
20: CRYSTALLINE POLYMER

Thermal Transition of Typical PAEKP



DMA of Arylmax® P3000 & P7000

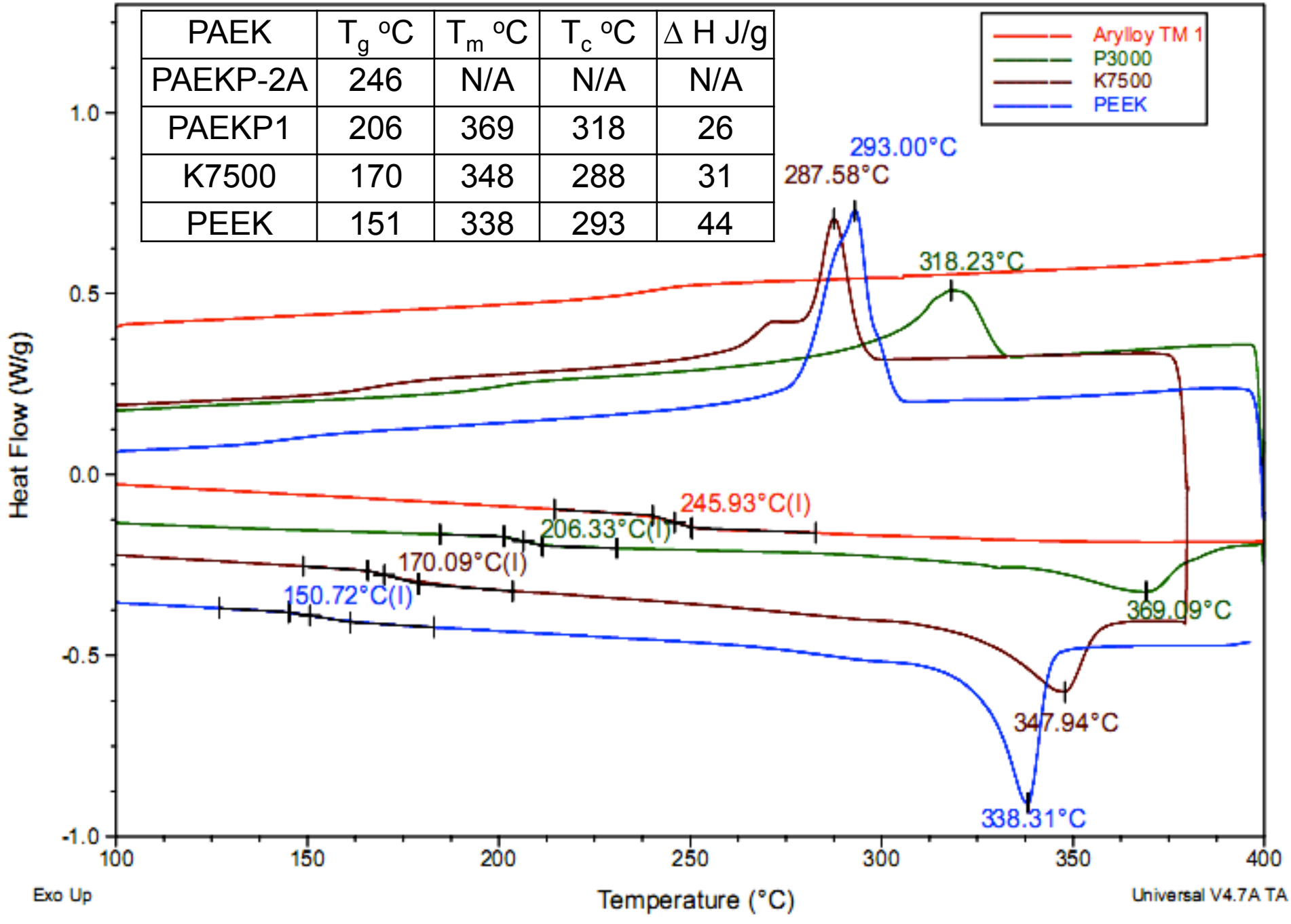




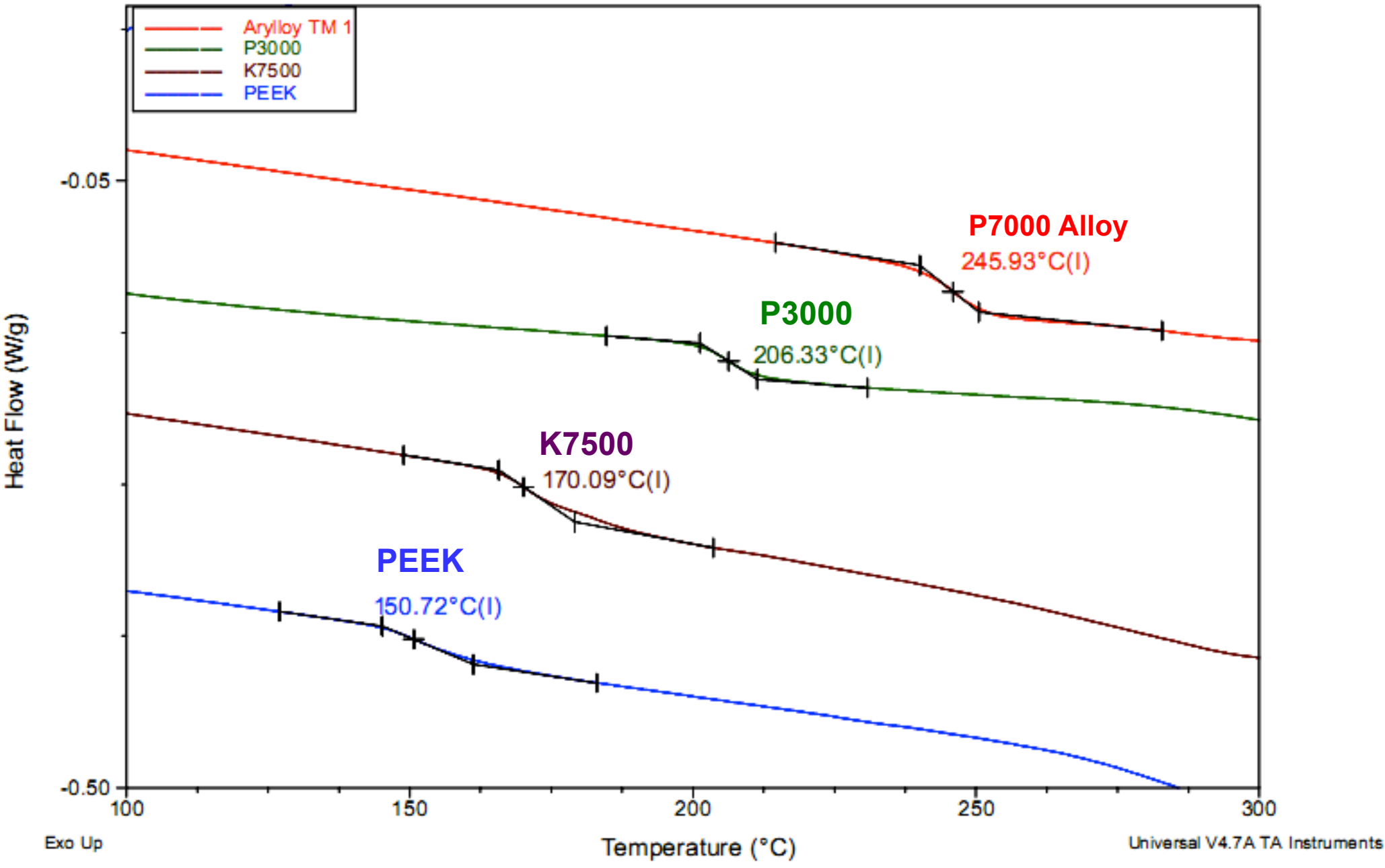
- Measured on annealed samples
- P7000-single cantilever, P3000 on 3 point

