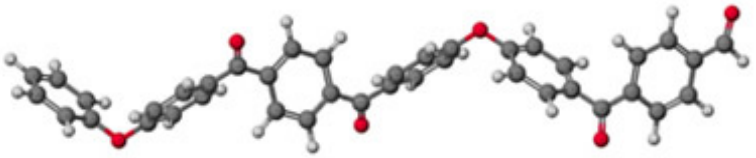


Polymics
Concept to Solution

Effect of high-temperature steam on the mechanical properties of PAEK polymers & alloy

Energy Rubber Group, 2014 Fall Technical Meeting
San Antonio, TX
September 18, 2014

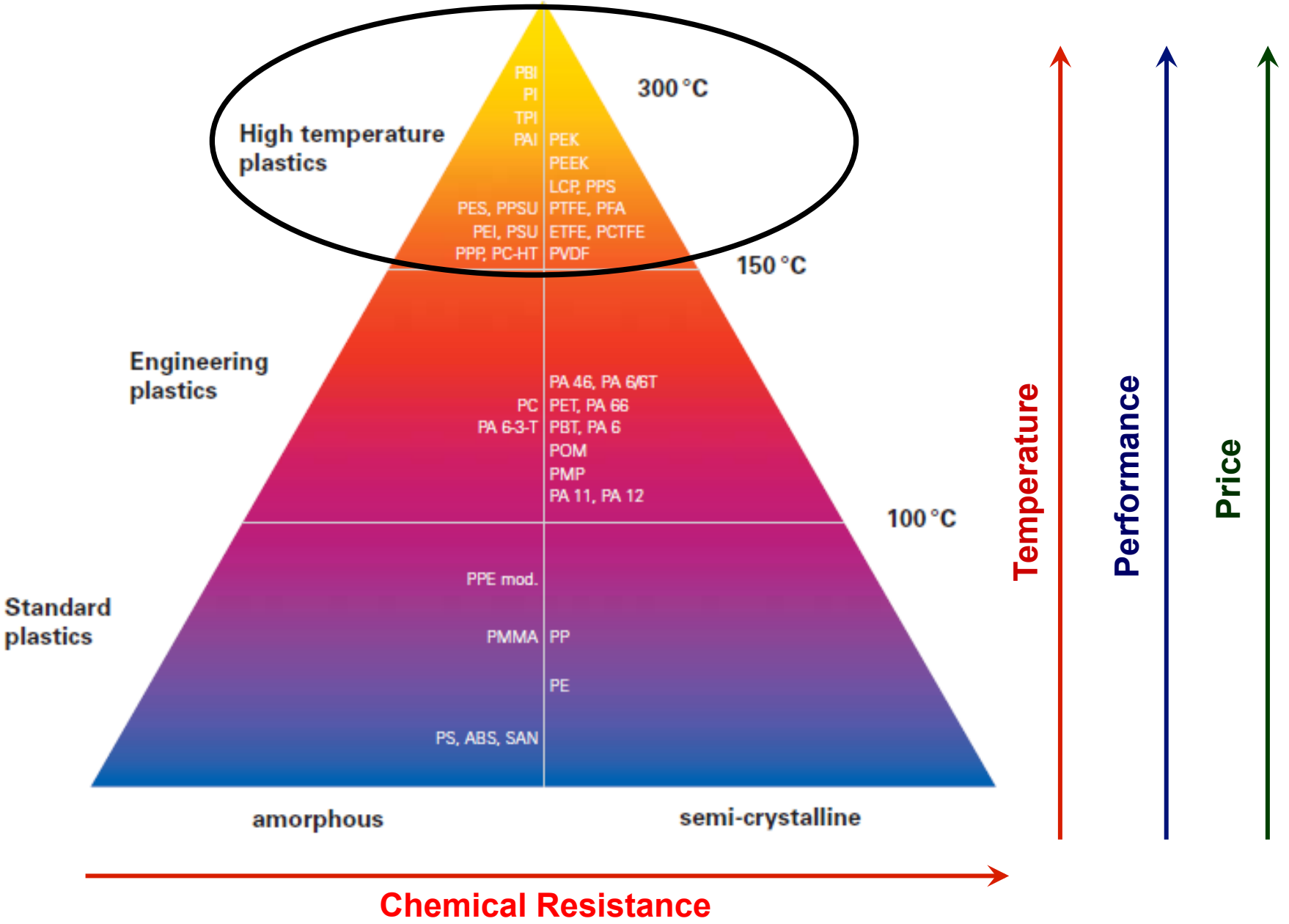
By Tim Hsu, Ph.D.

Outline

- **Introduction & Background**
  - Statement of the problem for corrosive HPHT fluid handling components.
  - Material options for PEEK & Beyond® : PAEK, Copolymers, Blends & Alloys
  - Effect of processing on properties. INJ, HCM, CAM, EXT.
- **Hot water screening of potential polymer candidates**
- **Steam as corrosive medium for polymers**
  - **Experimental**
  - **500 °F/72 hrs: appearance, water uptake, property retention**
  - **600 °F/24 hrs: appearance, water uptake, property retention**
- **Summary & conclusion**
- **Discussion**

Introduction & Background

Polymer Pyramid



Supply Chain of Polymeric Products

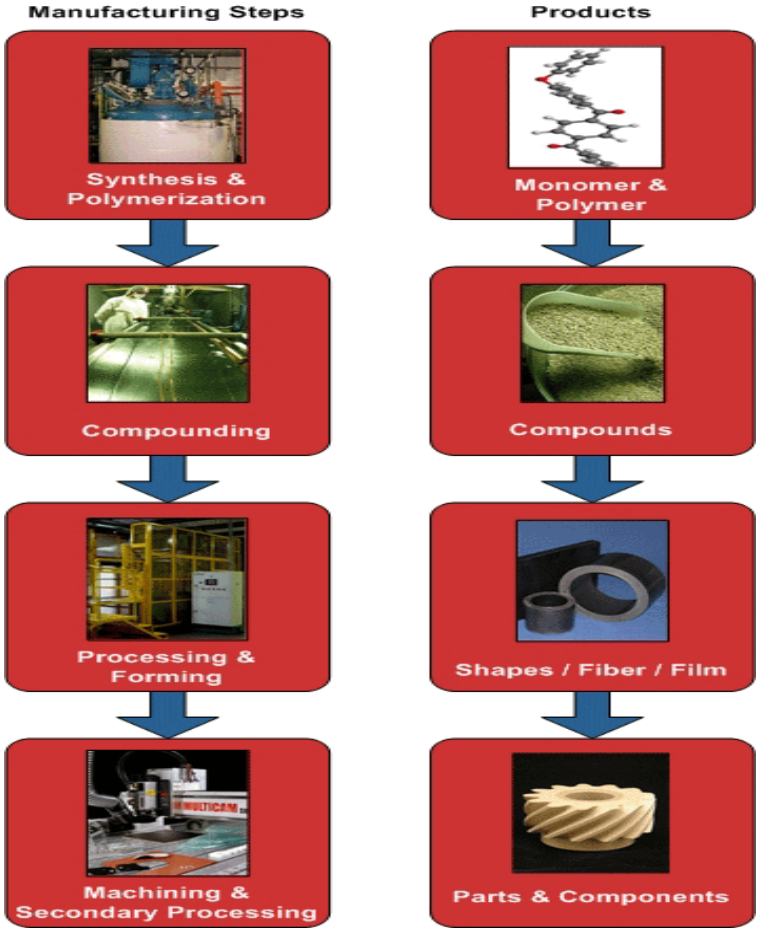
Engineering and Application Development

Polymerization → Compounding → Material Conversion → Application Development - Engineering → Manufacturing & Assembly → End User Products / Market Requirements

Polymer:
- PEEK
- PAEK's
- PAES's
- TPI
- PBI

Compounds:
- Carbon fiber
- Glass fiber
- Mineral fillers

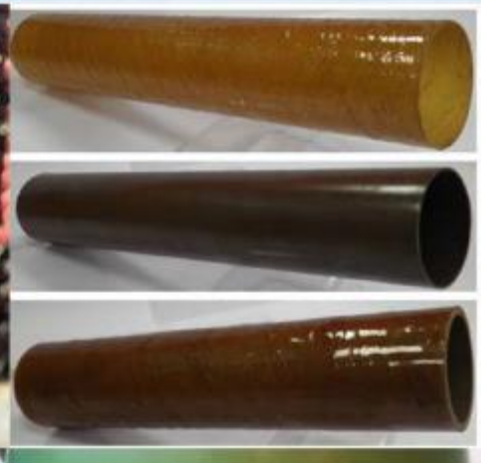
Stock Shapes:
- Tubes
- Bushings
- Sheet
- Rod
- Films



Polymer in Oil & Gas Application

Fluid Handling and Other Critical Components

Drilling	Logging	Completion	Production	Workover
Drill Pipes	Logging Tool	Cementing Tools	Sucker Rods	Bridge Plugs
Spoolable Tube	Construction	Frac Plugs	Oil Tubing	Frac Plugs
		Frac Balls	Seal Components	Injection Tubes



Polymics
Concept to Solution

High-temperature steam treatment

- HT steam is a screening medium for evaluating material performance in corrosive, HPHT environments

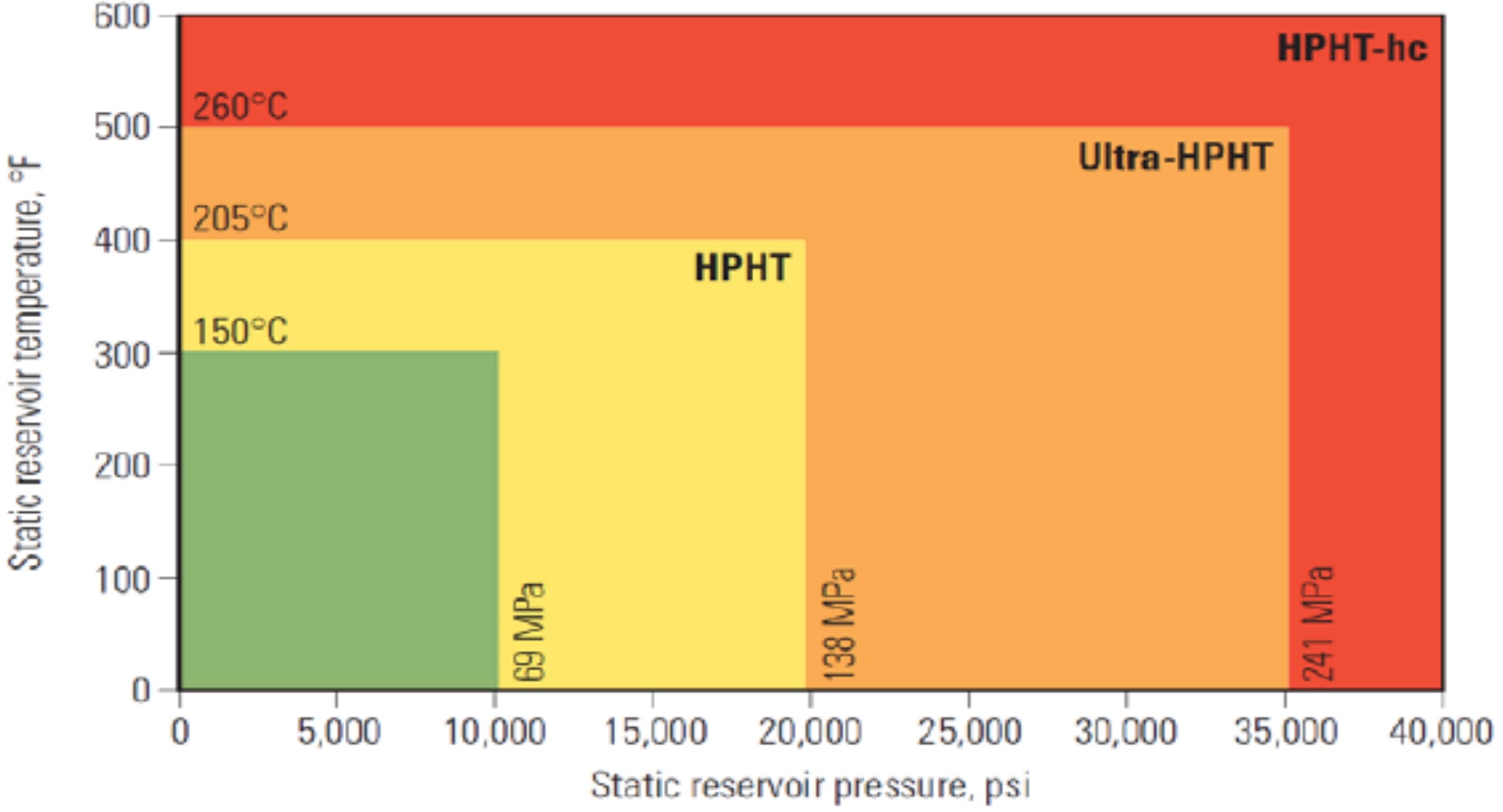
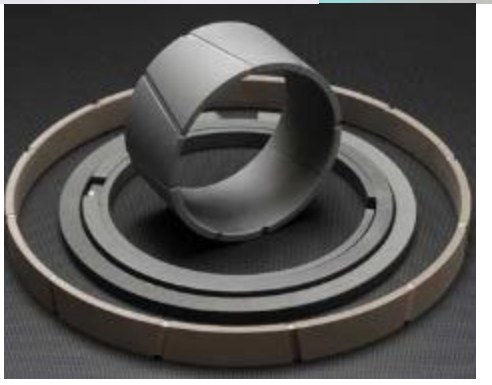
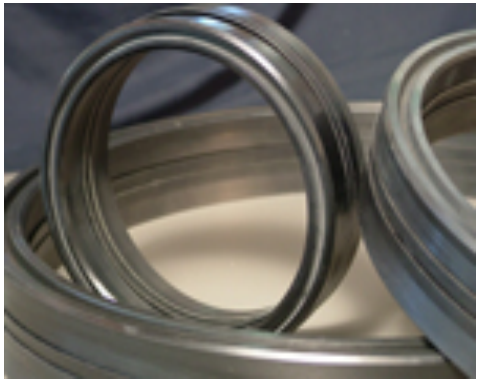


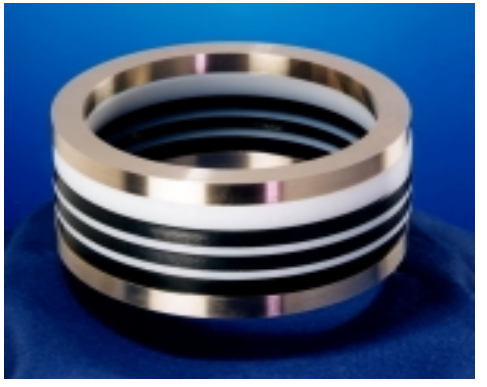
Image reproduced from: High Pressure, High Temperature Technologies, “Oilfield Review” (Schlumberger), p. 46

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.

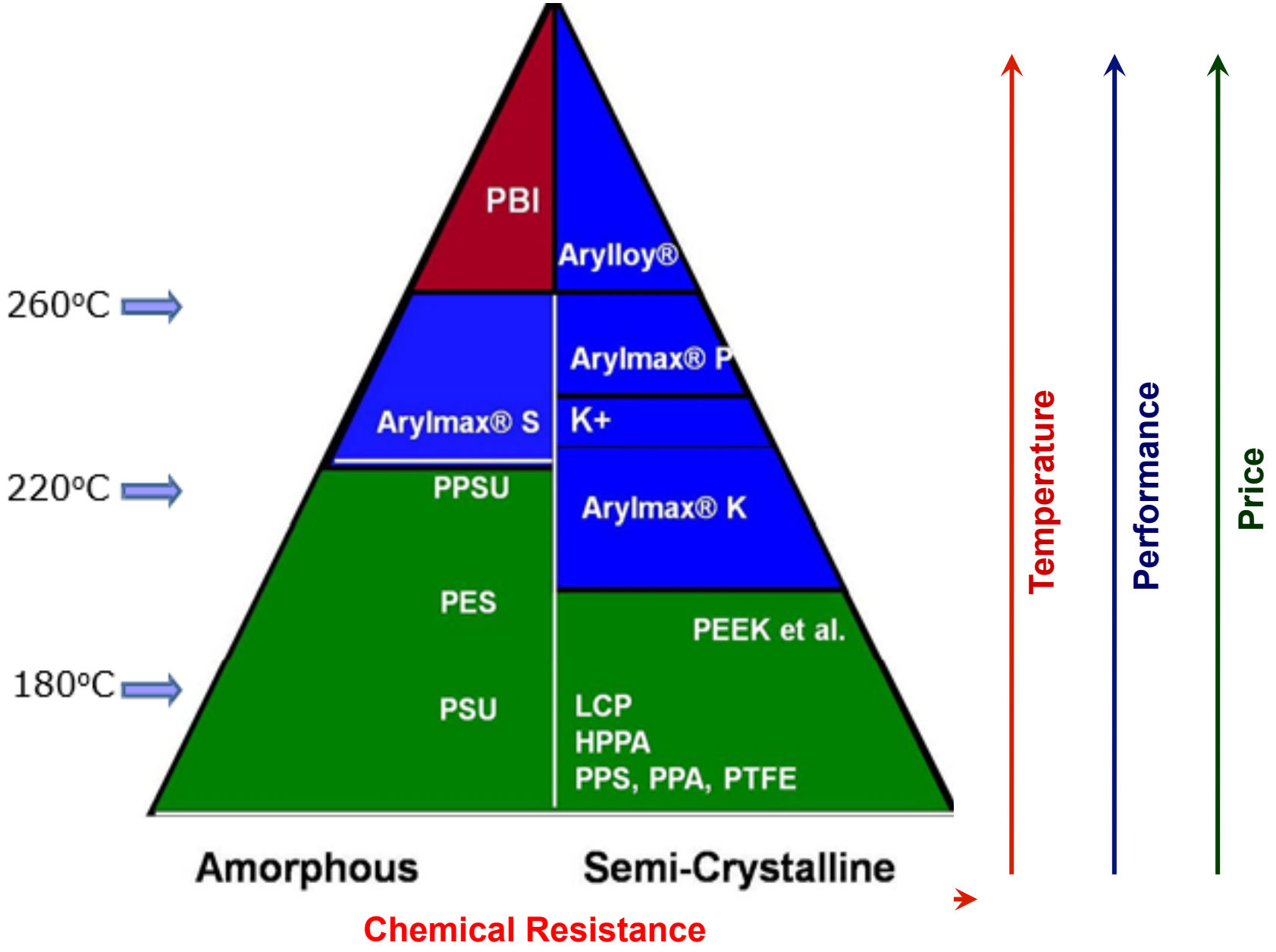
Potential Solution(s):