Comparison of PAEK's Thermal Transitions

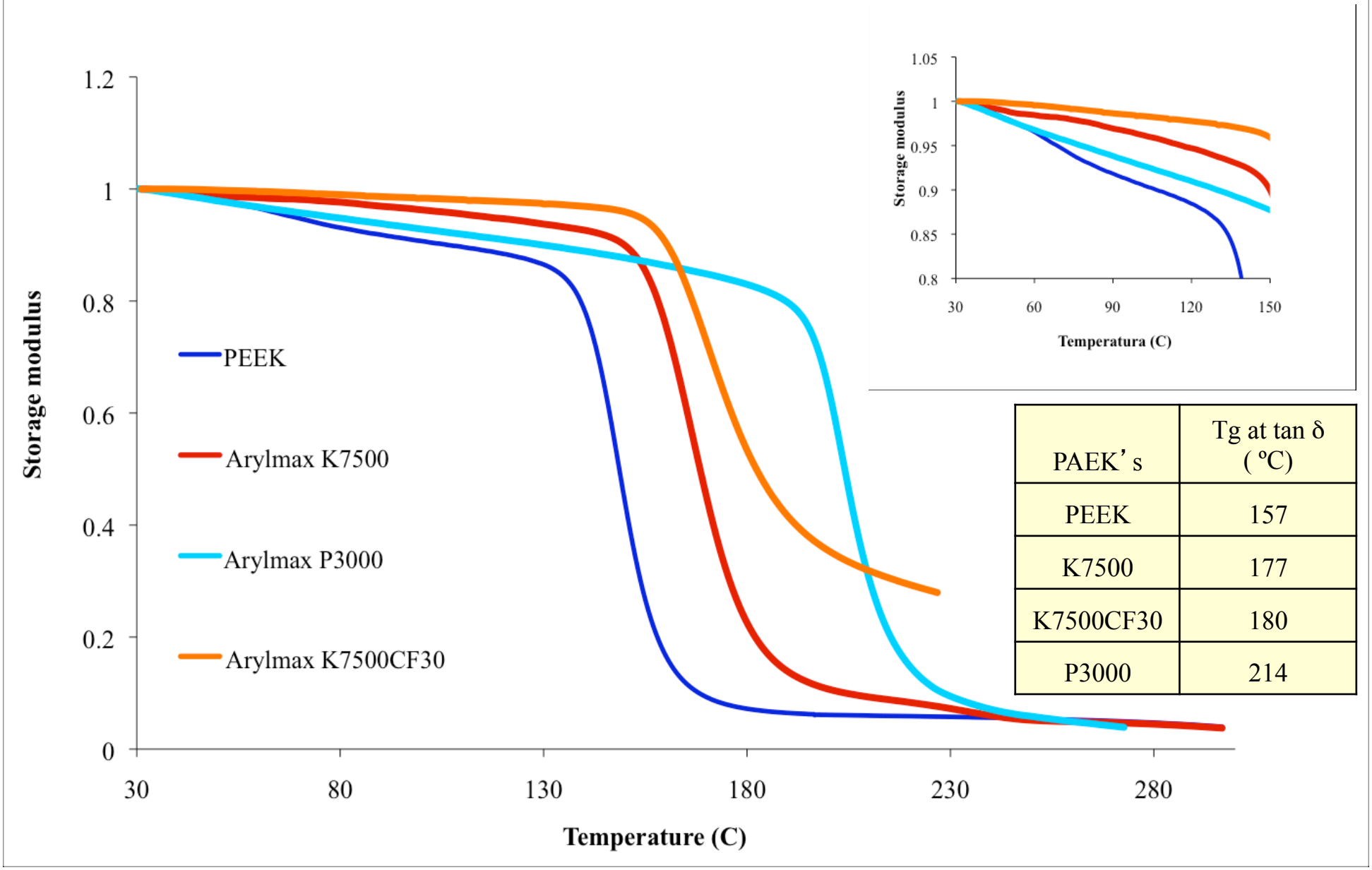
PAEK	T_g °C	T_m °C	T_c °C	Δ H J/g
PAEKP-2A	246	N/A	N/A	N/A
PAEKP1	206	369	318	26
K7500	170	348	288	31
PEEK	151	338	293	44



Comparison of PAEK's Tg's



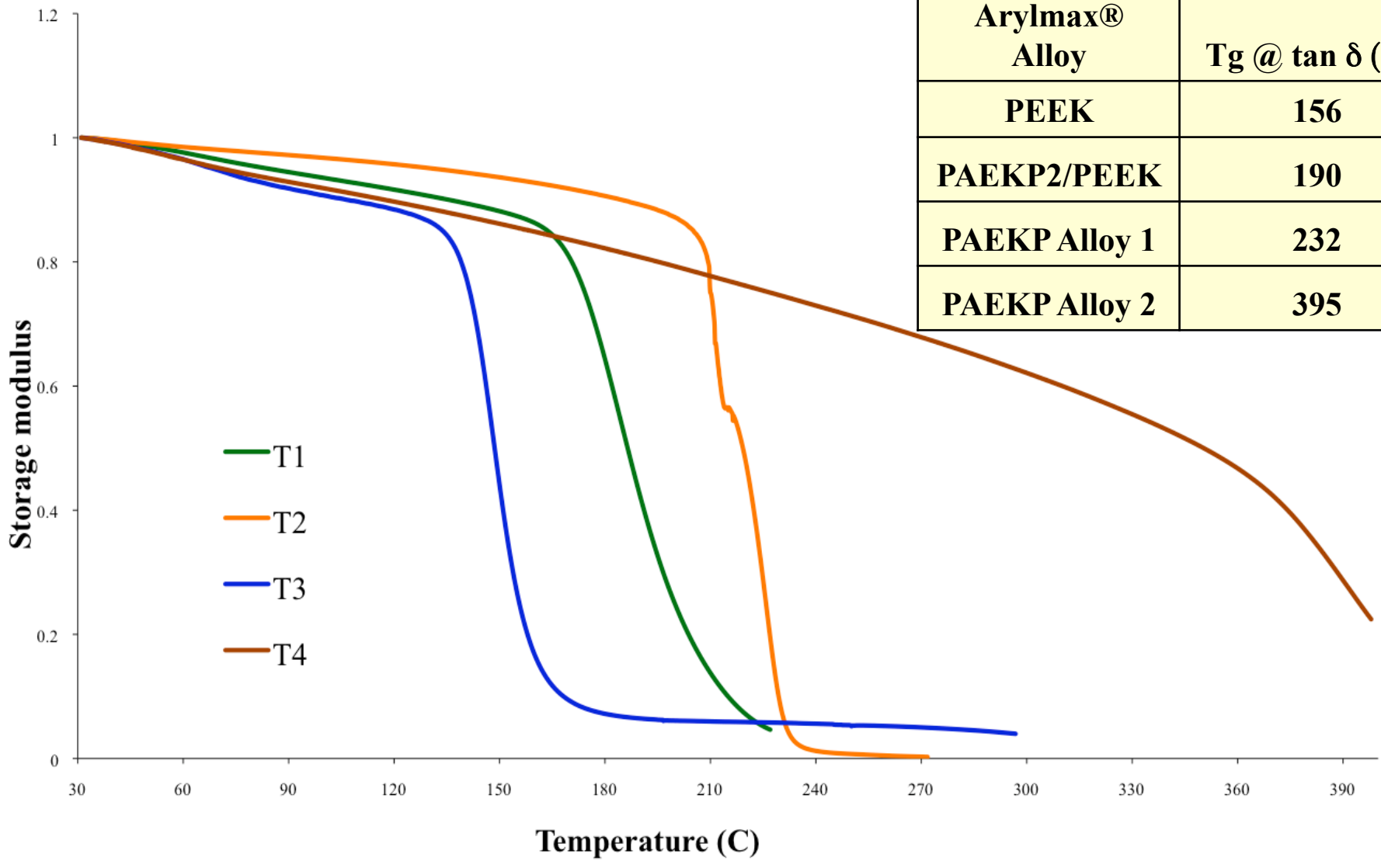
DMA of High Tg Arylmax® P3000 & Commercial PAEK's



PAEK's	Tg at tan δ (°C)
PEEK	157
K7500	177
K7500CF30	180
P3000	214

Measurements made on annealed samples using 3 point bend fixture
(except Arylmax K7500CF30 measured (annealed) using single cantilever fixture)

DMA of High Tg's Arylmax® P7000 Alloy & Blend

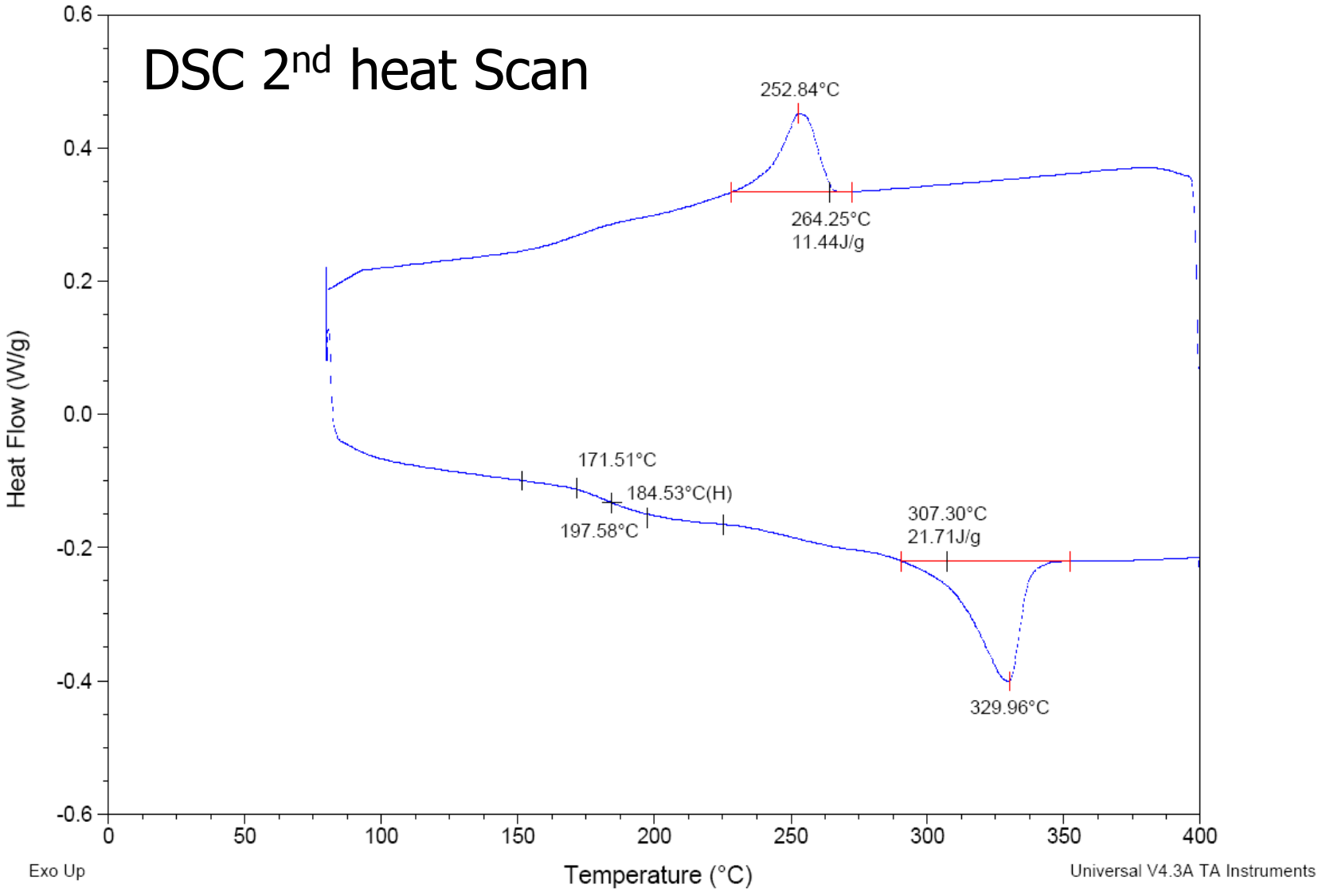


Arylmax® Alloy	Tg @ tan δ (°C)
PEEK	156
PAEKP2/PEEK	190
PAEKP Alloy 1	232
PAEKP Alloy 2	395

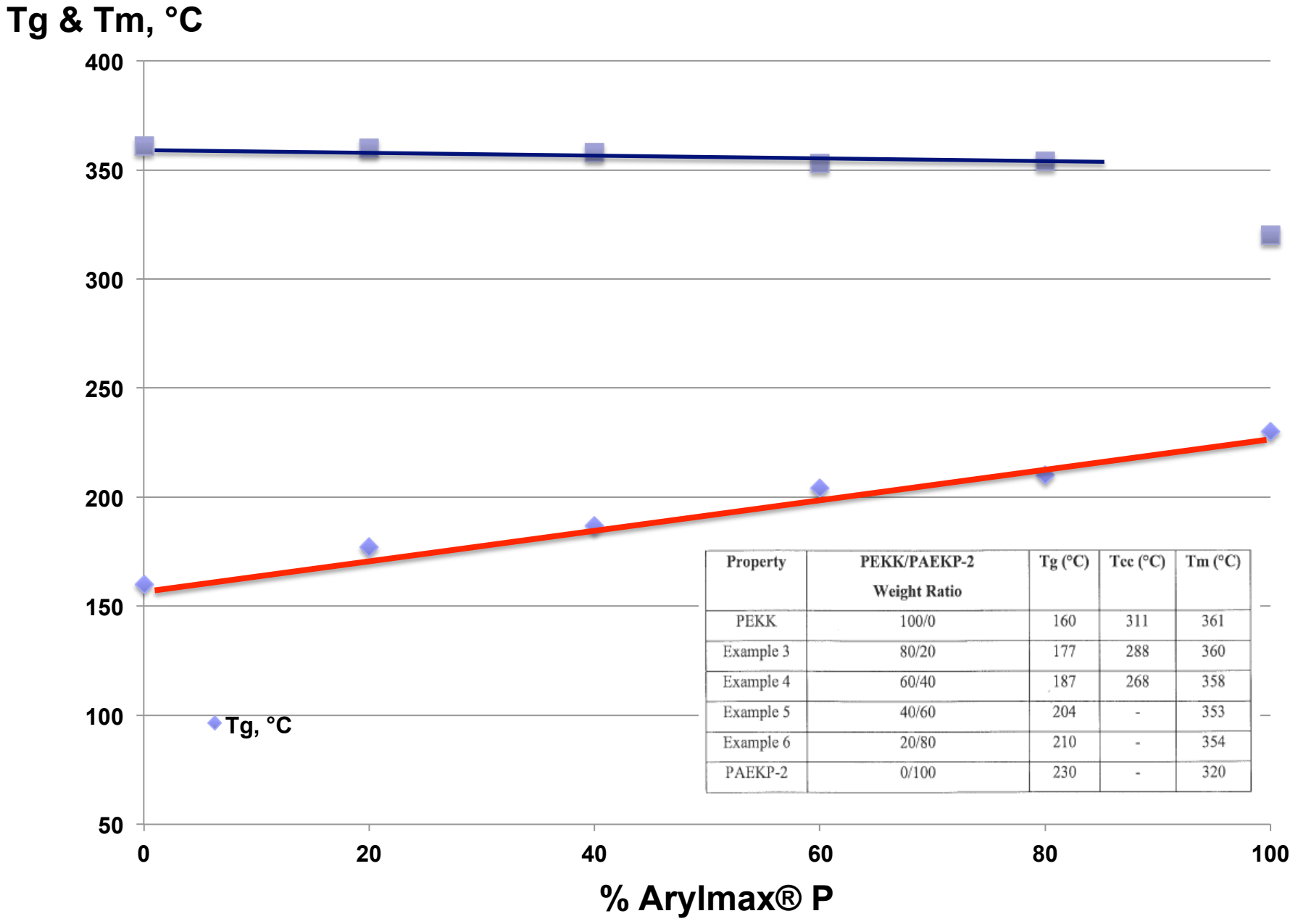
- Measured on annealed samples using single cantilever.

Arylmax® P Alloy & Blends

Arylmax® P & PEEK Blends



Arylmax® P & PEKK Blends



Property	PEKK/PAEKP-2 Weight Ratio	Tg (°C)	Tcc (°C)	Tm (°C)
PEKK	100/0	160	311	361
Example 3	80/20	177	288	360
Example 4	60/40	187	268	358
Example 5	40/60	204	-	353
Example 6	20/80	210	-	354
PAEKP-2	0/100	230	-	320

Why Use Blends & Alloys?

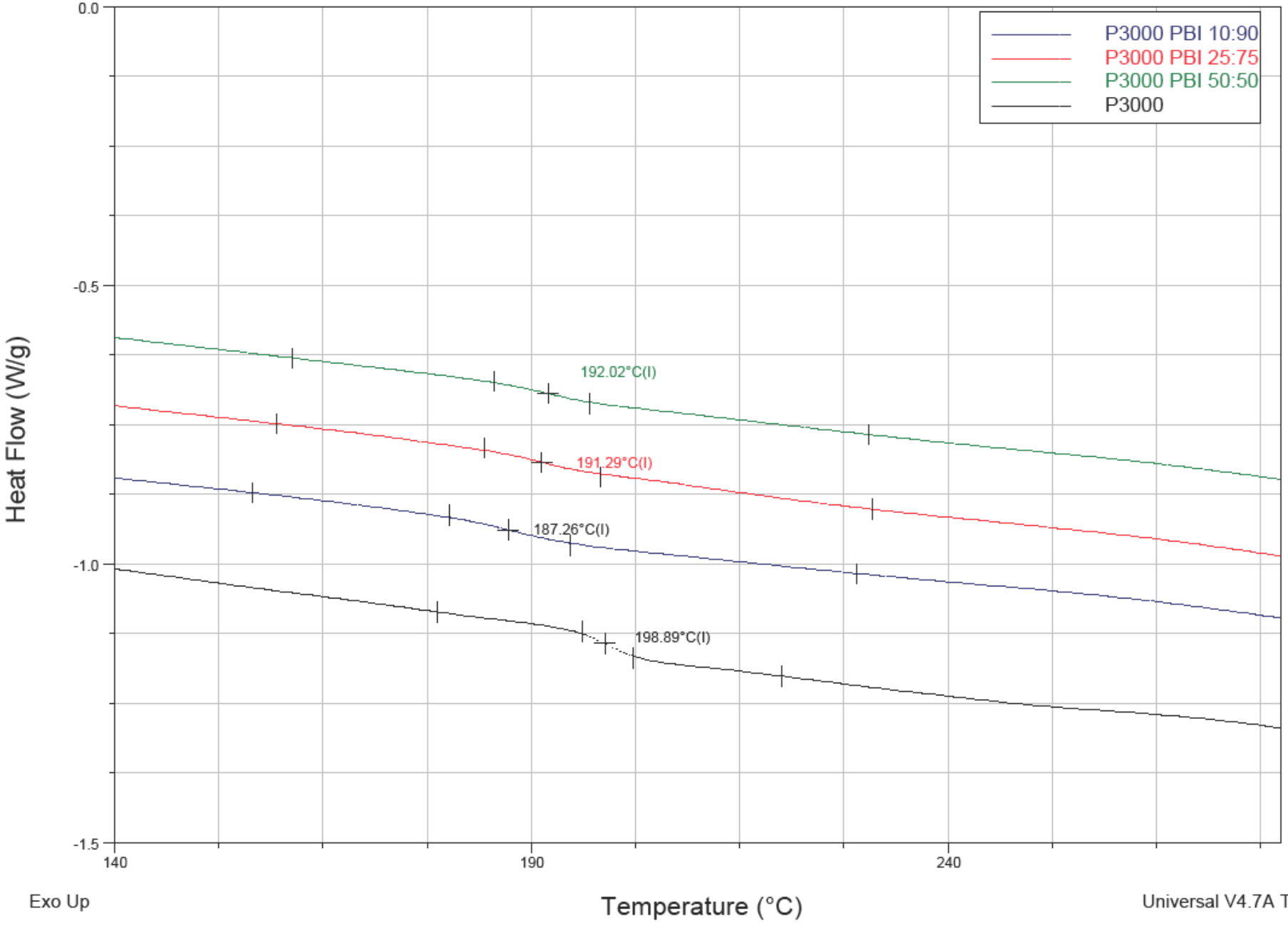
- Enhance strength at high temperature by increasing Tg with high Tg components
- Improve dimensional stability at high use temperature with high melting components
- Enhance chemical and corrosion resistance with more chemical resistance components
- Compatibilizer and Interfacial Agents for composite and coatings applications
- Modify processing characteristics and mechanical properties