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

Polymers for Corrosive HPHT Application

PAEK, its Blends & Alloys

High Heat Polymers



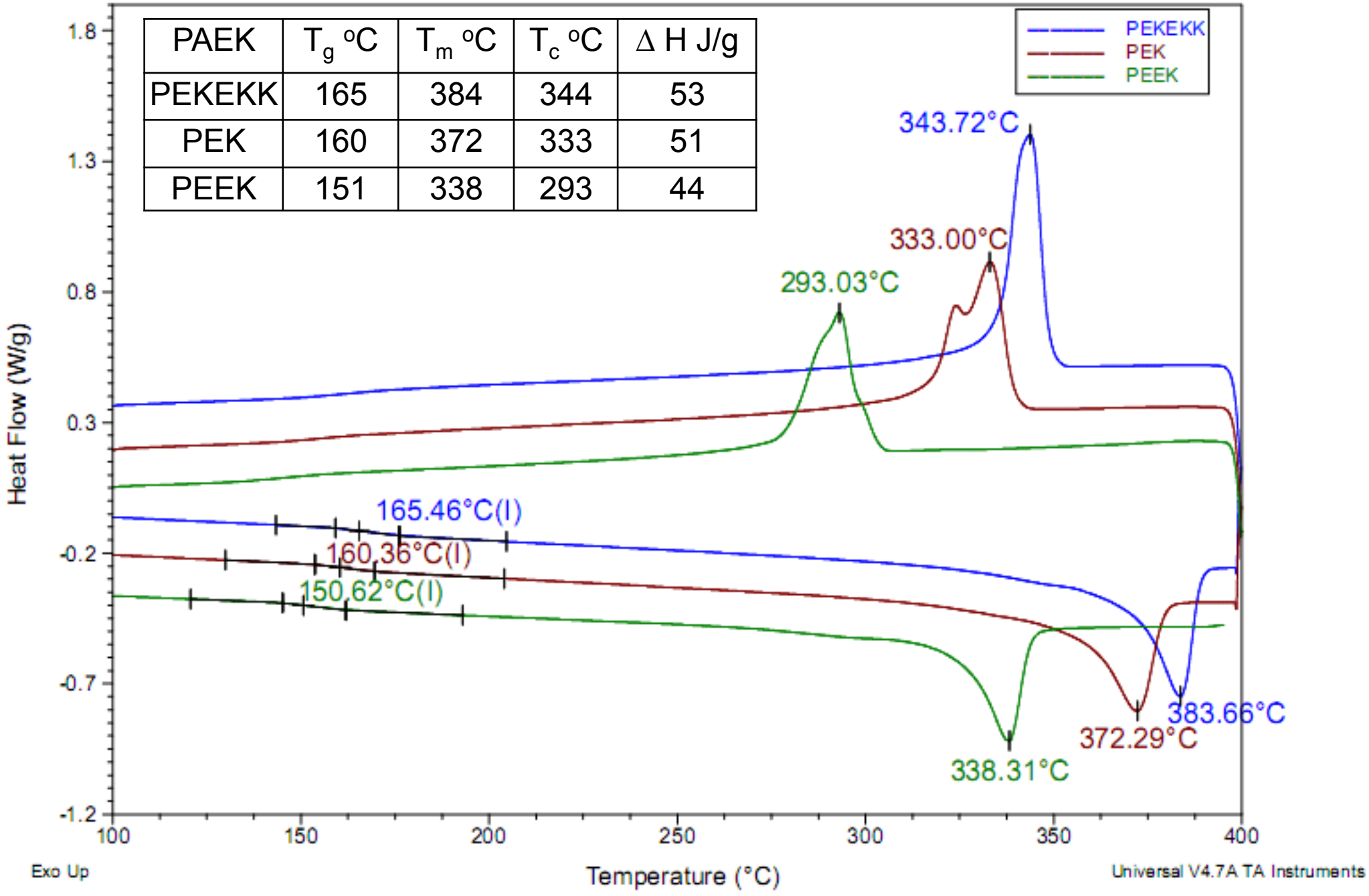
Commercial PAEK's

Generic Name	Trade Name
PEEK	Victrex®; Vestakeep® (Evonik); Ketaspire® (Solvay); Generic
PEK/PEEKK	PEEK-HT® (Victrex); Generic
PEKEKK	PEEK-ST® (Victrex); Ultrapek® (BASF)
PEKK **Other PAEK's**	Cypek® (Cytec), Oxpekk® (Arkema); Arylmax® K & P (Polymics)

® : tradename of respective company inside parenthesis

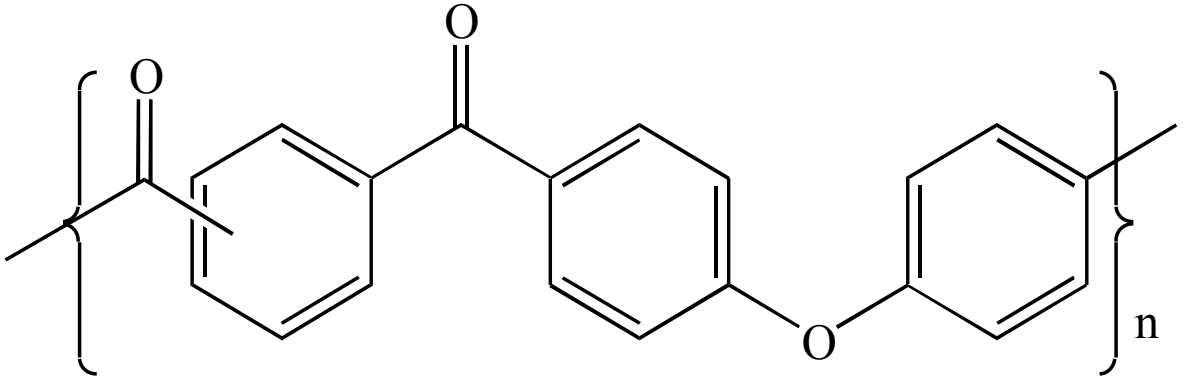
Thermal Transitions of Commercial PAEK's

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



Arylmax® K Resin

Poly(ether ketone ketone)

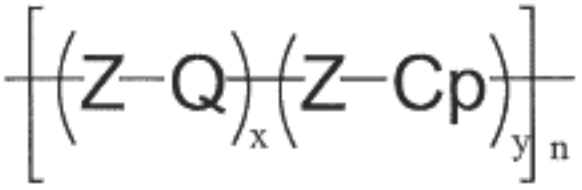


Tm = 310 – 380°C

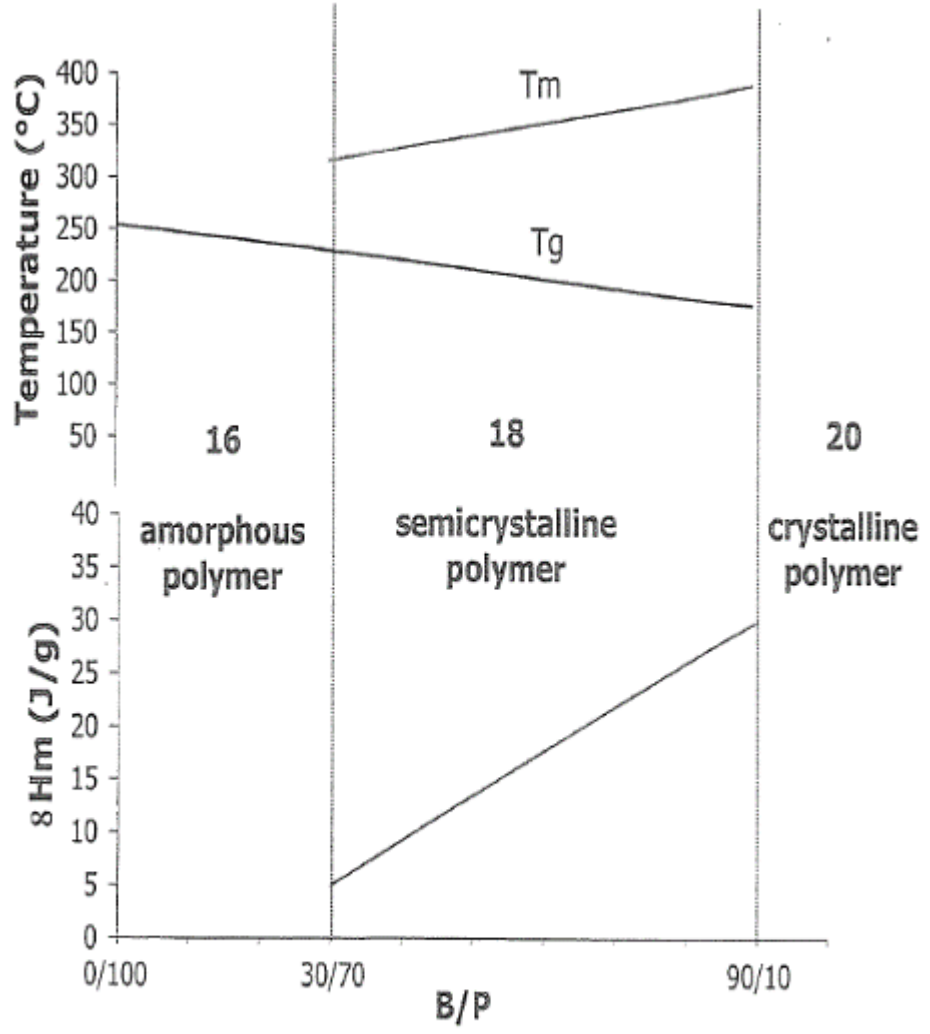
Arylmax® P Resin

- **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



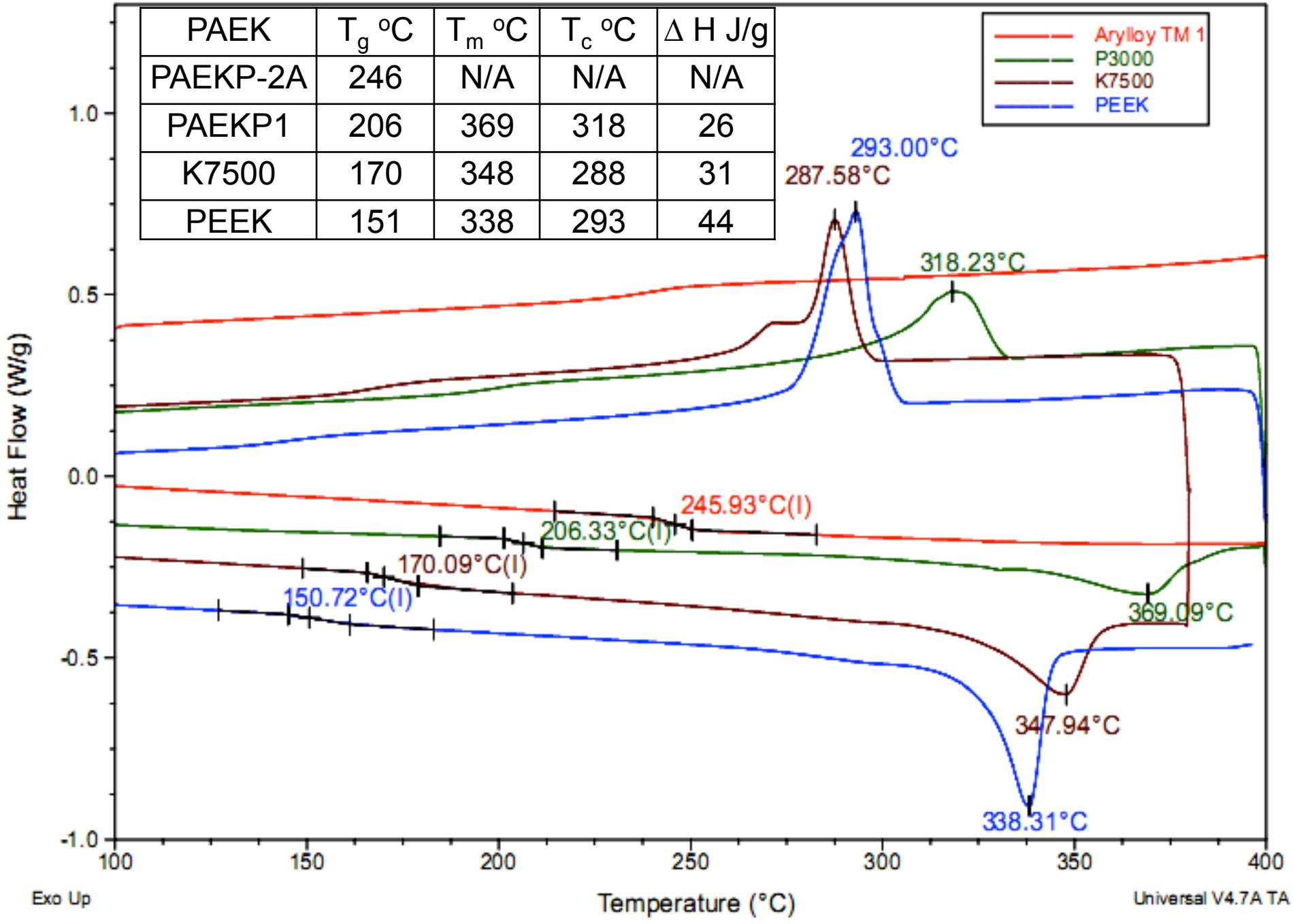
- Z = bisphenyl(di)ketone radical
- Q = bisphenol radical
- Cp = proprietary aromatic radical



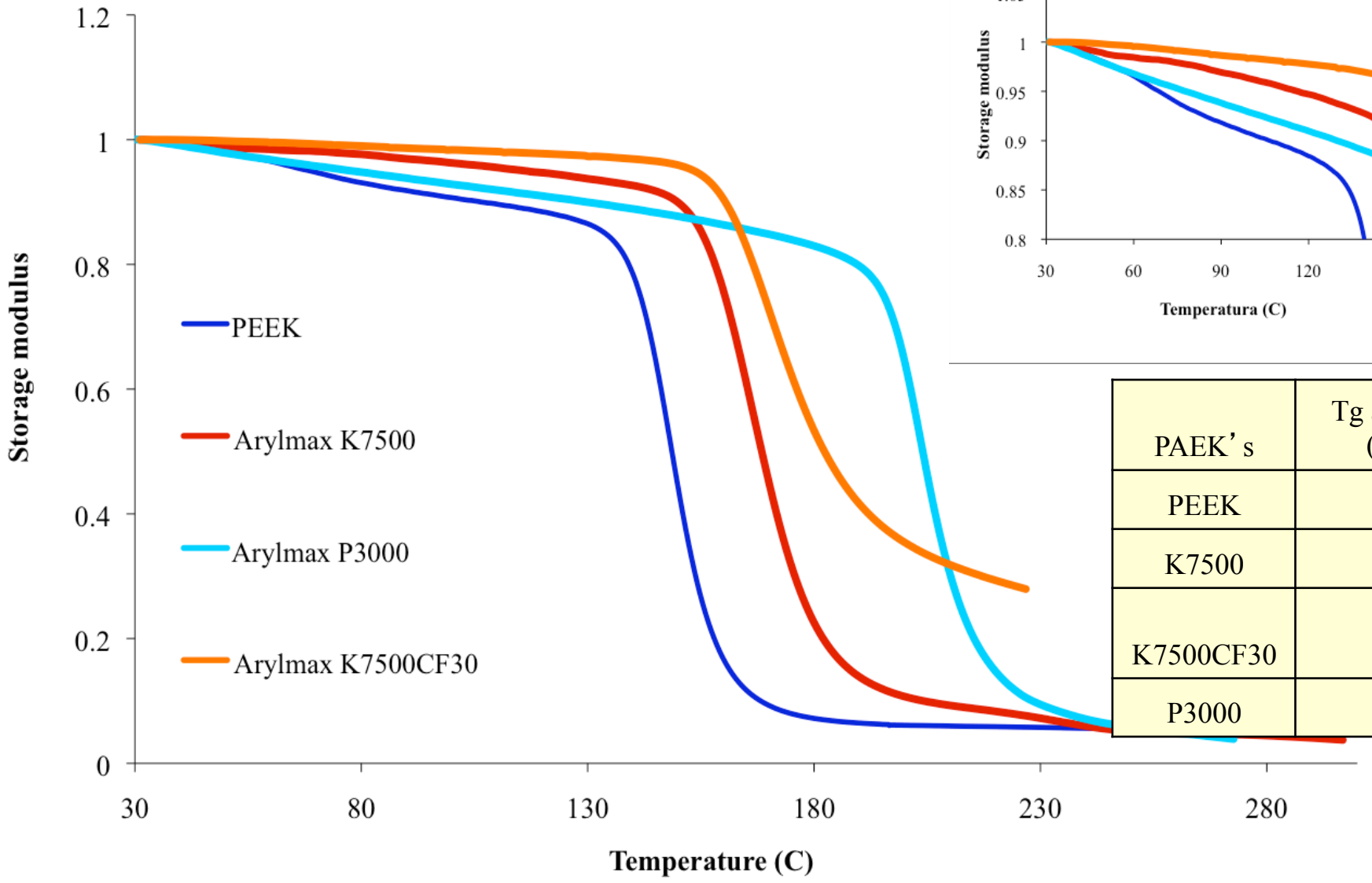
16: AMORPHOUS POLYMER
18: SEMICRYSTALLINE POLYMER
20: CRYSTALLINE POLYMER

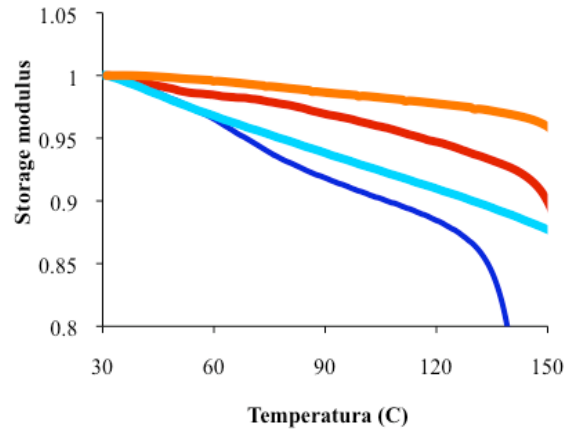
Comparison of PAEK's Thermal Transitions

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



DMA of High Tg Arylmax®K, P & Commercial PAEK's





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

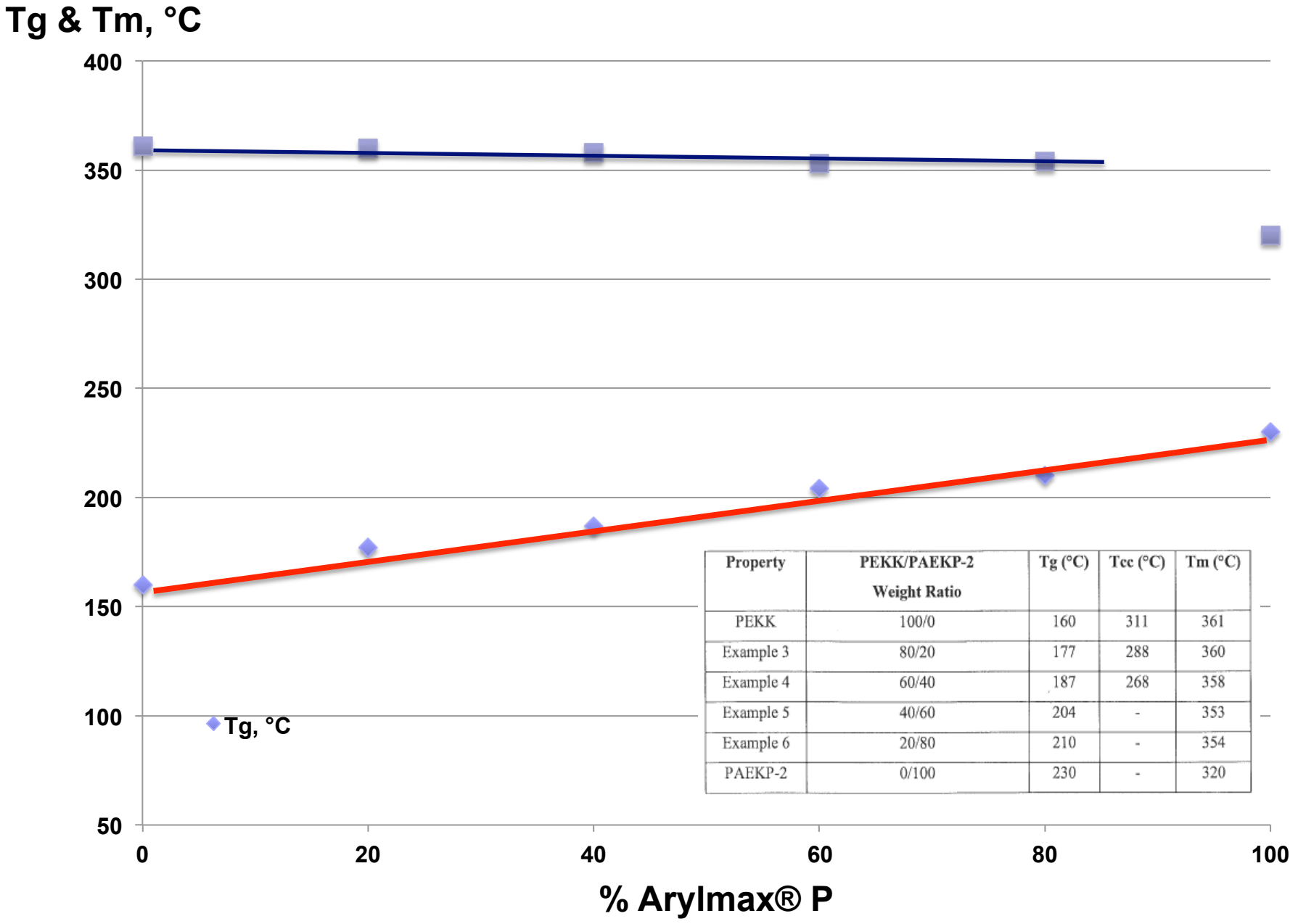
Measurements made on annealed samples using 3 point bend fixture
(except Arylmax K7500CF30 measured (annealed) using single cantilever fixture)

PBI and High Heat PAEK Enhanced Blends & Alloys

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

Arylmax® P & PEKK Blends

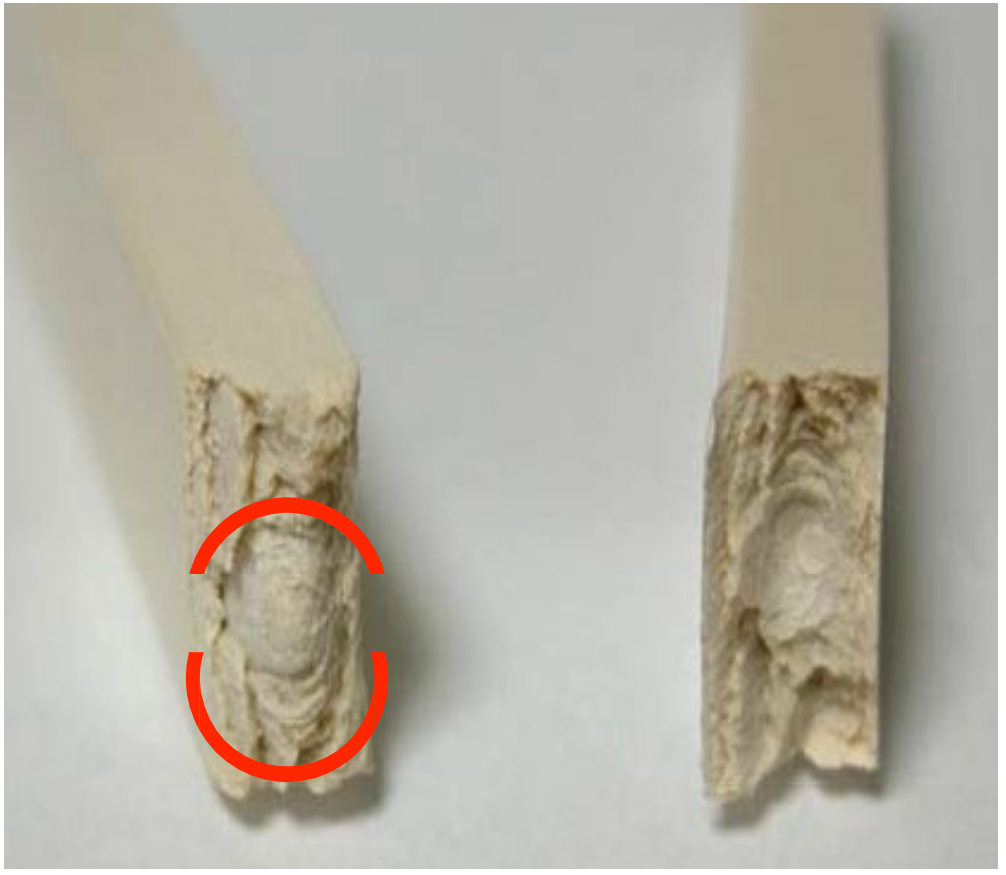


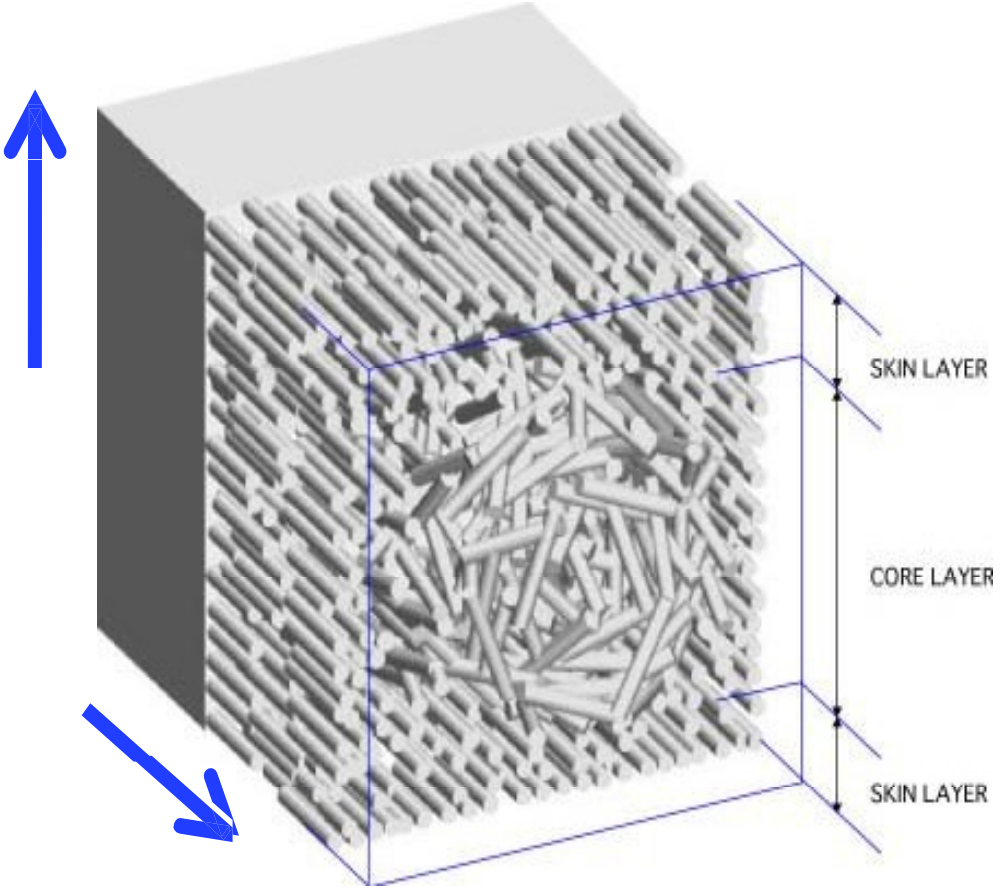
Property	PEKK/PAEKP-2 Weight Ratio	Tg (°C)	Tcc (°C)	Tm (°C)
PEKK	100/0	160	311	361
Example 3	80/20	177	288	360
Example 4	60/40	187	268	358
Example 5	40/60	204	-	353
Example 6	20/80	210	-	354
PAEKP-2	0/100	230	-	320

Processing & Properties

Effect of Processing on Morphology

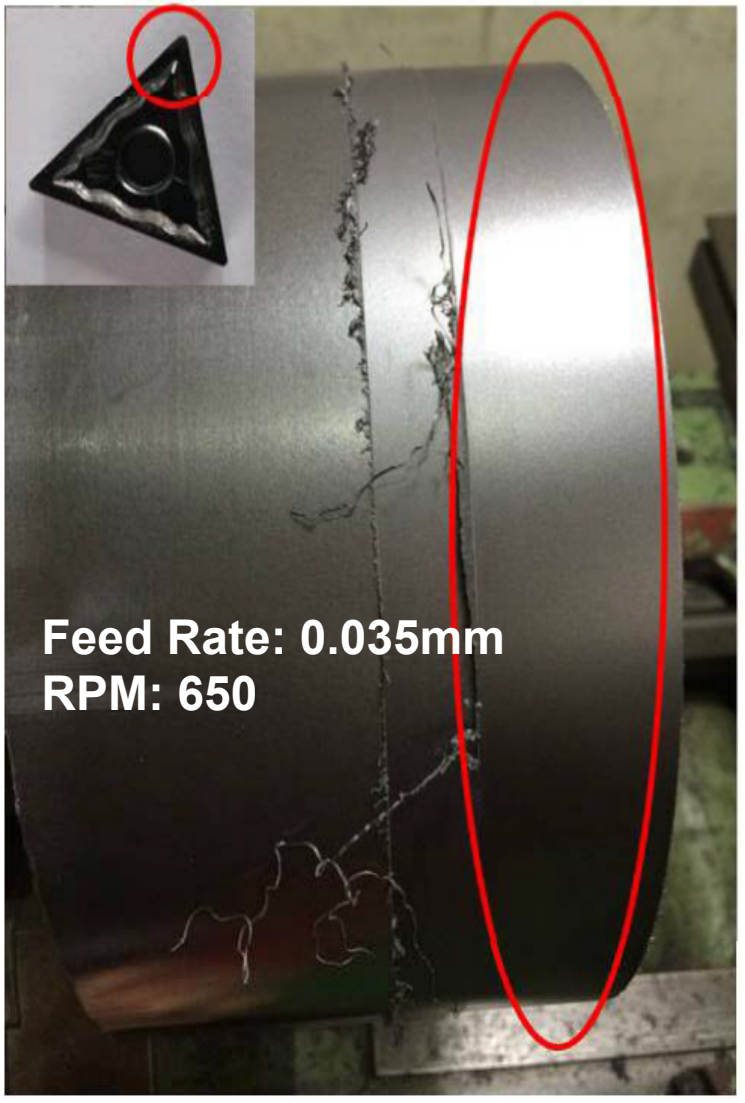
(Neat & Reinforced)