Example of Arylmax® P Alloys
- PBI Enhanced PAEKP

Arylmax® P & PBI Alloys

Man code	Material	Composition	Process ID	Lot #	Comment
P3000 based					
EX5159-A01	PBI / P3000	10 / 90	P02	EE007-11I-01	
EX5159-A02	PBI / P3000	25 / 75	P02	EE007-11I-02	
EX5159-A03	PBI / P3000	50 / 50	P02	EE007-11I-03	
EX5159-A04	PBI / P3000	90 / 10	HCM	CC001-11I-26	
EX5159-A06	PBI / P3000	20/80	P01b	BB11I-01	
EX5159-A08	P3000	100	HCM	CC002-11I-01	Polymics
EX5069-A06	P3000	100	P01b	BB11I-04	Polymics
P7000 based					
EX5159-A05	PBI / P7000	20/80	P01b	BB11I-02	
EX5159-A07	PBI / P7000	95 / 5	HCM	CC001-11I-25	
EX5069-A05	P7000	100	P01b	BB11I-03	Polymics
Reference					
EX5159-A09	PBI/PEEK	50/50	PO1b	SJ4566-MU1-02	TU60
EX5159-A10	PEEK	100	As received pellets	40064	Vestakeep 4000G
EX5159-A11	PBI	100	HCM	MJ4751-MU3-01/03 and CC014-08L-01	U60

P3000/PBI Alloys Thermal Transitions

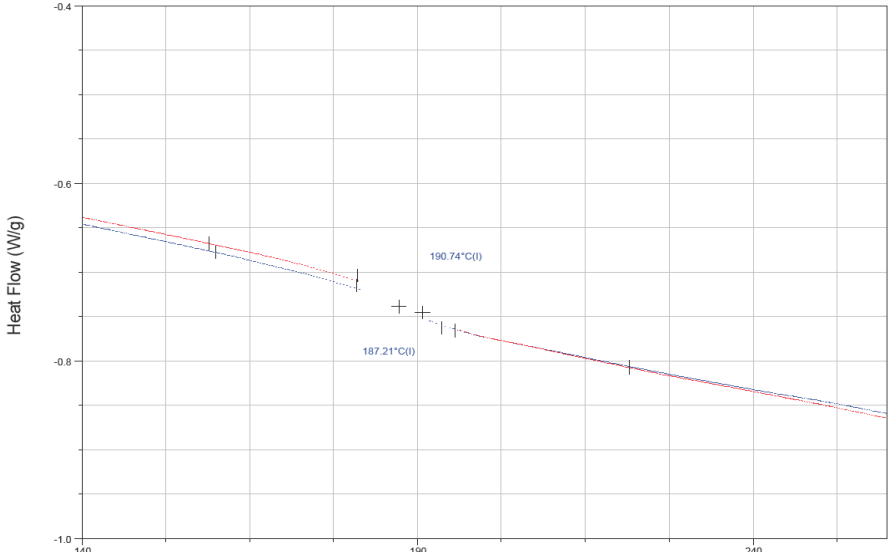


P3000/PBI Alloys Dsc Multiscan

Sample: EX5159-A01-1
Size: 5.0000 mg
Method: K7500
Comment: EE007-11I-04

DSC

File: C:...\DSC\Uma\J5159\EX5159-A01-1.
Operator: Kevin
Run Date: 14-Sep-2011 16:04
Instrument: DSC Q20 V24.8 Build 120



Sample: EX5159-A03-1
Size: 5.1000 mg
Method: K7500
Comment: EE007-11I-06

DSC

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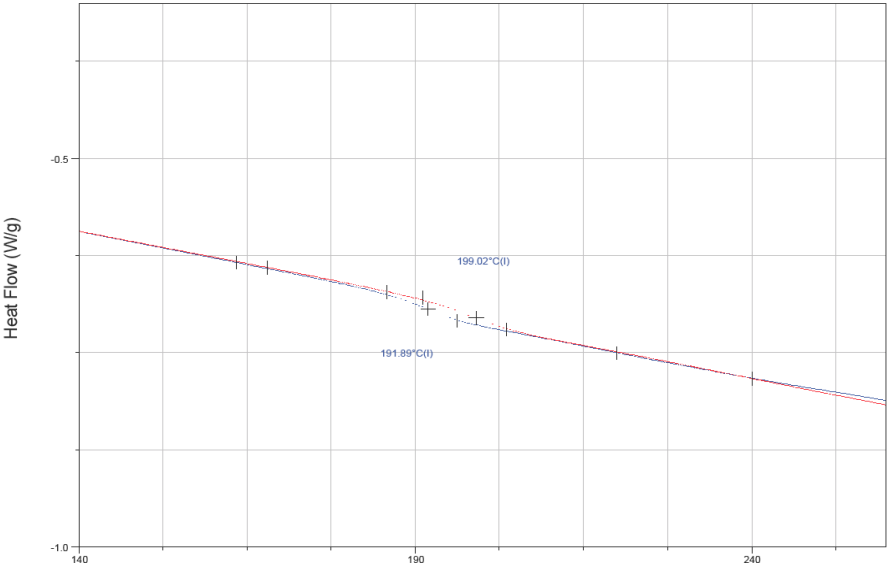
Operator: Kevin
Run Date: 15-Sep-2011 00:11
Instrument: DSC Q20 V24.8 Build 120



Sample: EX5159-A02-1
Size: 3.9000 mg
Method: K7500
Comment: EE007-11I-05

DSC

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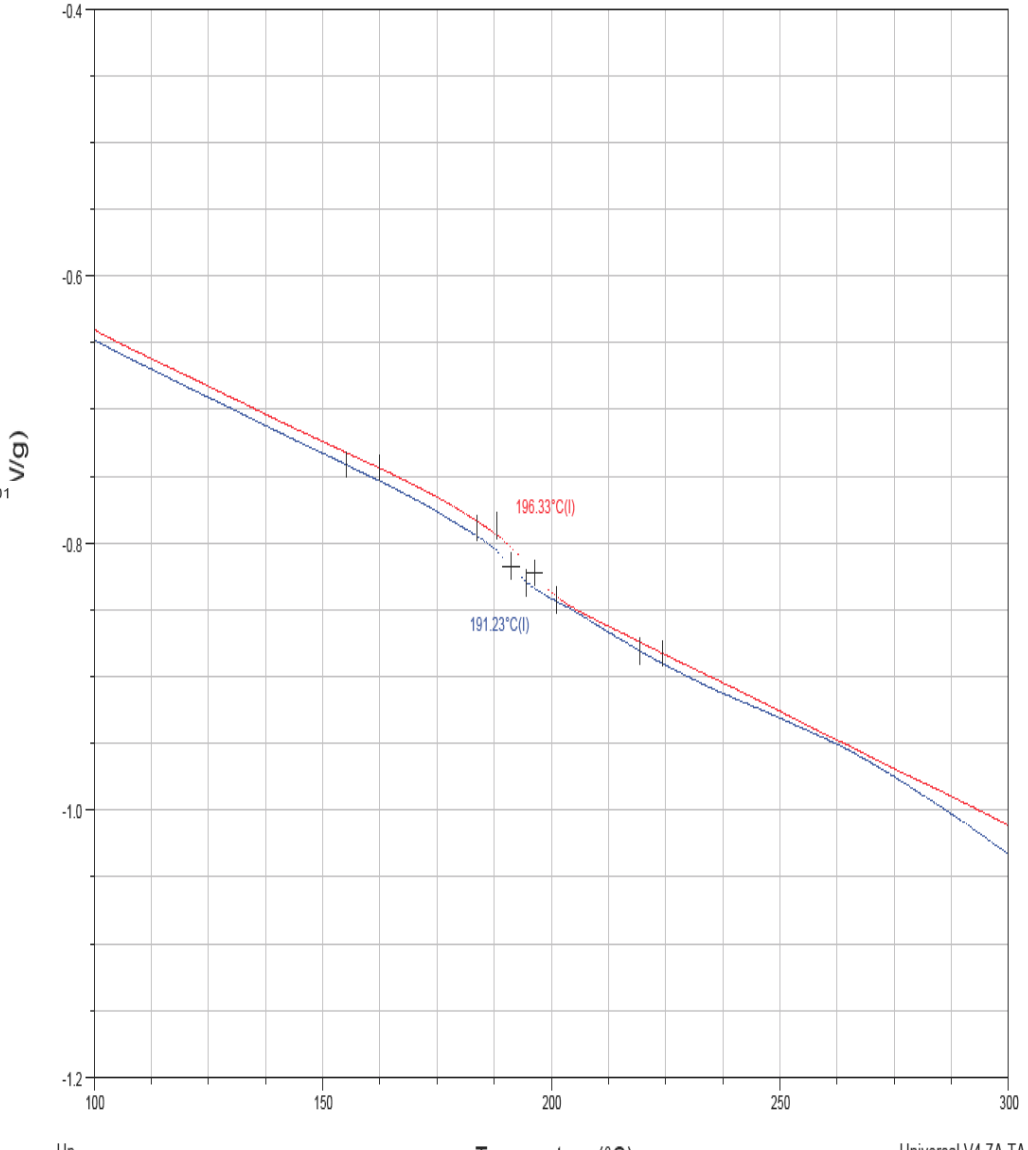
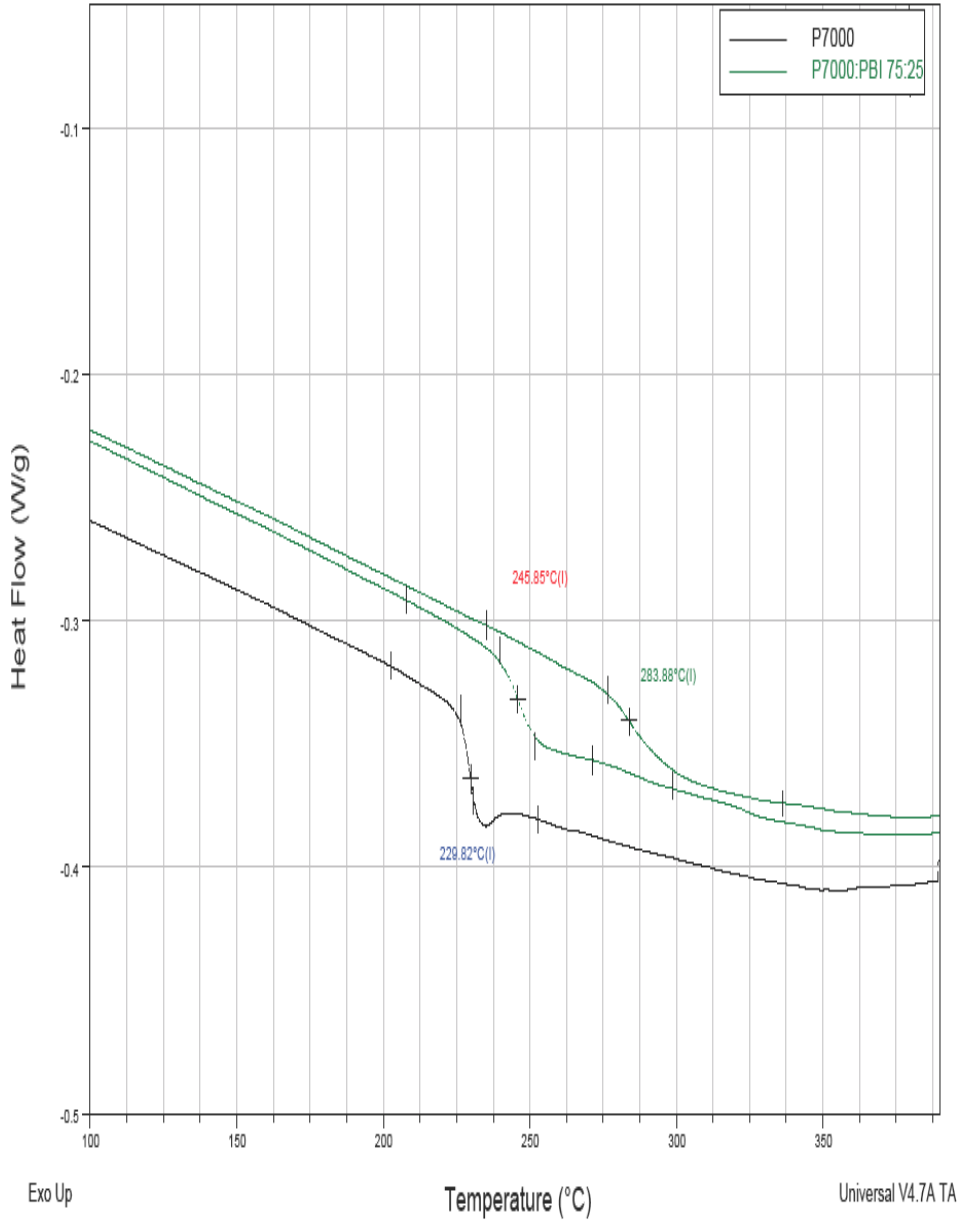
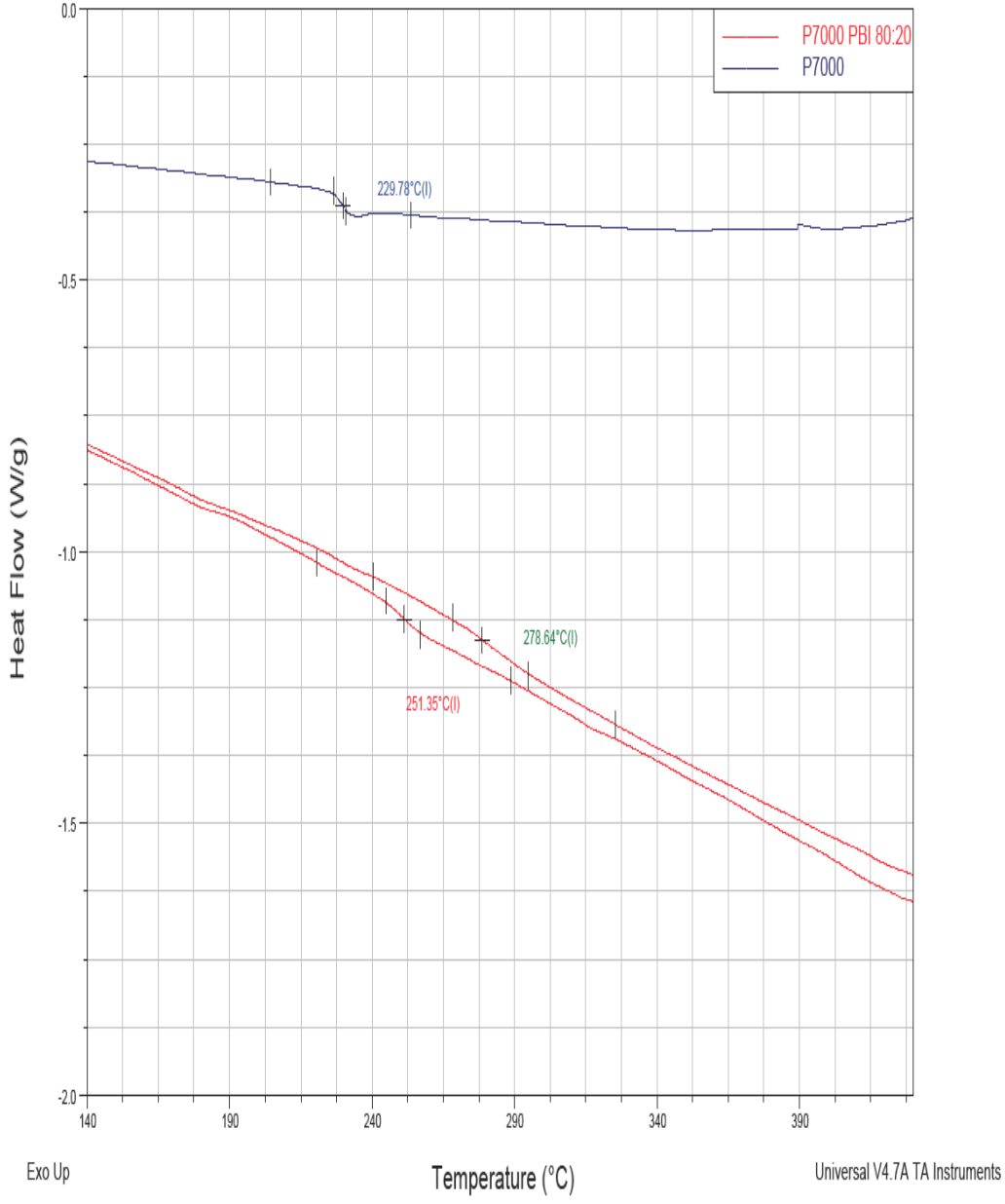
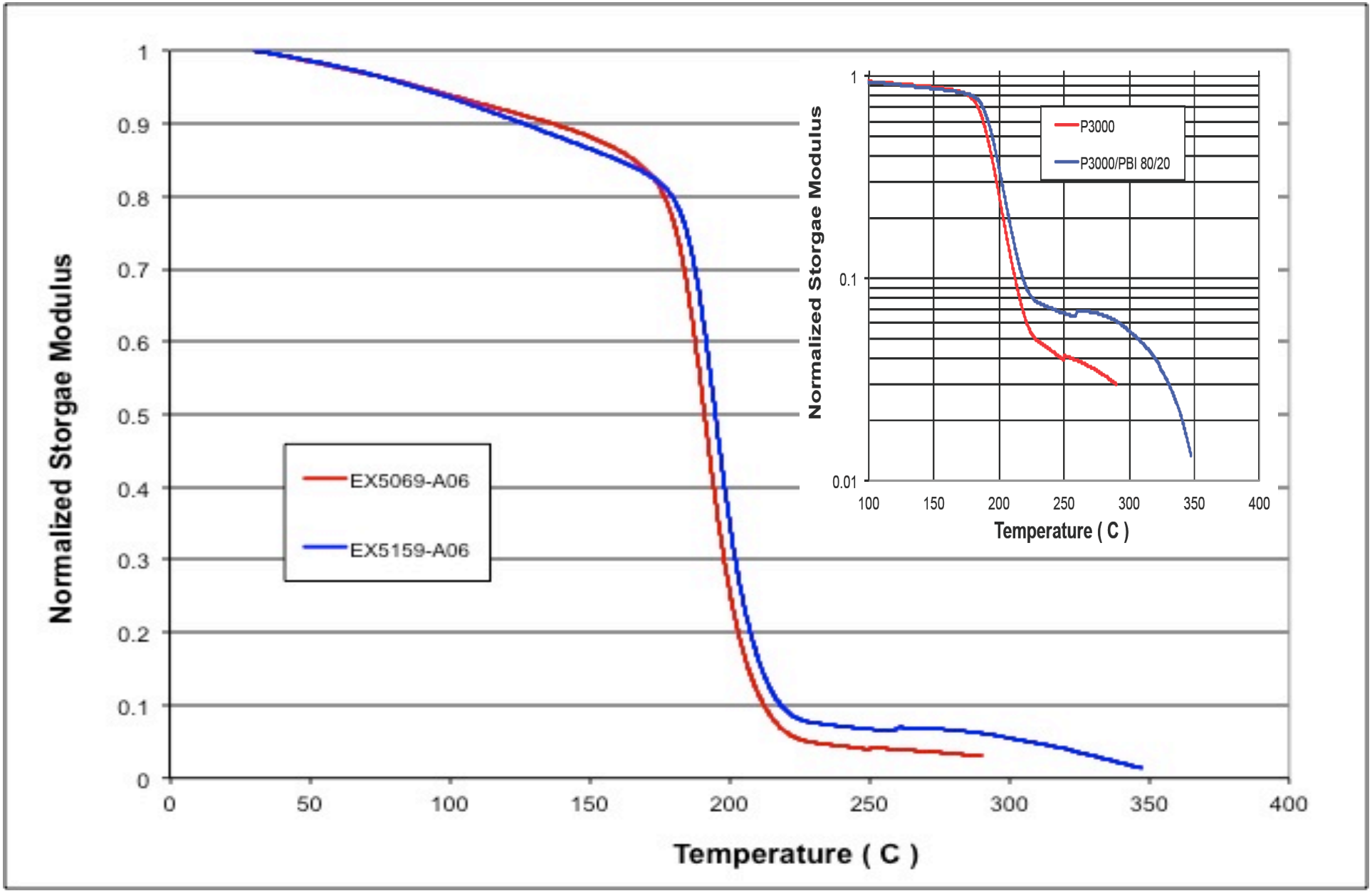