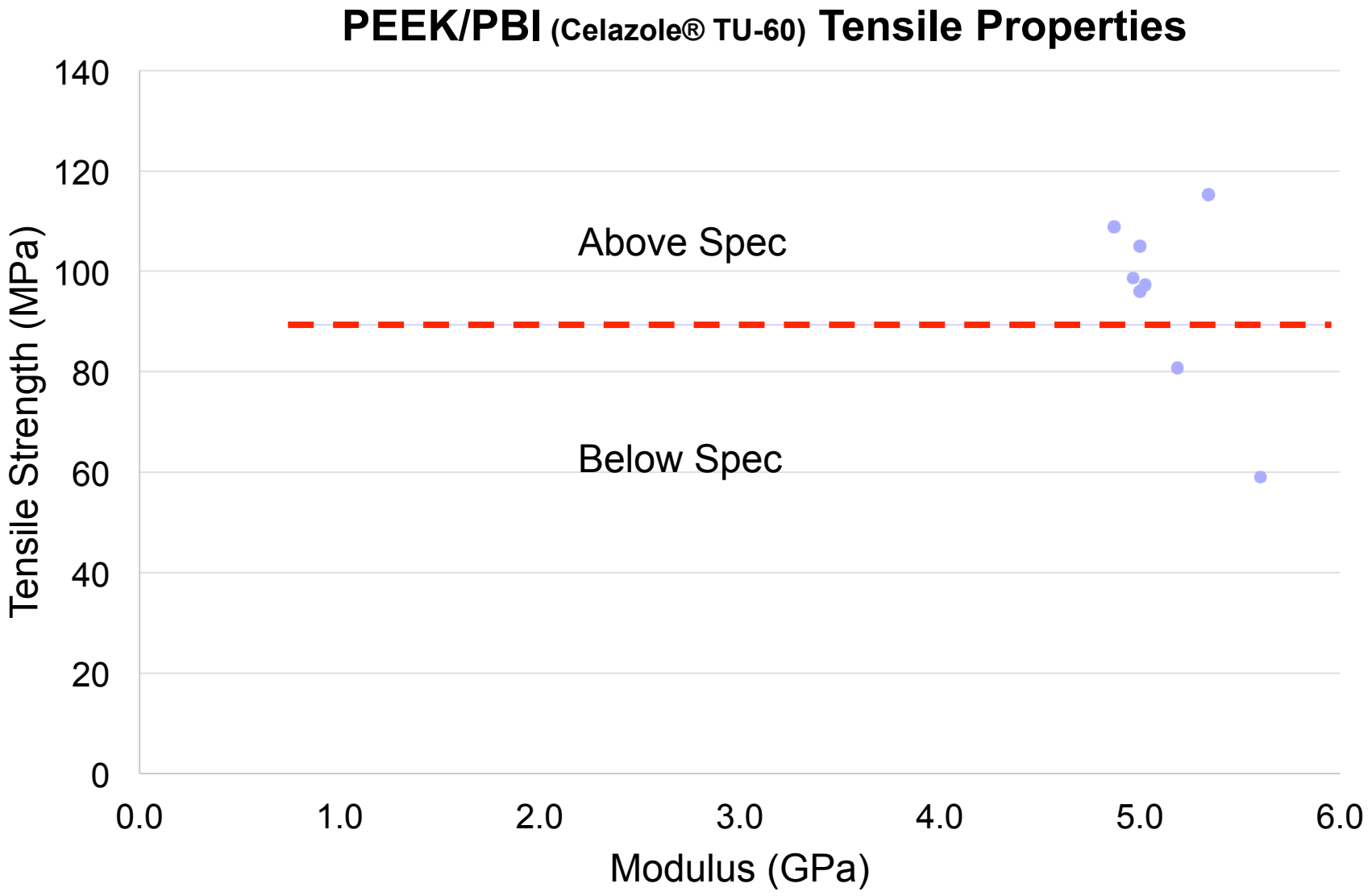


Polymics
Concept to Solution

Effect of Machining on Components



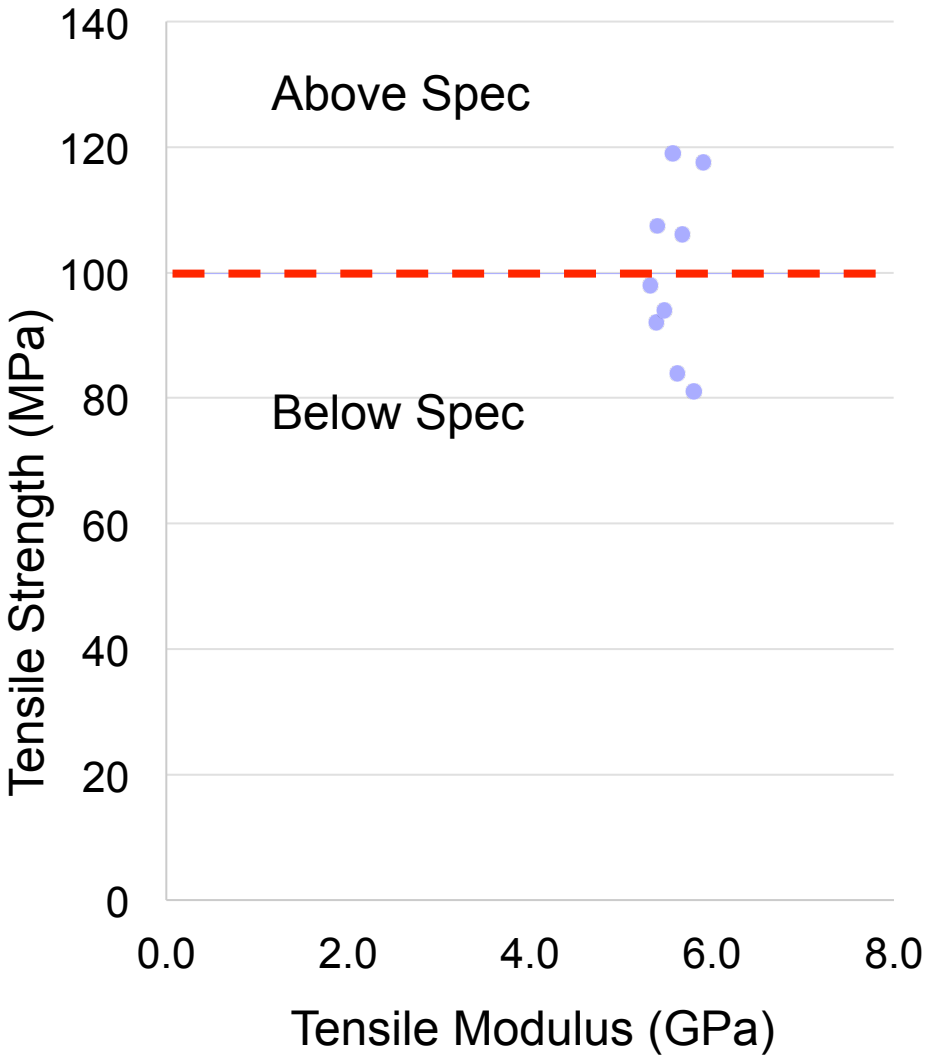
Effect of Compounding on Mechanical Properties

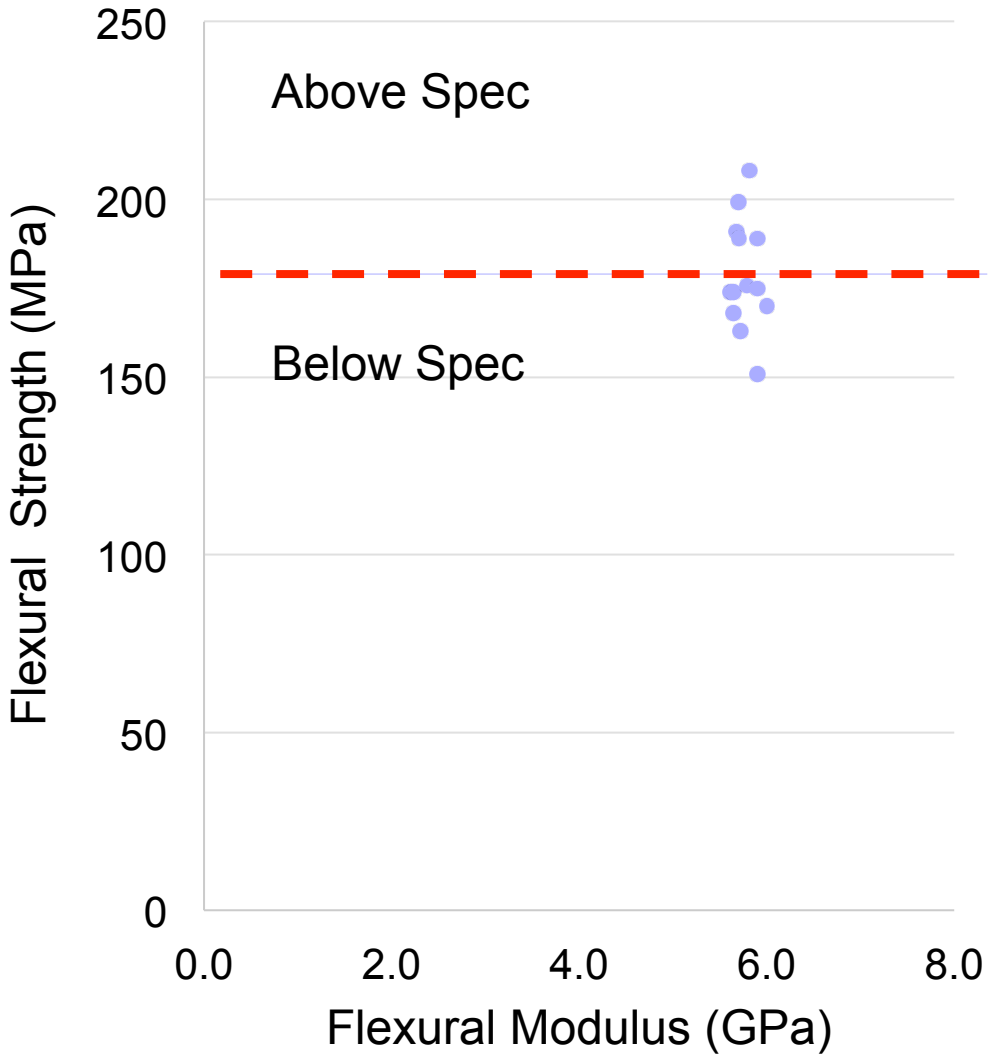


- **Compounding conditions has significant impact on tensile properties**

Effect of Compounding on Mechanical Properties

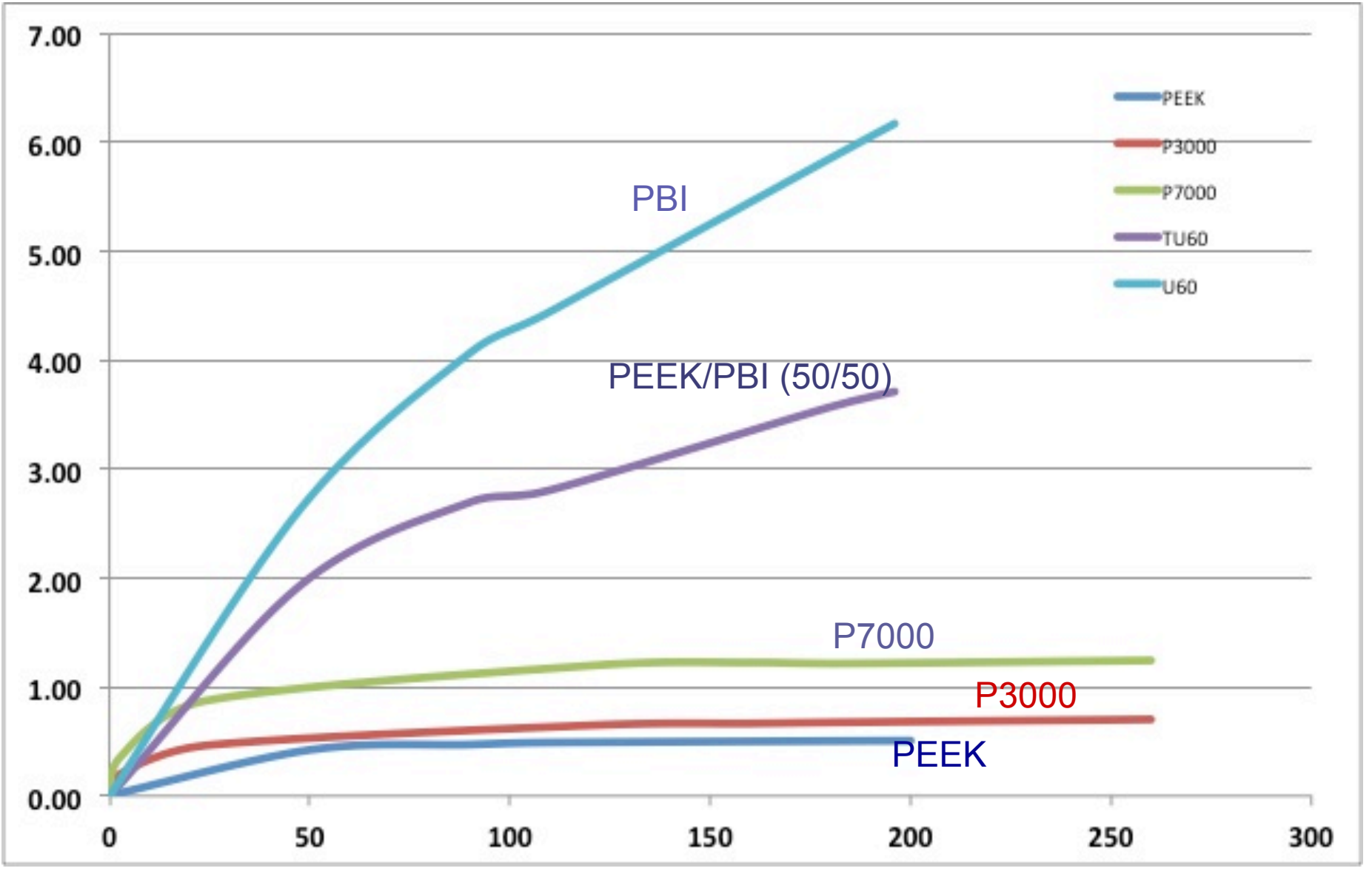
PEKK/PBI
(Arylmax K7522PB60)





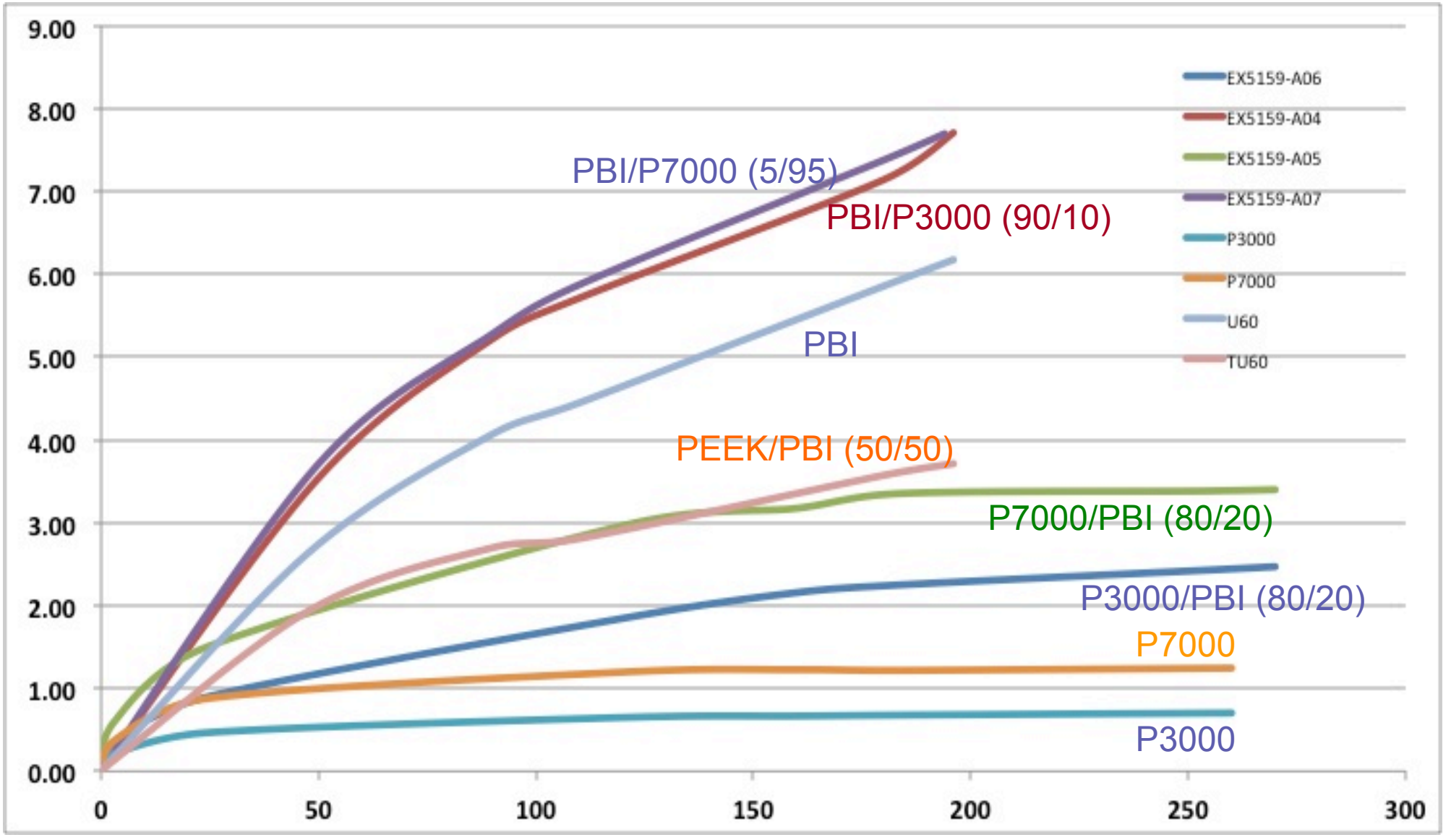
Steam & Hot Water Performance

Water Uptake (@60 °C) of PAEK



- 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.

Experimental Plan for Steam Treatment

Material matrix by PAEK family:

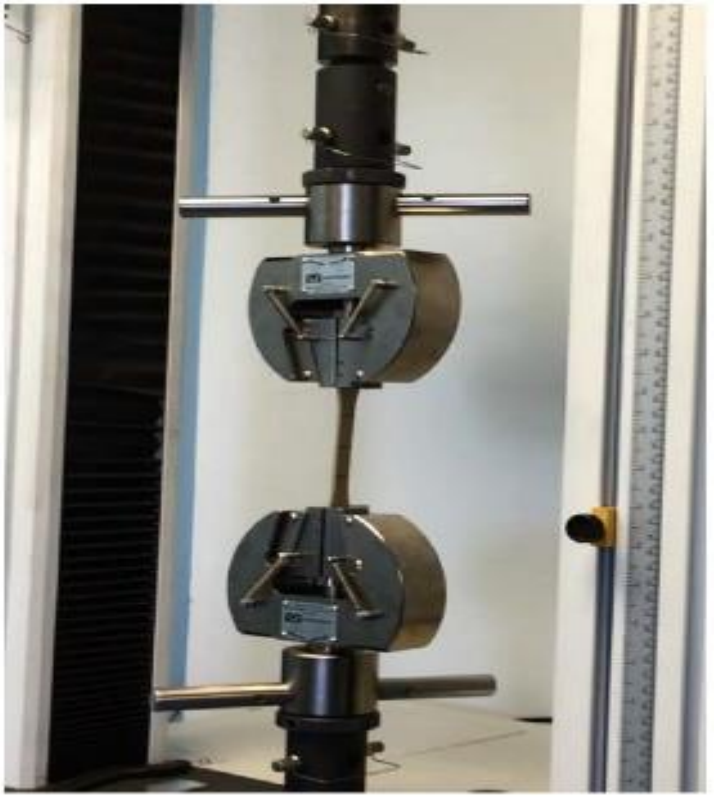
PEEK	PEKK (Arylmax® K)	PAEK blends & alloys (Arylloy ®)
PEEK (Victrex 450G) PEEK HMW (Vestakeep) PEK (Victrex PEEK HT) PEEK/PBI (Celazole TU-60)	PEKK (K7522) PEKK HMW (K7500) PEKK/PBI (Arylmax K7522PB10) PEKK/PBI (Arylmax K7522PB50) PEKK/PBI (Arylmax K7522PB60)	PEKK/PAEK (Arylmax K7520/P3000) PAEK/PBI (Arylmax P3000/PBI)

Condition I. Steam treatment at 500°F (260 °C) for 72 hrs

Condition II. Steam treatment at 600°F (315 °C) for 24 hrs

Experimental Set-up for Steam Treatment

- High pressure, high temperature autoclave with temperature control
- ASTM tensile bar specimens



Steam Treatment @ 500°F/72 hrs

PEEK
(Victrex PEEK 450G)

PEEK HMW
(Vestakeep)