P7000/PBI Alloys Thermal Transitions



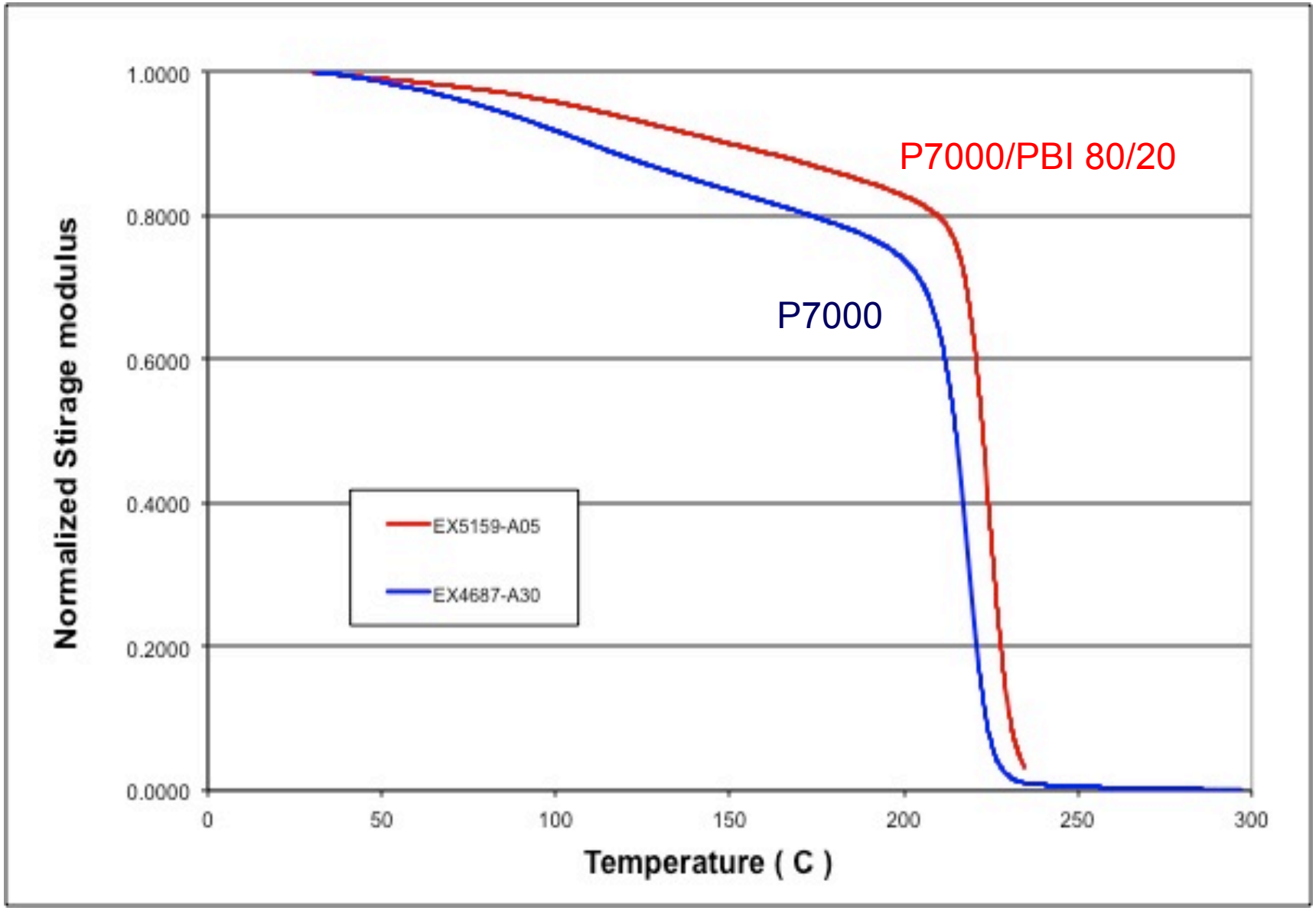


P3000/PBI Dynamic Mechanical Property



- Measured on annealed samples using single cantilever.

P7000/PBI Dynamic Mechanical Property

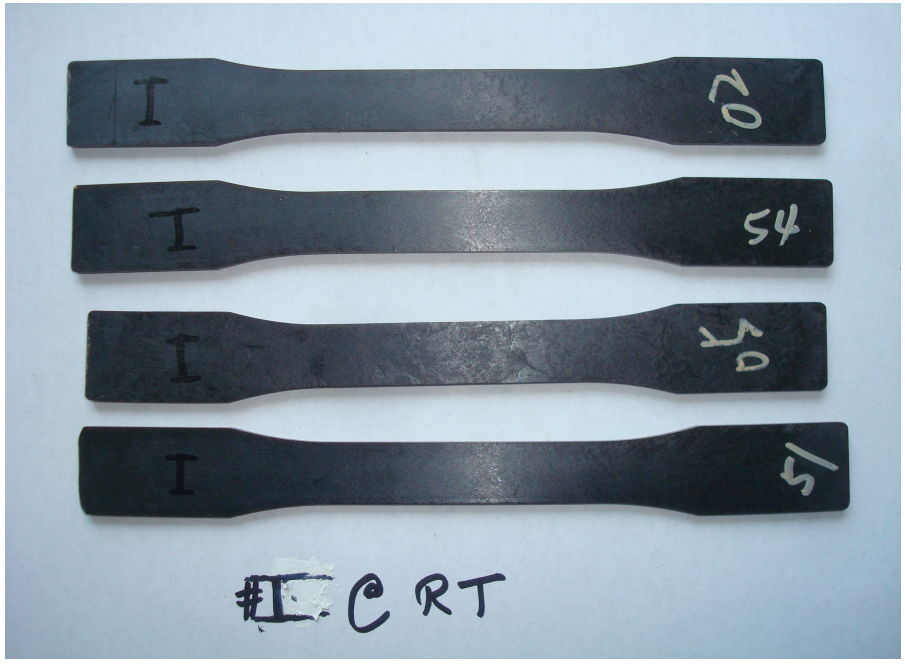


- Measured on annealed samples using single cantilever.