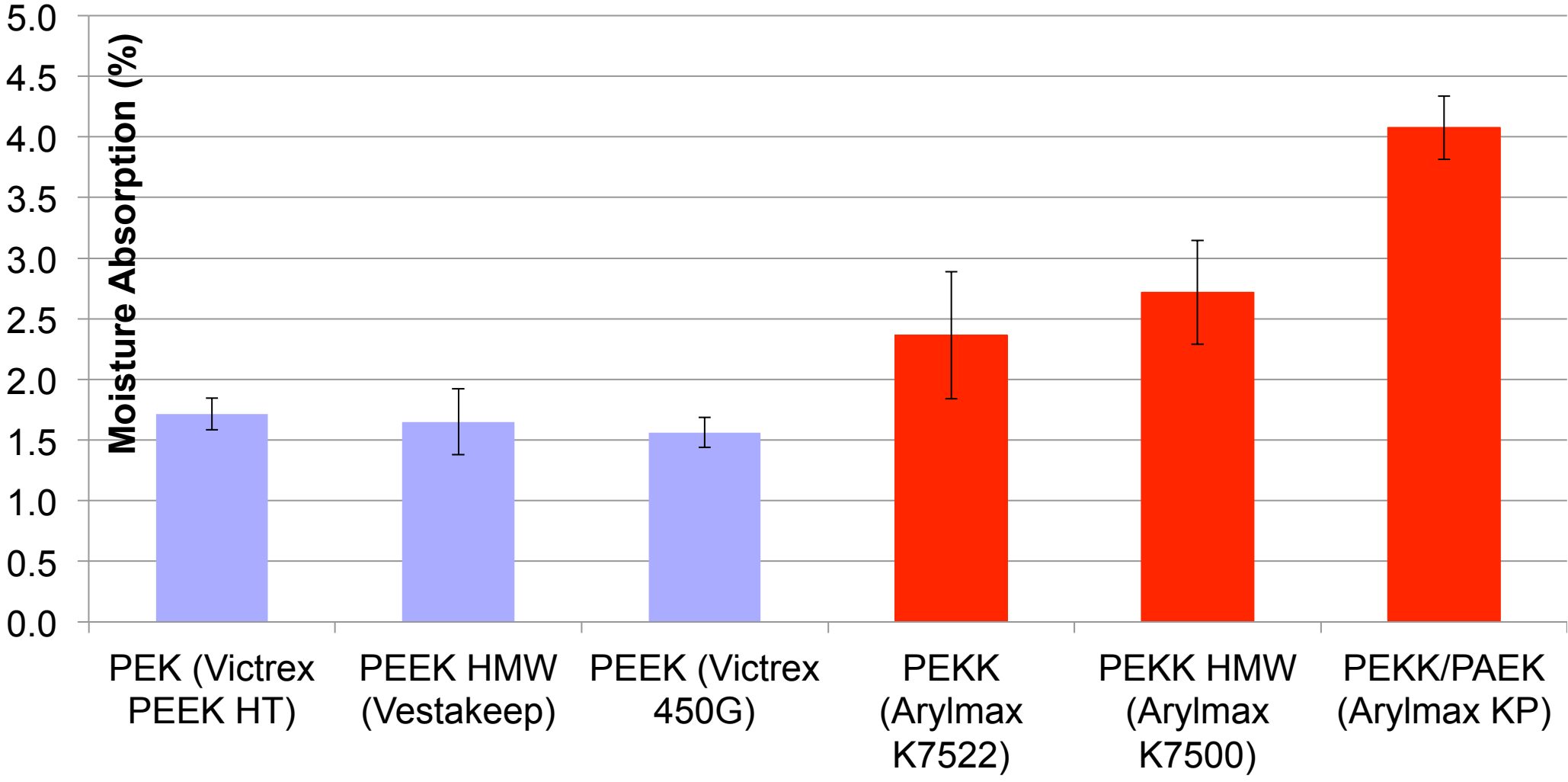
PEK
(Victrex PEEK HT)

PEKK HMW
(Arylmax K7500)

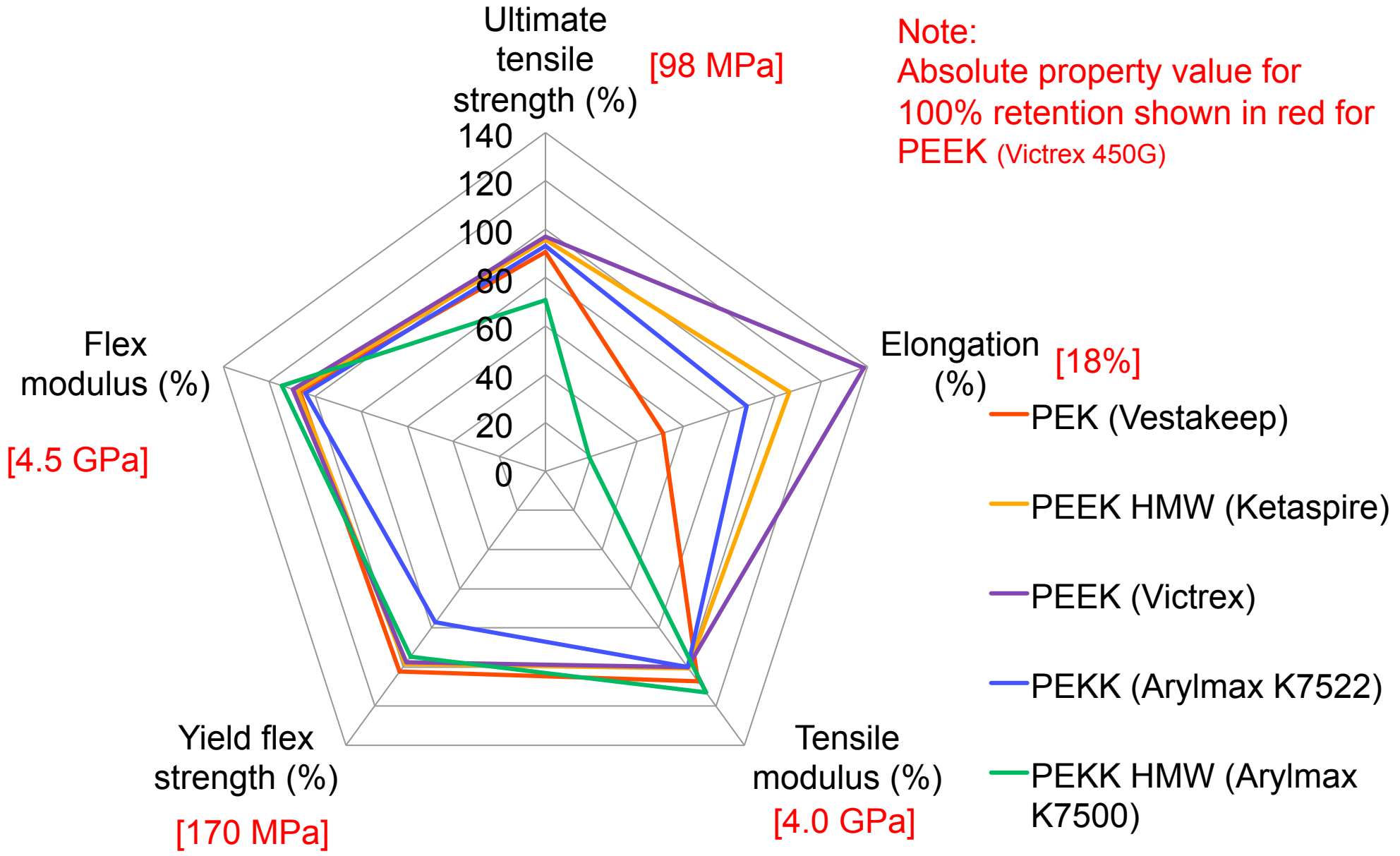
PEKK
(Arylmax 7522)

PEKK/PAEK
(Arylmax KP)

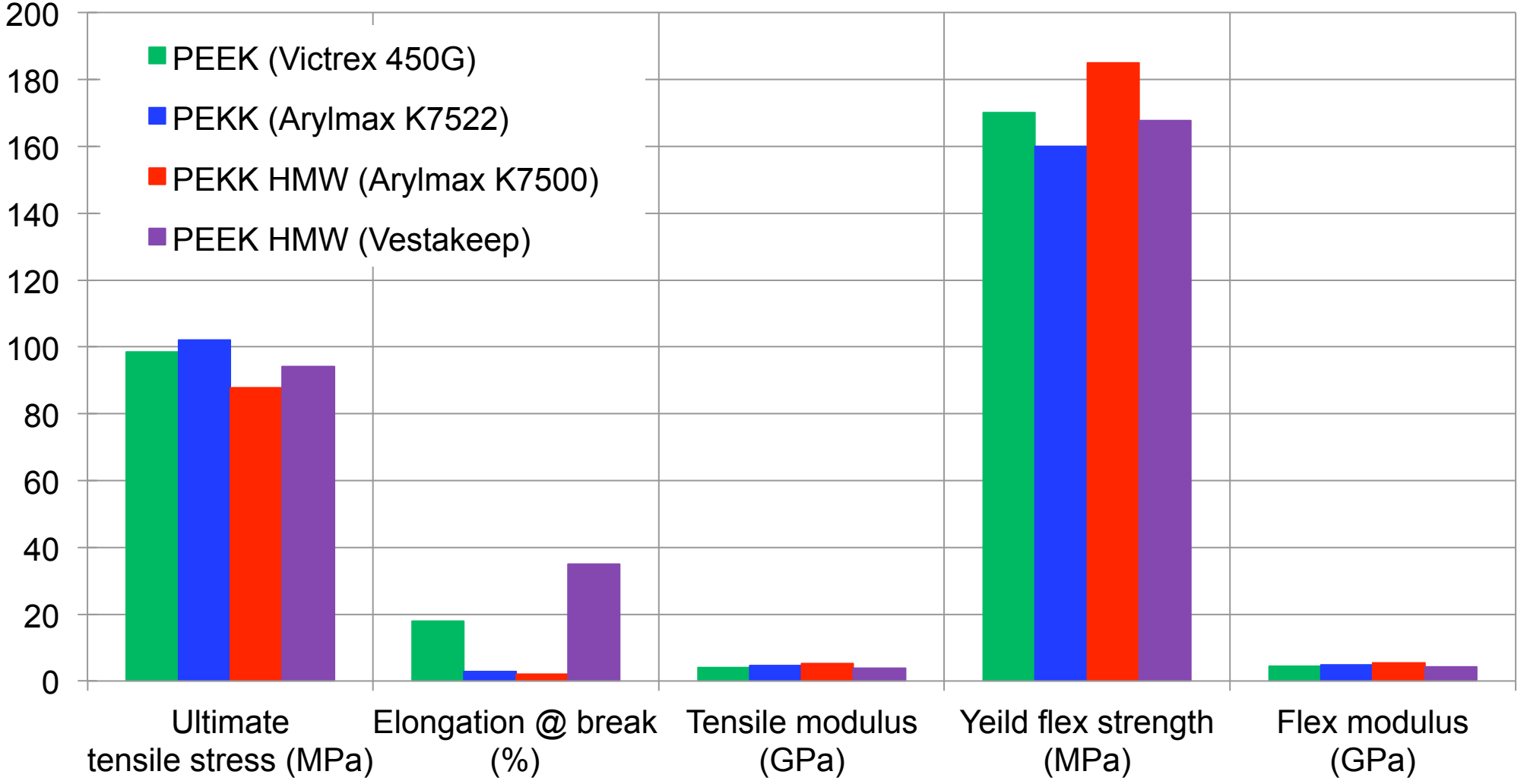
Water Absorption
(Stream Treated PAEK @ 500°F/72 hrs)



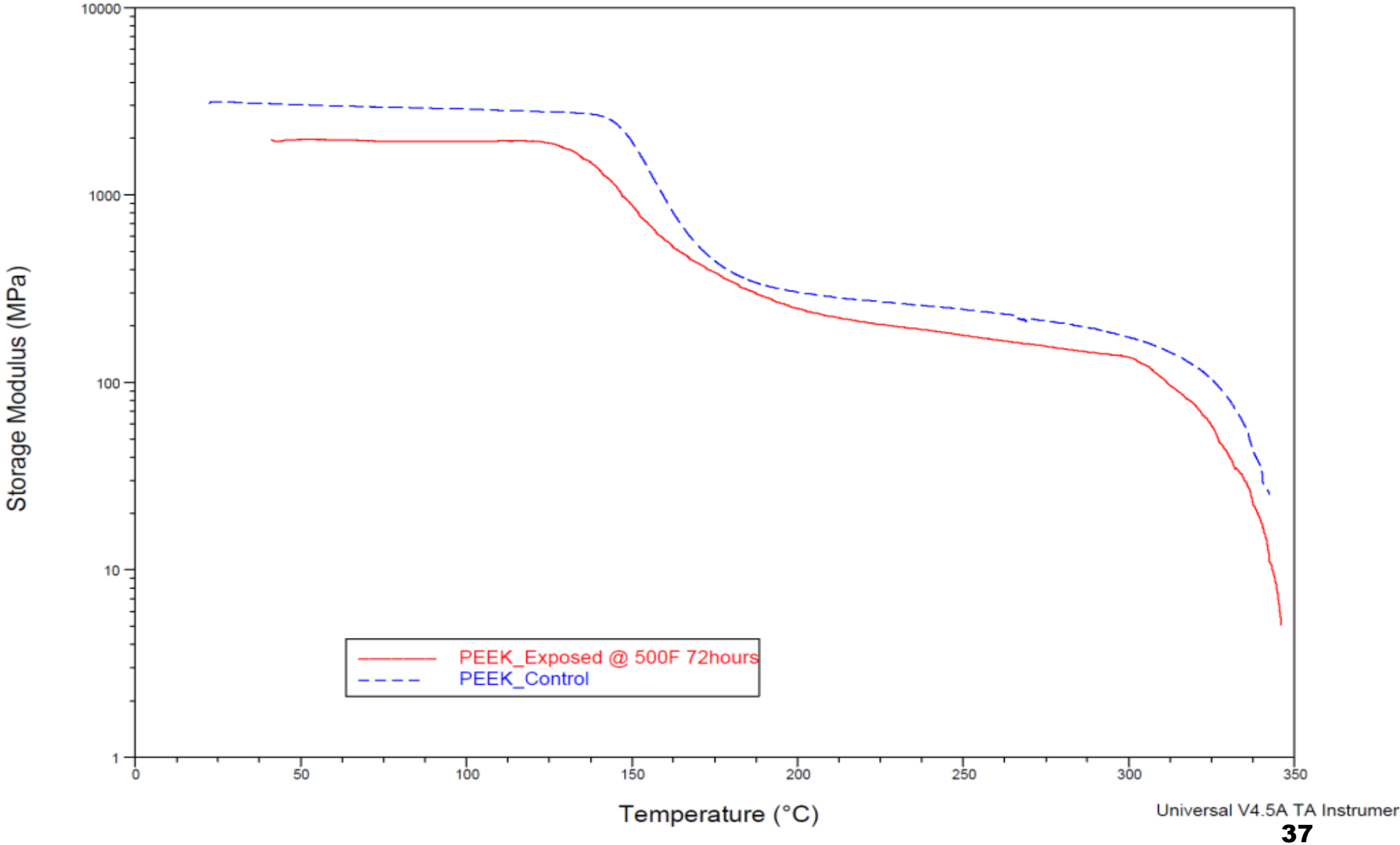
Mechanical Property Retention
(Steam Treated PAEK @ 500 °F/72 hrs)



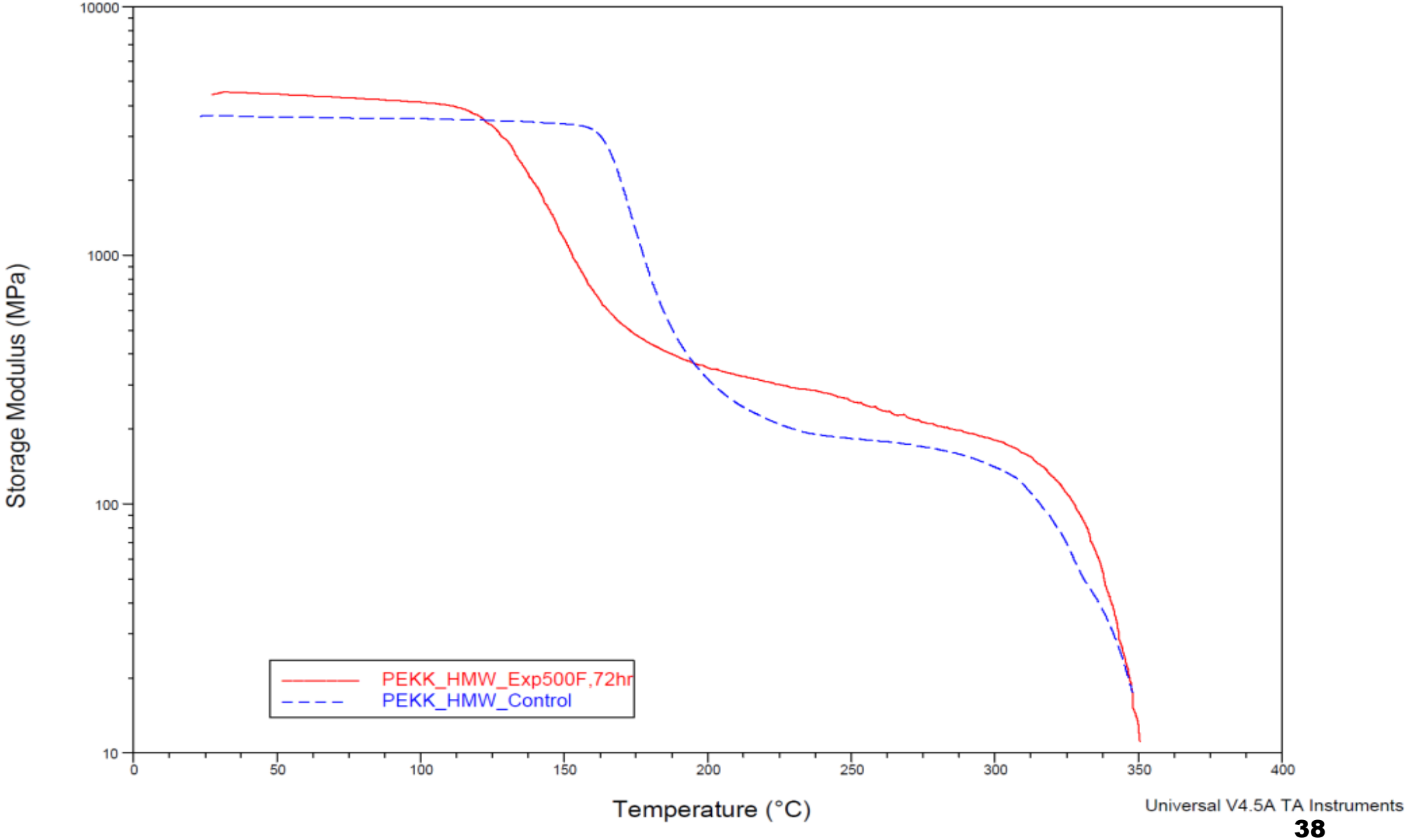
Mechanical properties
(Steam Treated PAEK @ 500 °F/72 hrs)