Water & Acid Immersion Tests

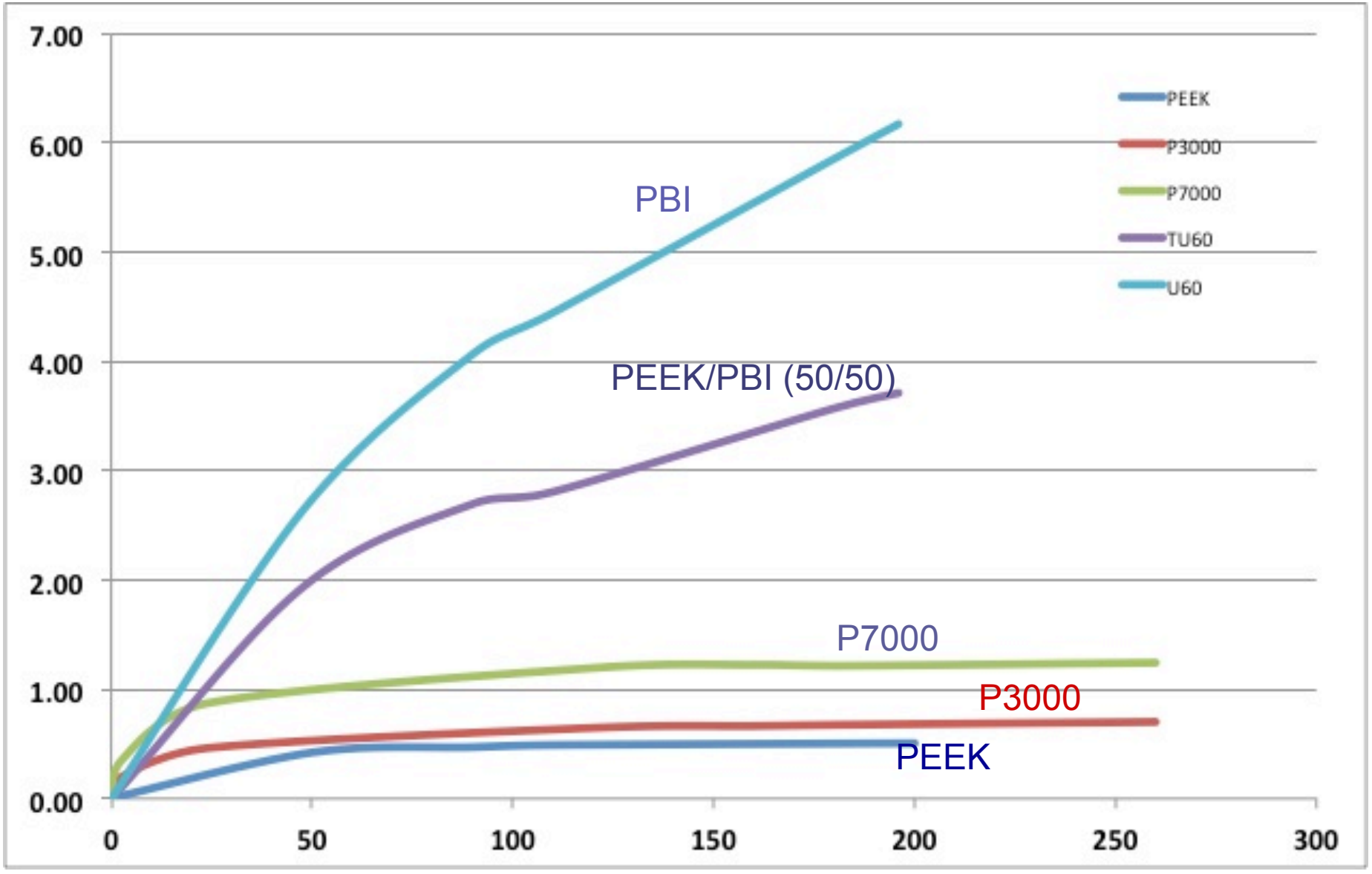
Water Immersion @ 60 °C

Control



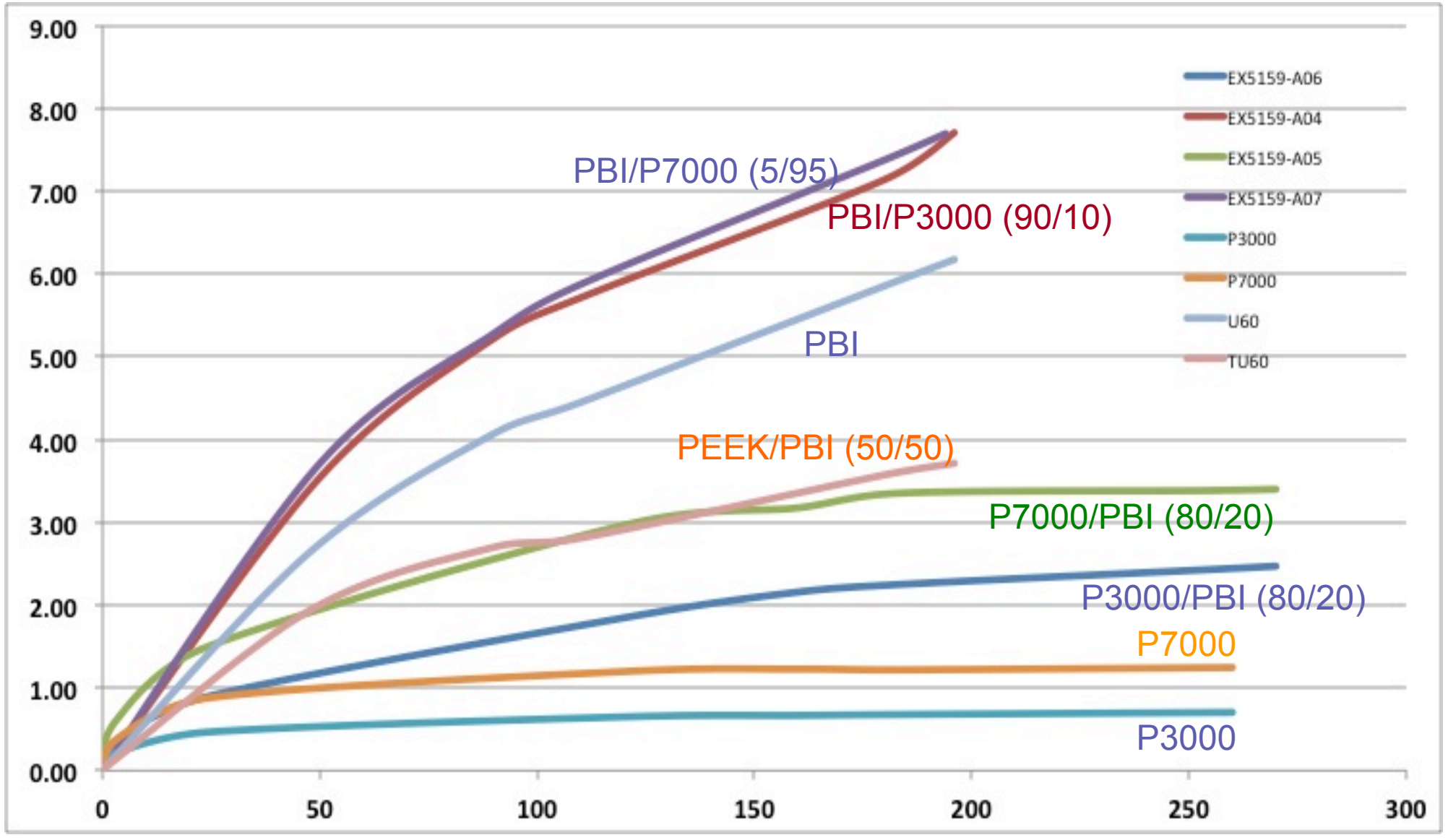
Acid Immersion @ 40% Sulfuric Acid

Water Uptake (@60 °C) of Arylmax® P Alloy



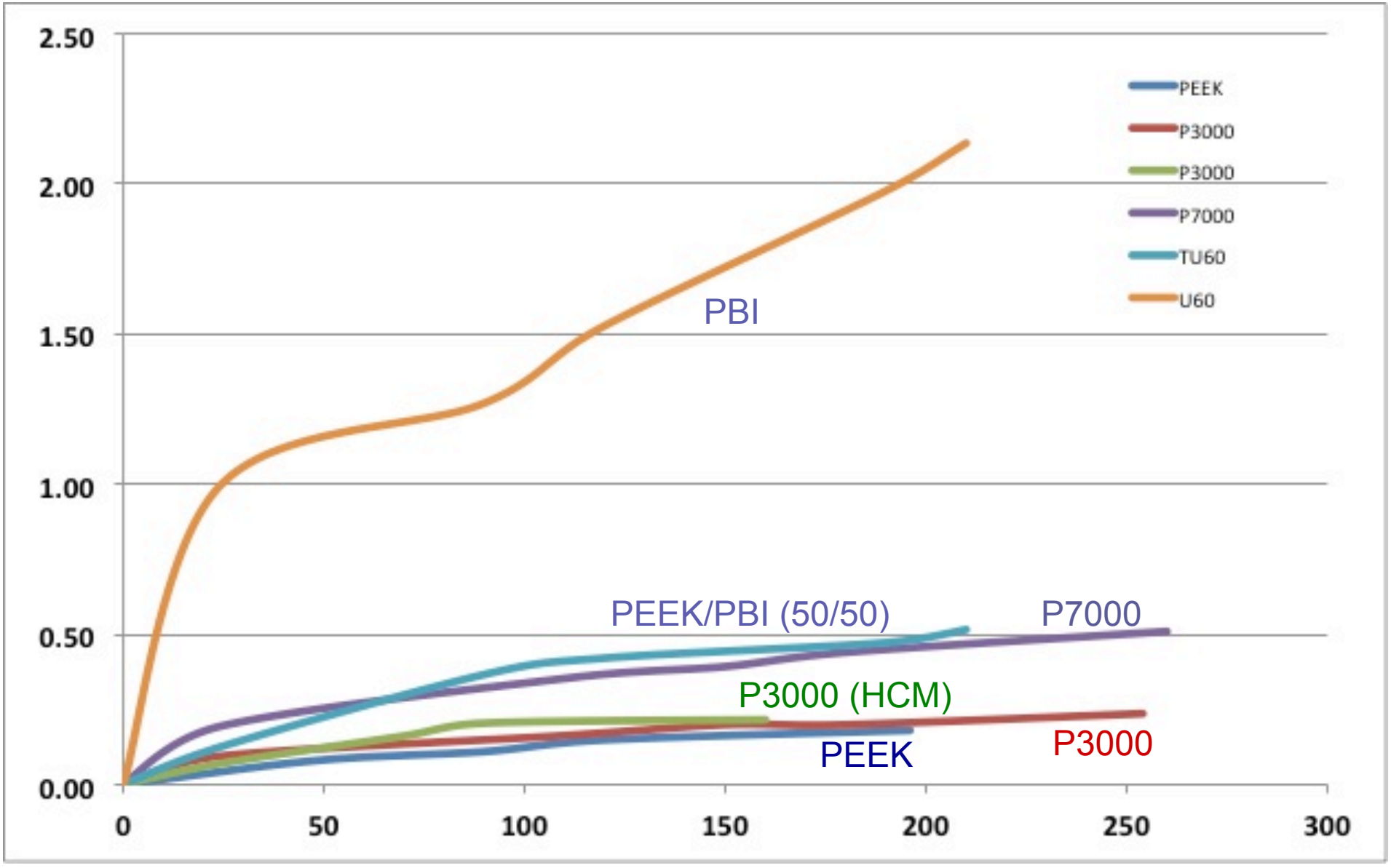
- Average of three Specimen immersed in Water @ 60 °C; Dimensions and Hardness was also checked.

Water Uptake (@60 °C) of Arylmax® P Alloy



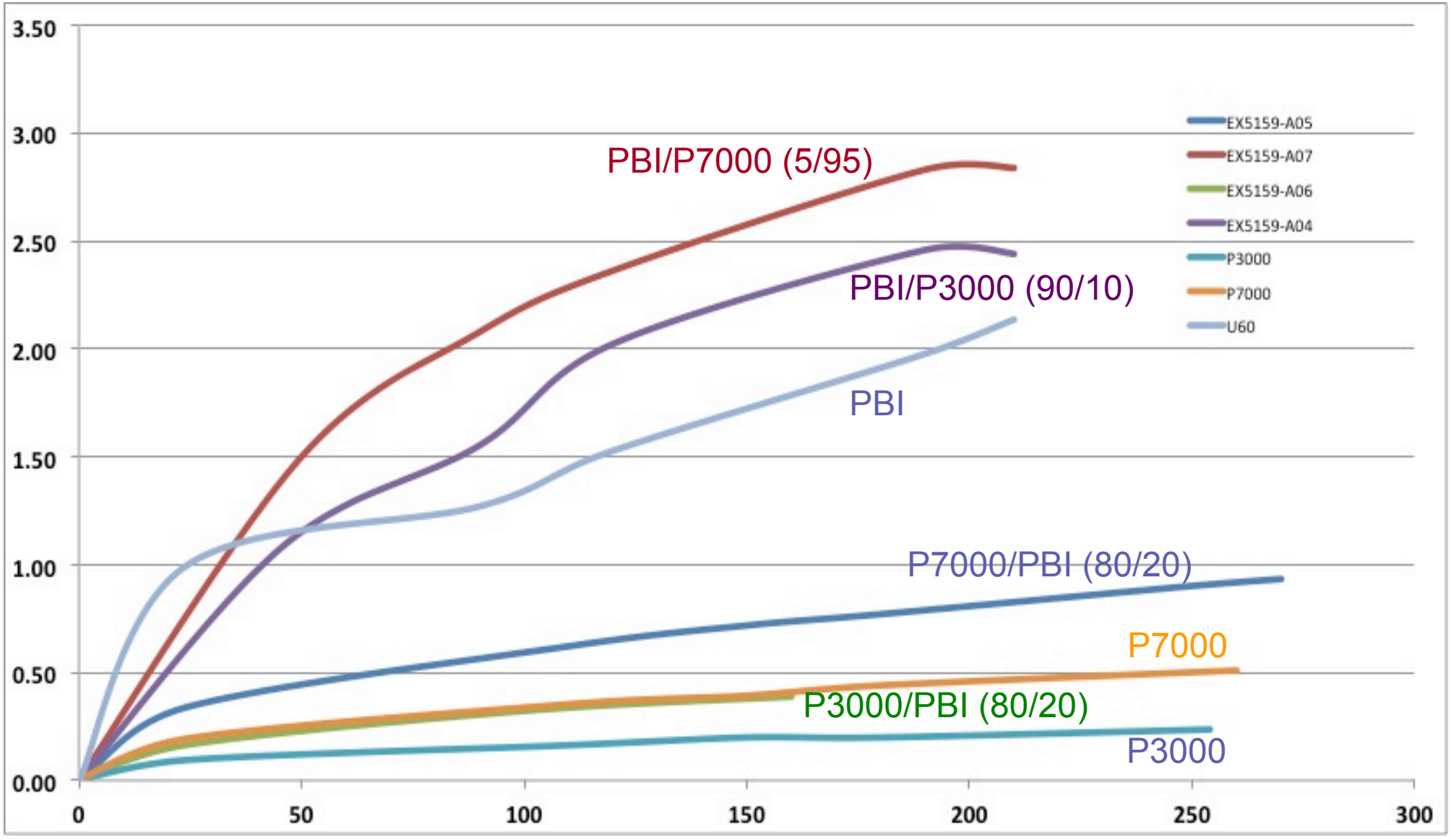
- Average of three Specimen immersed in Water @ 60 °C; Dimensions and Hardness was also checked.

Acid Immersion (40% H_2SO_4) of Arylmax® P Alloy



- Average of three Specimen immersed in 40% Sulfuric acid; Dimensions and Hardness was also checked.

Acid Immersion (40% H_2SO_4) of Arylmax® P Alloy



- Average of three Specimen immersed in 40% Sulfuric acid; Dimensions and Hardness was also checked.

Summary

- Arylmax® P polymers forms miscible blends (Alloy) with most high temperature polymer systems including PAES, TPI, and PAEK.
- It's possible to further enhance thermal and mechanical properties by high Tg polymers such as PBI.
- There is no evidence of degradation or hydrolytical degradation based on dimensional and hardness measurements by water and acid immersion tests. Actual mechanical properties tests will be further reported.
- Miscibility may play an important role in the proper design of high Tg polymer alloys with improved plateau moduli, and enhanced environmental resistance for high pressure, high temperature oil & gas applications.