PEEK
(Victrex® 450G)



PEKK HMW
(Arylmax® K7500)



PEKK/PBI
(Arylmax K7522PB)

PEKK/PBI (K7522PB10)

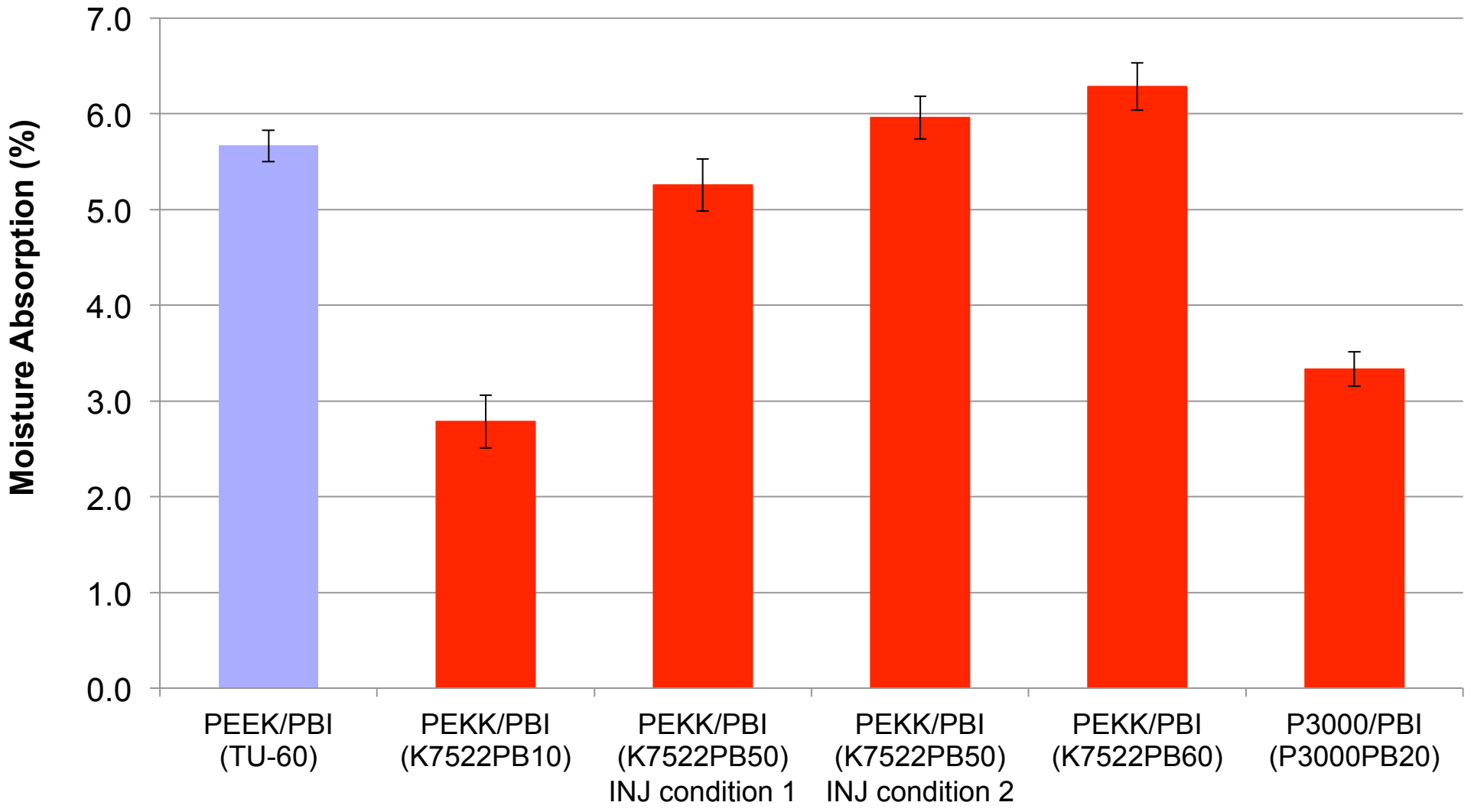
PEKK/PBI (K7522PB50)

PEKK/PBI (K7522PB60)

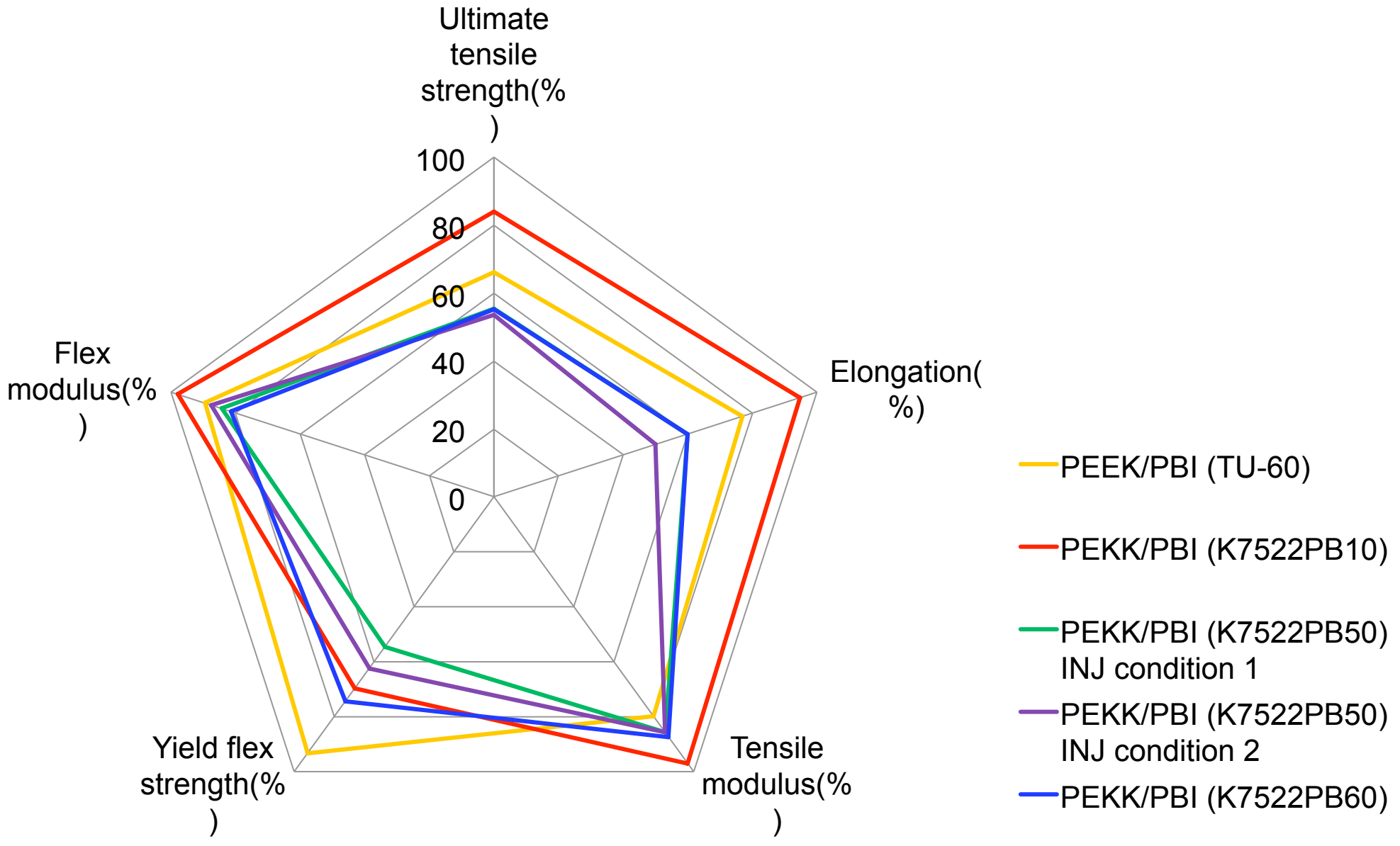
PAEK
(Arylmax P3000)

PAEK/PBI
(Arylmax P3000/PBI)

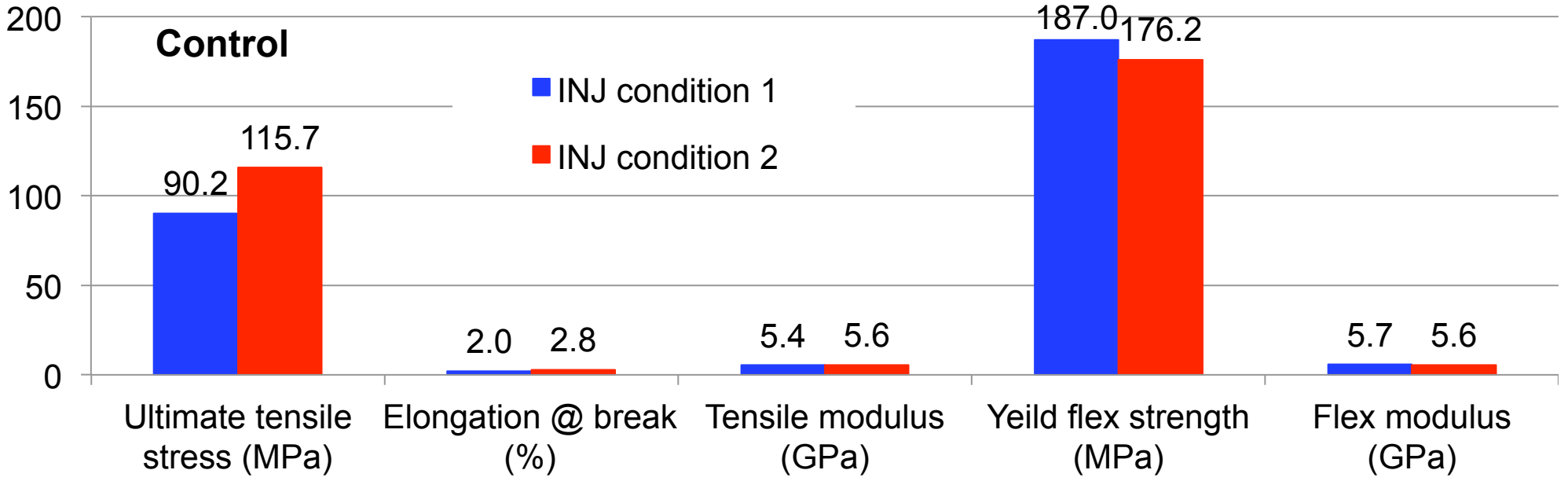
Water Absorption
(Stream Treated PAEK/PBI Blends @ 500°F/72 hrs)

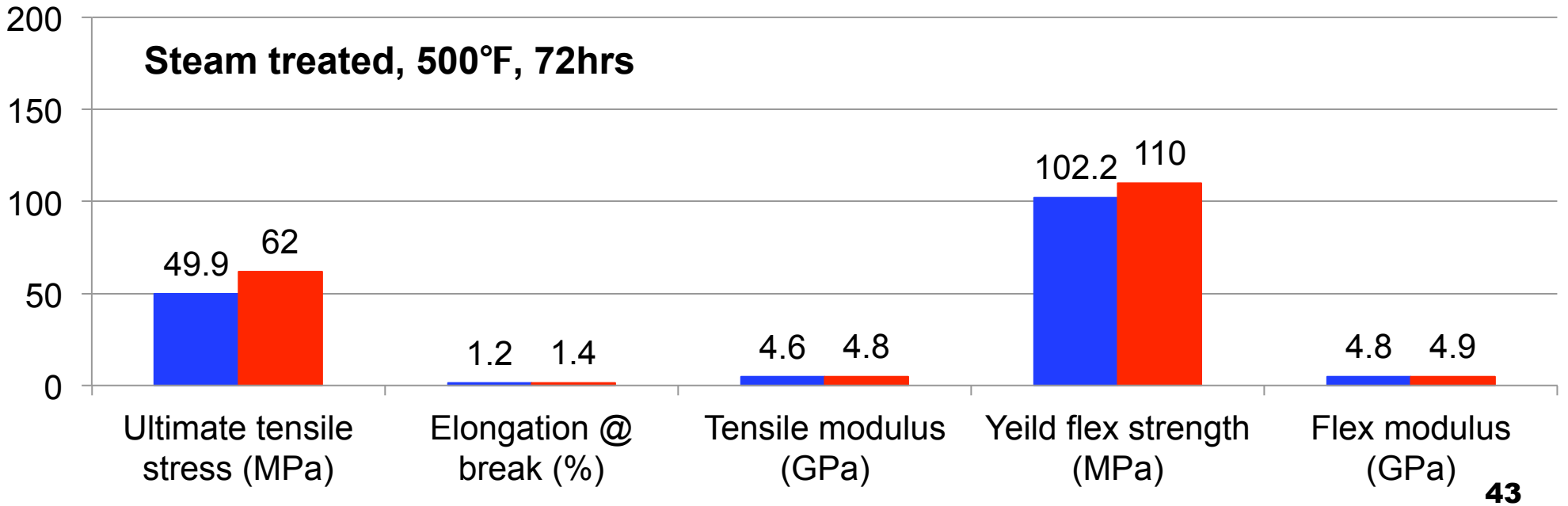


Mechanical Properties Retention
(Steam Treated PAEK/PBI Blends @ 500 °F/72 hrs)

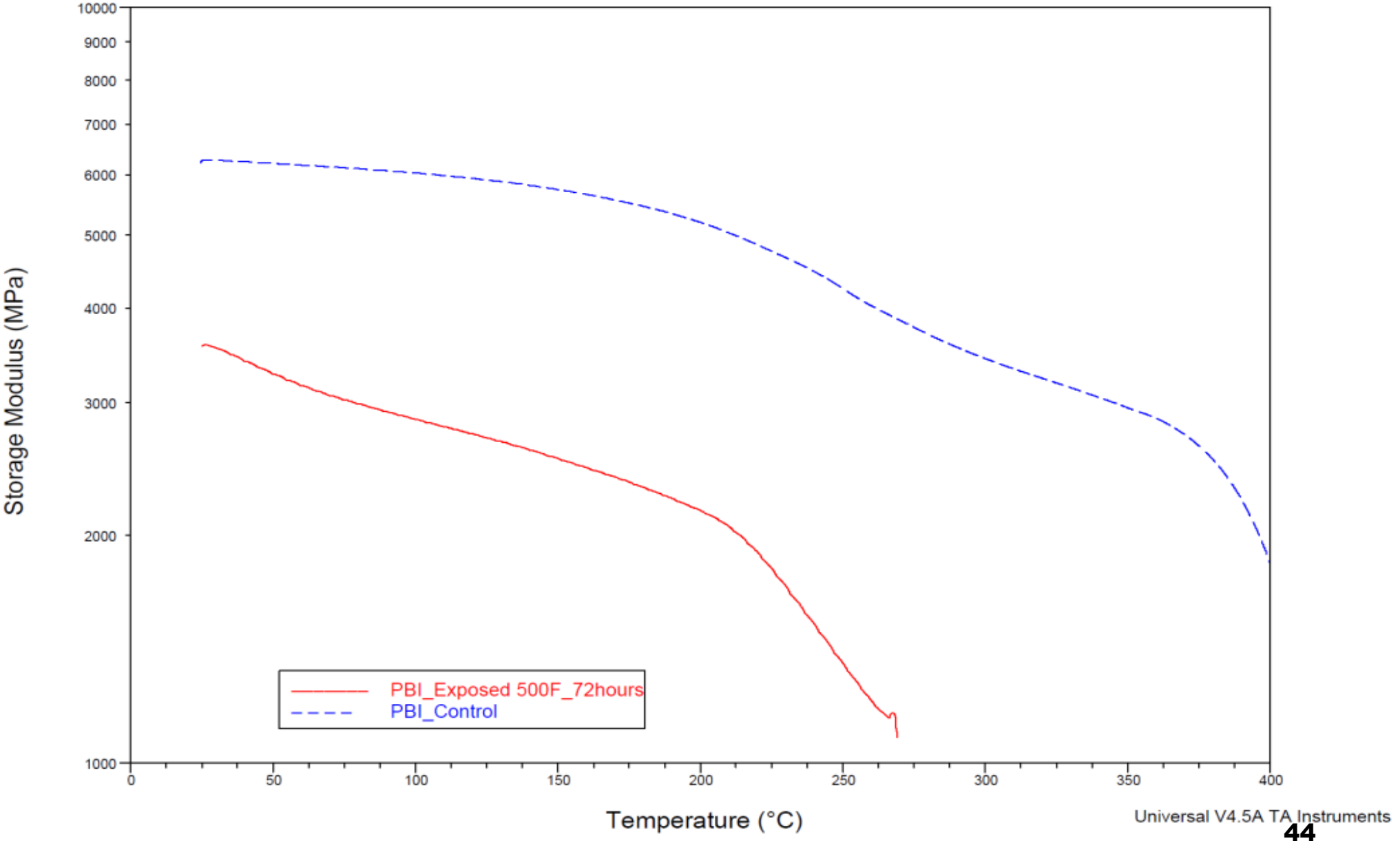


PEKK/PBI
(Arylmax K7522PB50)

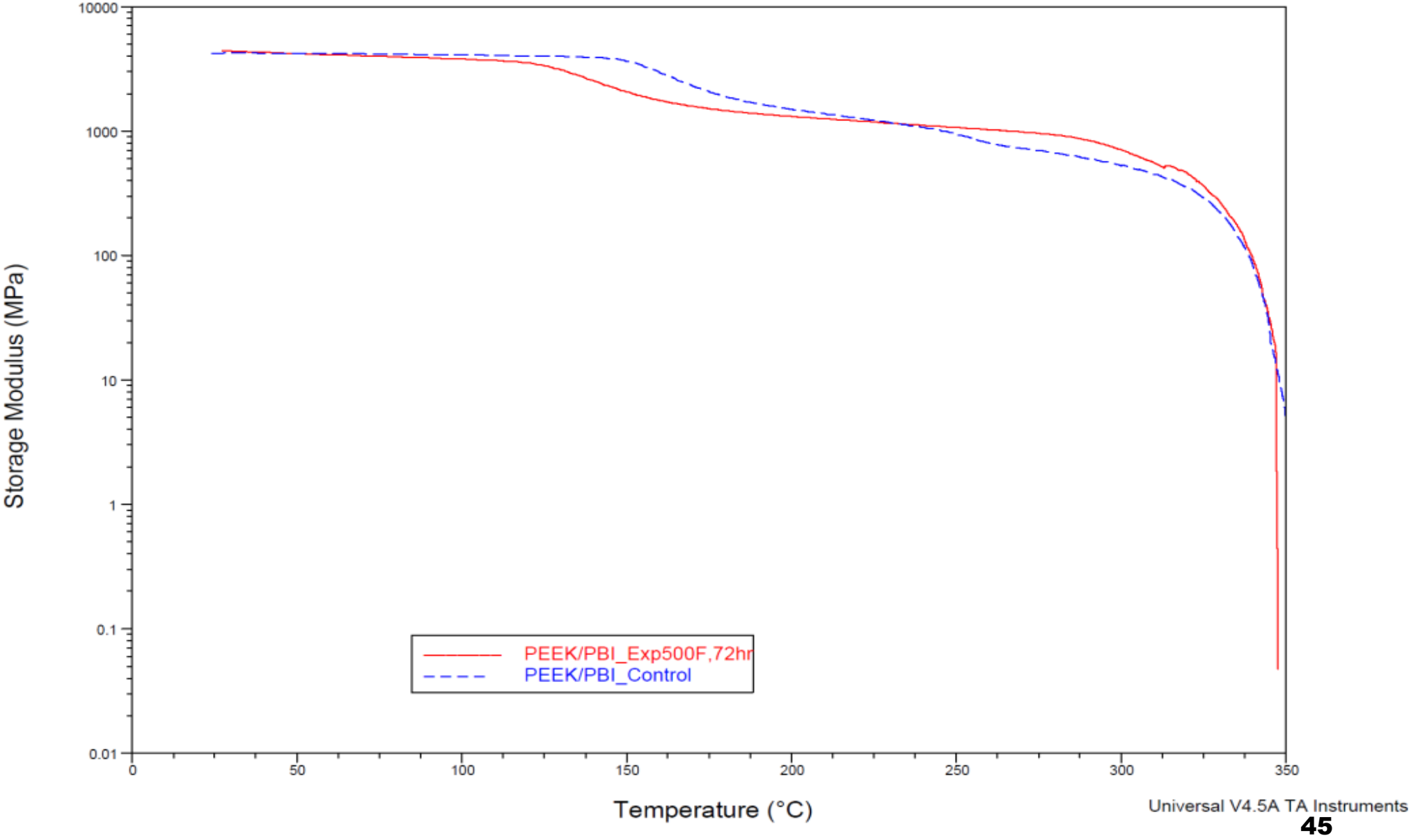




PBI
(Celazole® U60)

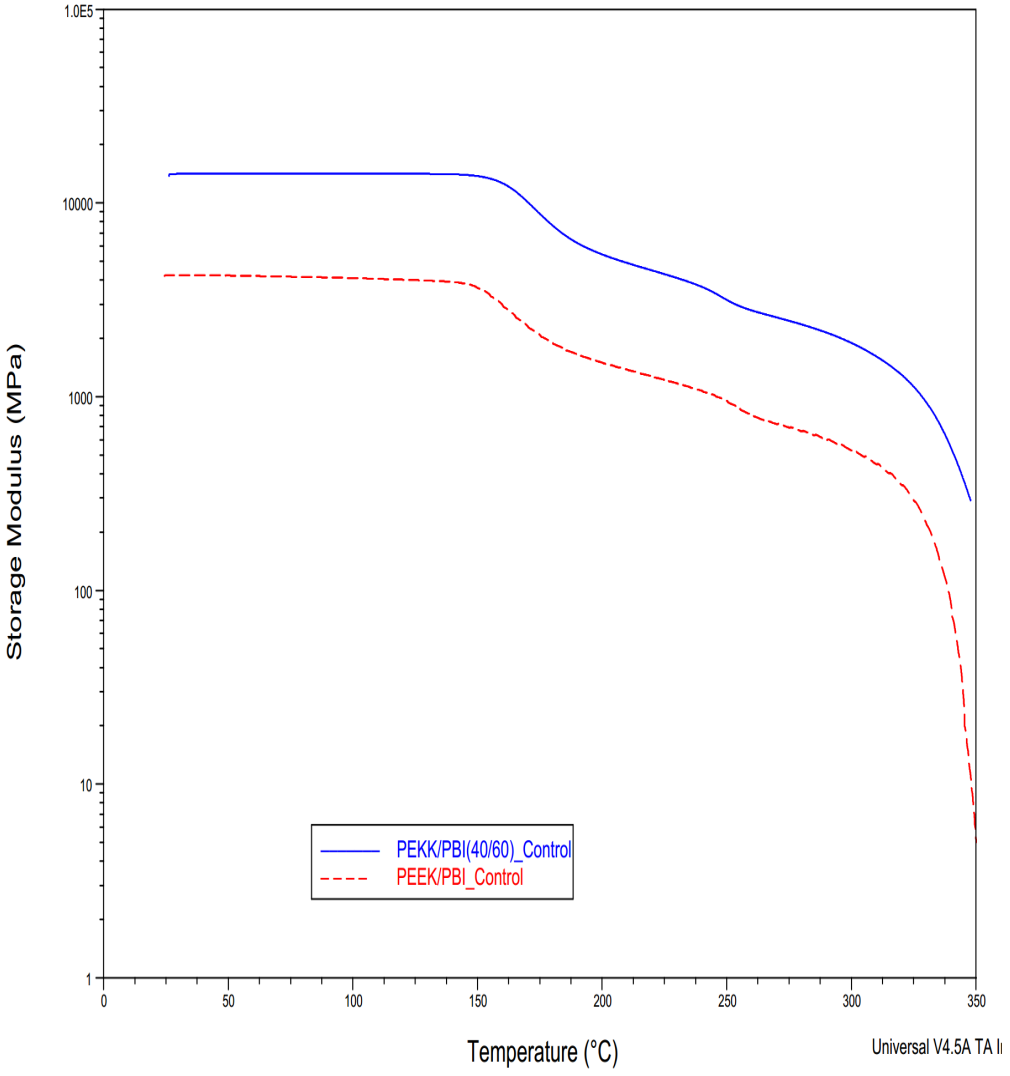


PEEK/PBI
(Celazole® TU-60)

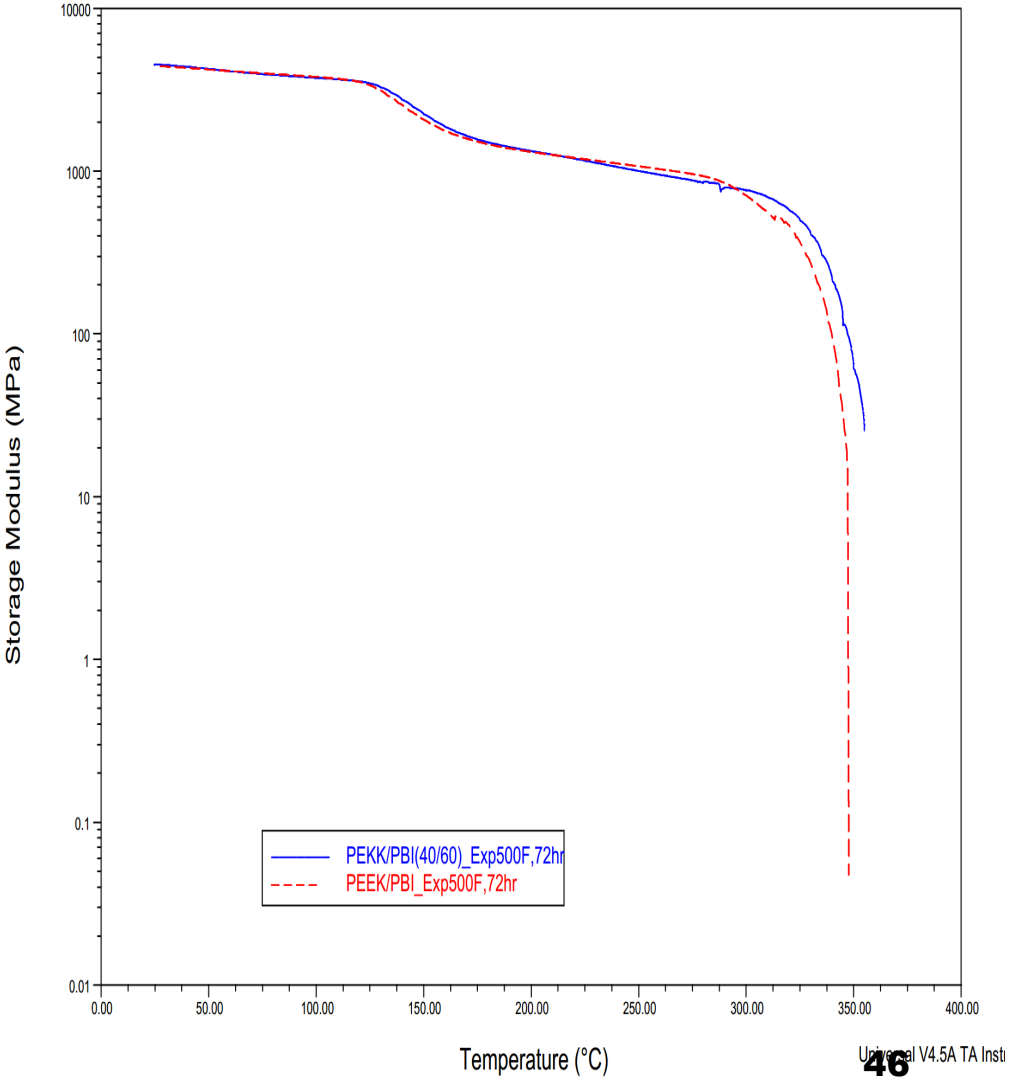


PEKK/PBI (Arylmax K7522PB50) vs. PEEK/PBI (Celazole® TU-60)

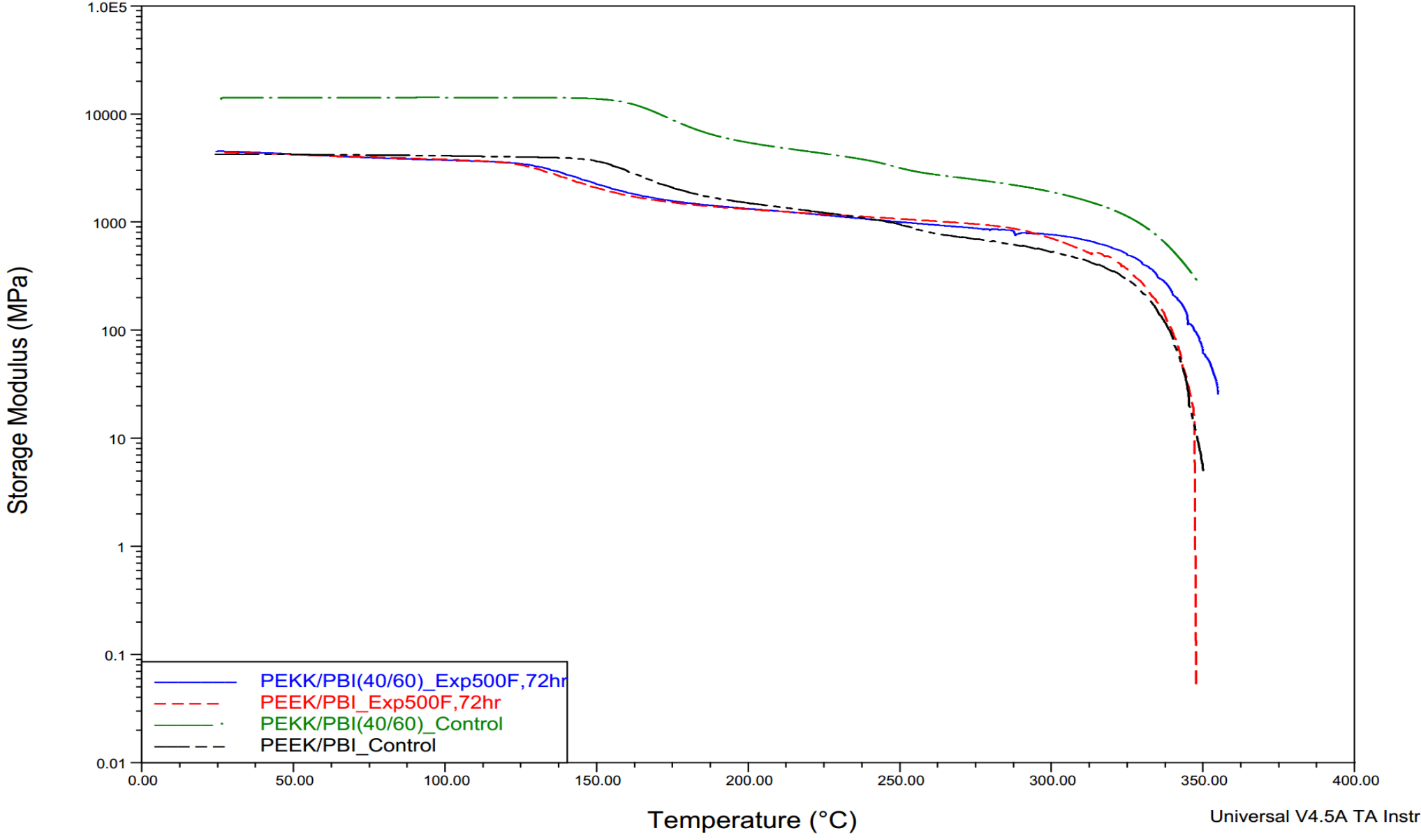
Control



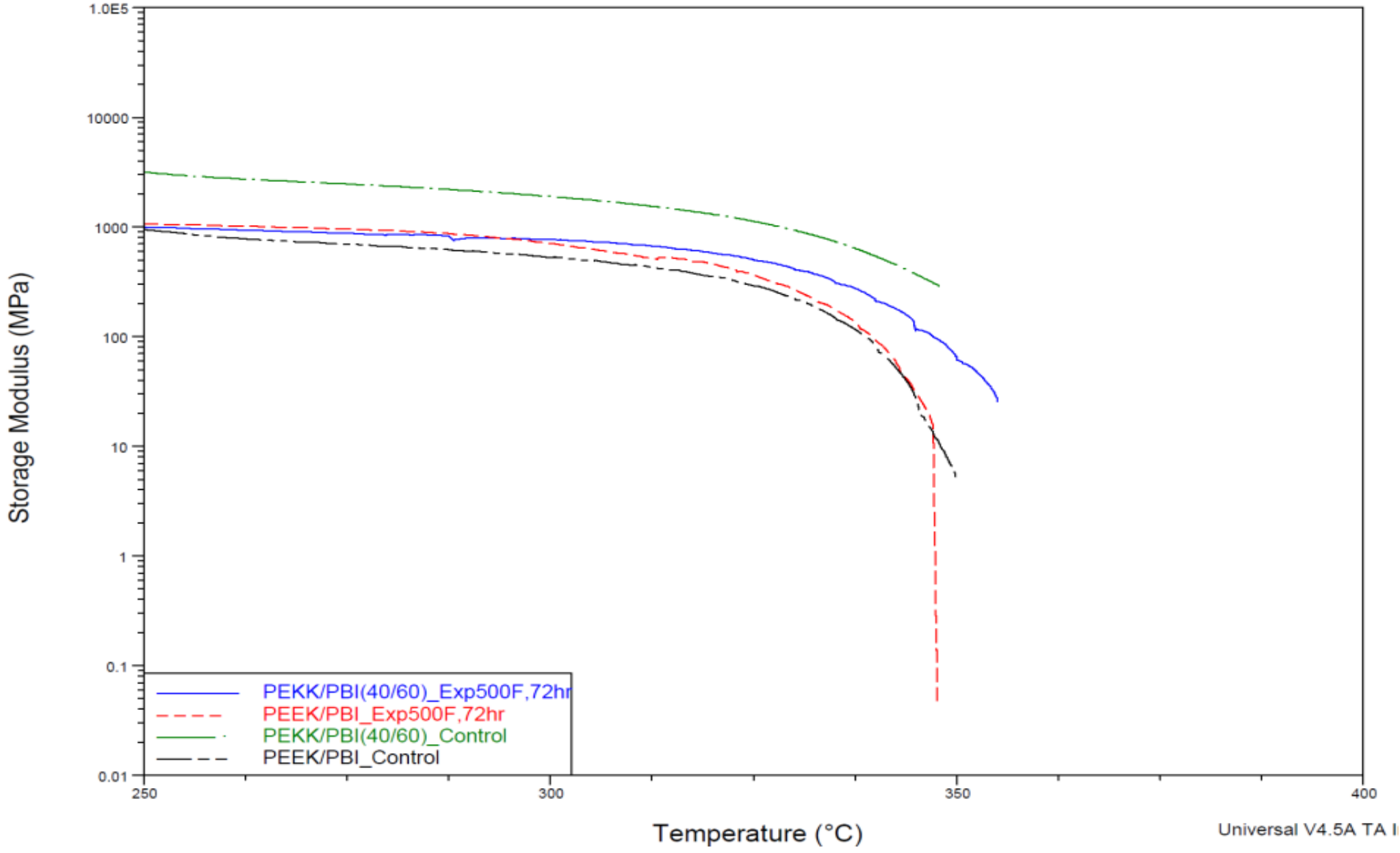
Steam Treated @ 500F/72 hrs



PEKK/PBI (Arylmax K7522PB60) vs. PEEK/PBI (Celazole® TU-60)

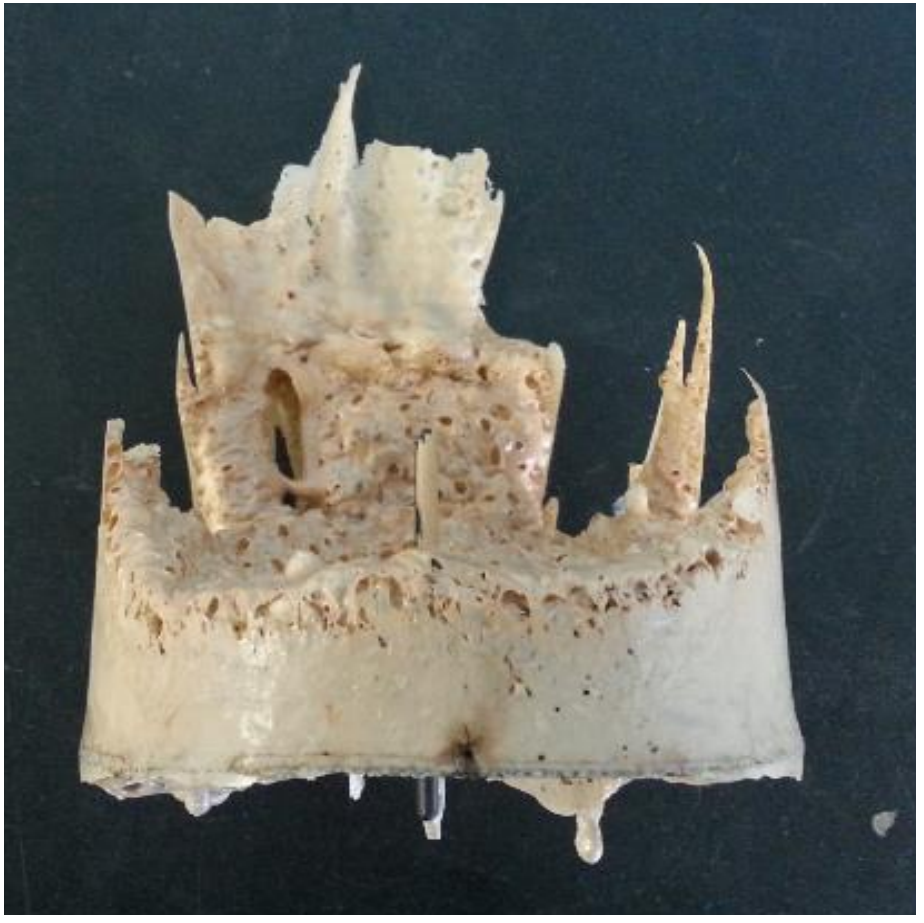


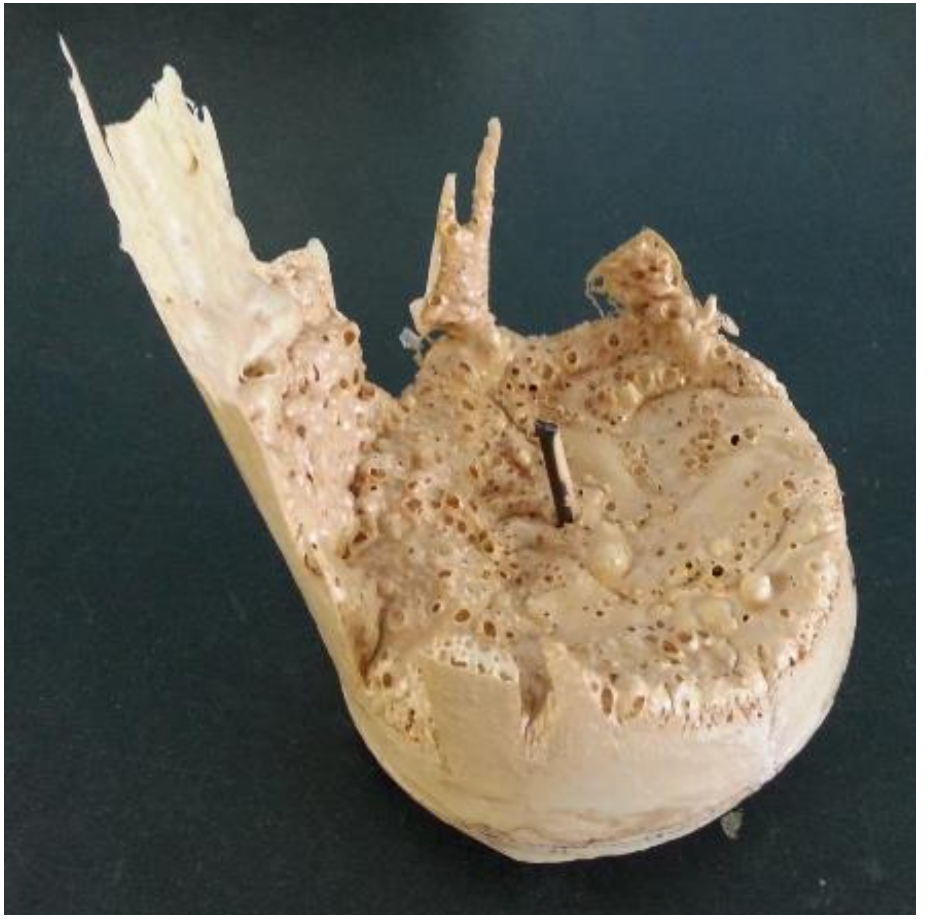
PEKK/PBI (Arylmax K7522PB60) vs. PEEK/PBI (Celazole® TU-60)



Steam Treatment @ 600°F/24 hrs

PEEK
(Victrex PEEK450G)
(Steam Treated @ 600 °F/24 hrs)





PAEK CF Compound
(Steam treated @ 600°F/24 hrs)

PAEK (CF reinforced)

30% CF Filled PEEK (KD2250)

PAEK/PBI
(Steam Treatment @ 600°F/24 hrs)

PEKK/PAEK
(Arylmax KP)

PEKK/PBI
(Arylmax K7522PB60)

PEKK HMW
(Arylmax K7500)

PEKK
(Arylmax K7522)

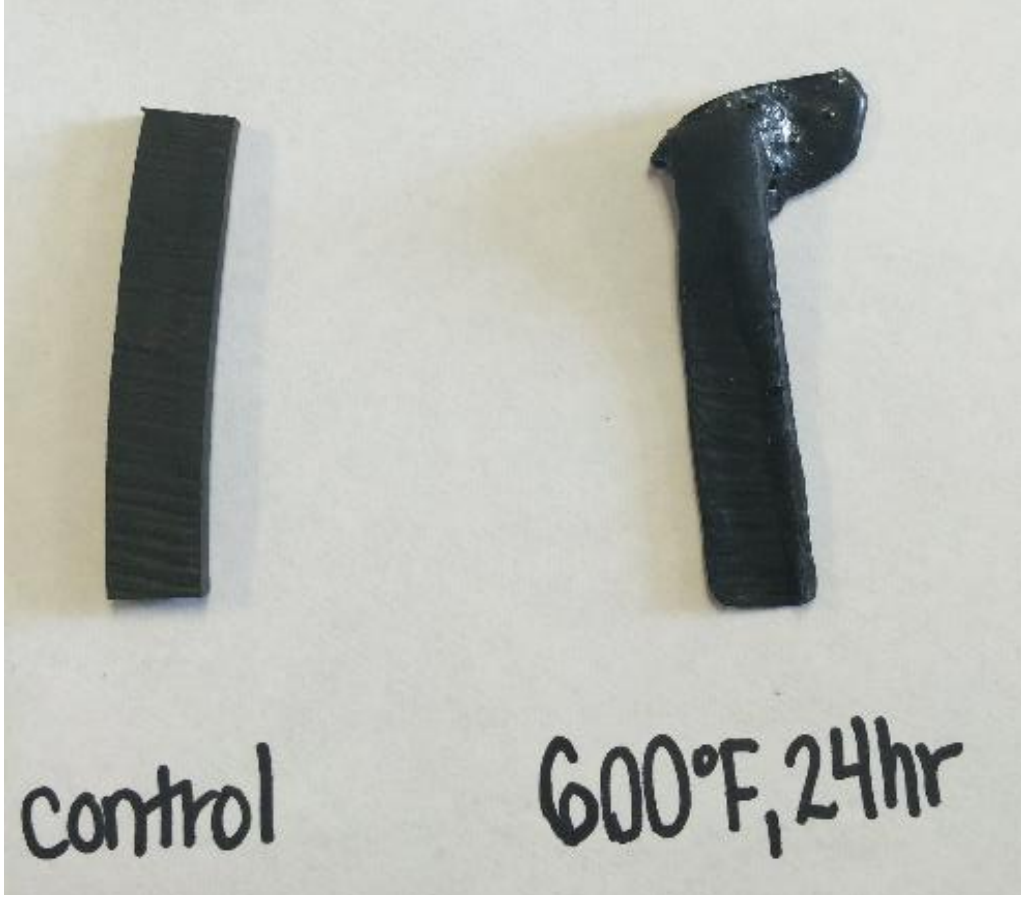
PEEK/PBI
(TU-60)

PAEK/PBI
(Arylmax P3000PB20)

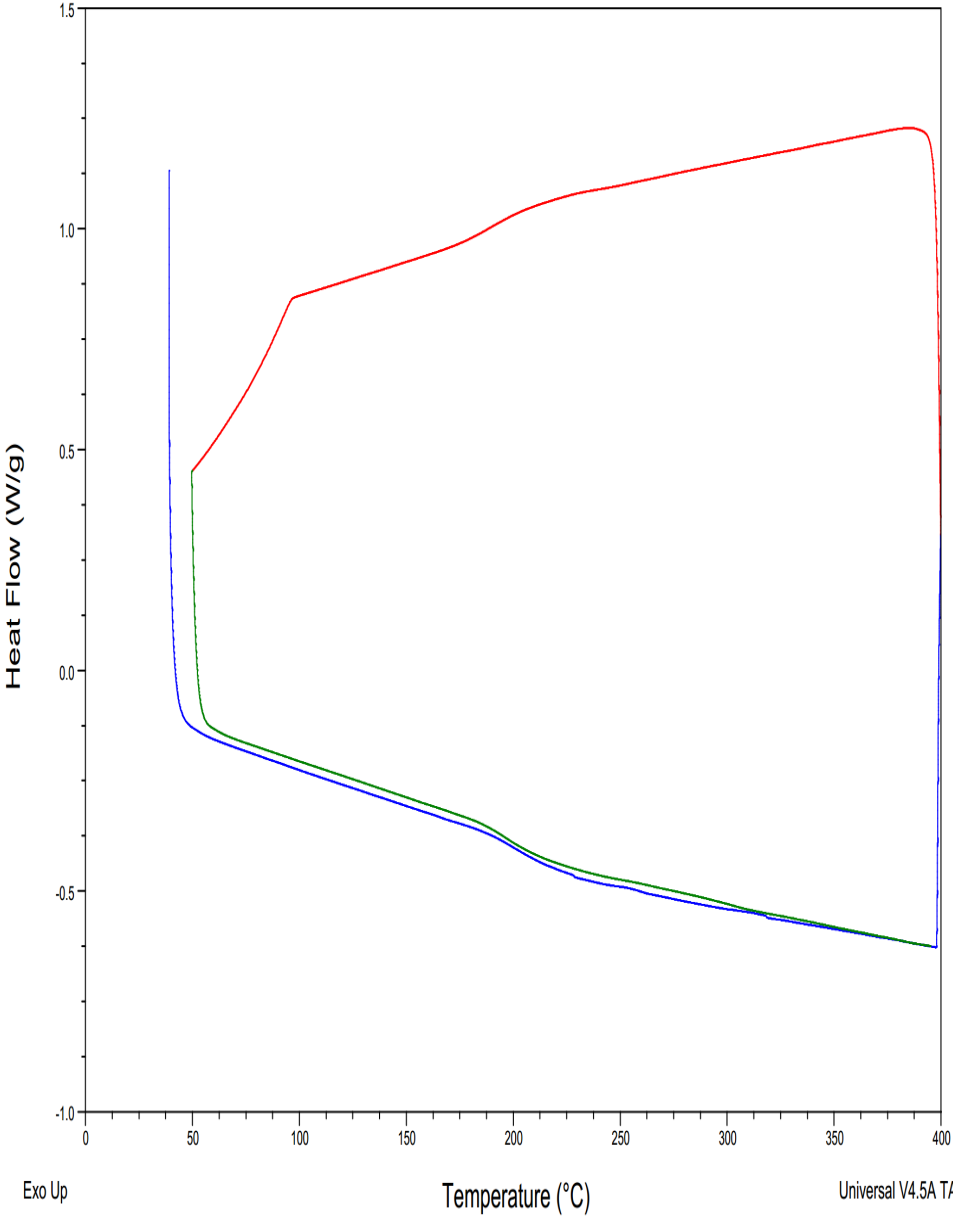
PEKK/PBI
(Arylmax K7522PB60)

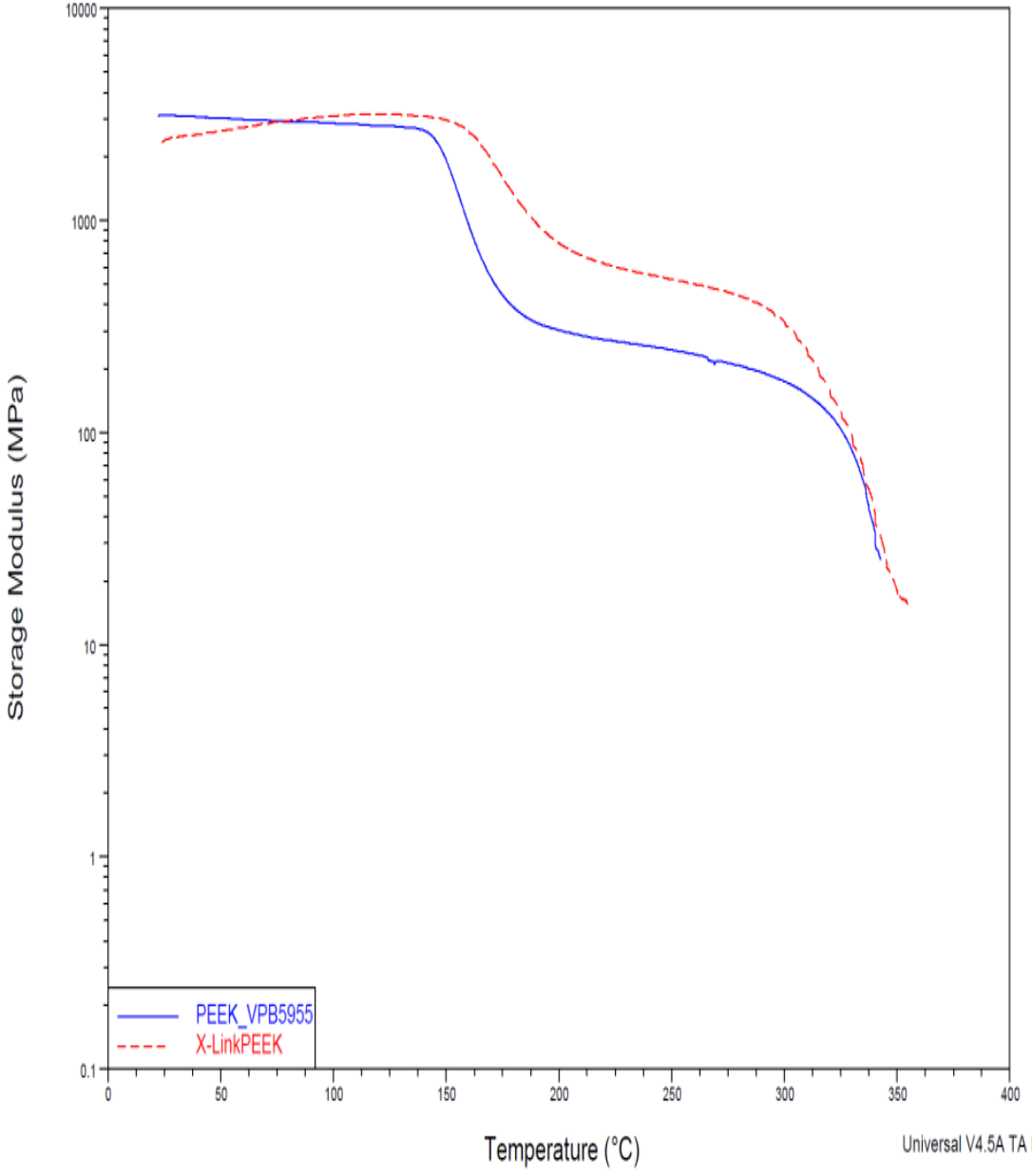
Enhance Thermal Performance of PAEK Through Cross-linking

- Preliminary results of cross-linked PEEK
  - DMA (control, 600F)
- Cross-linked PAEK



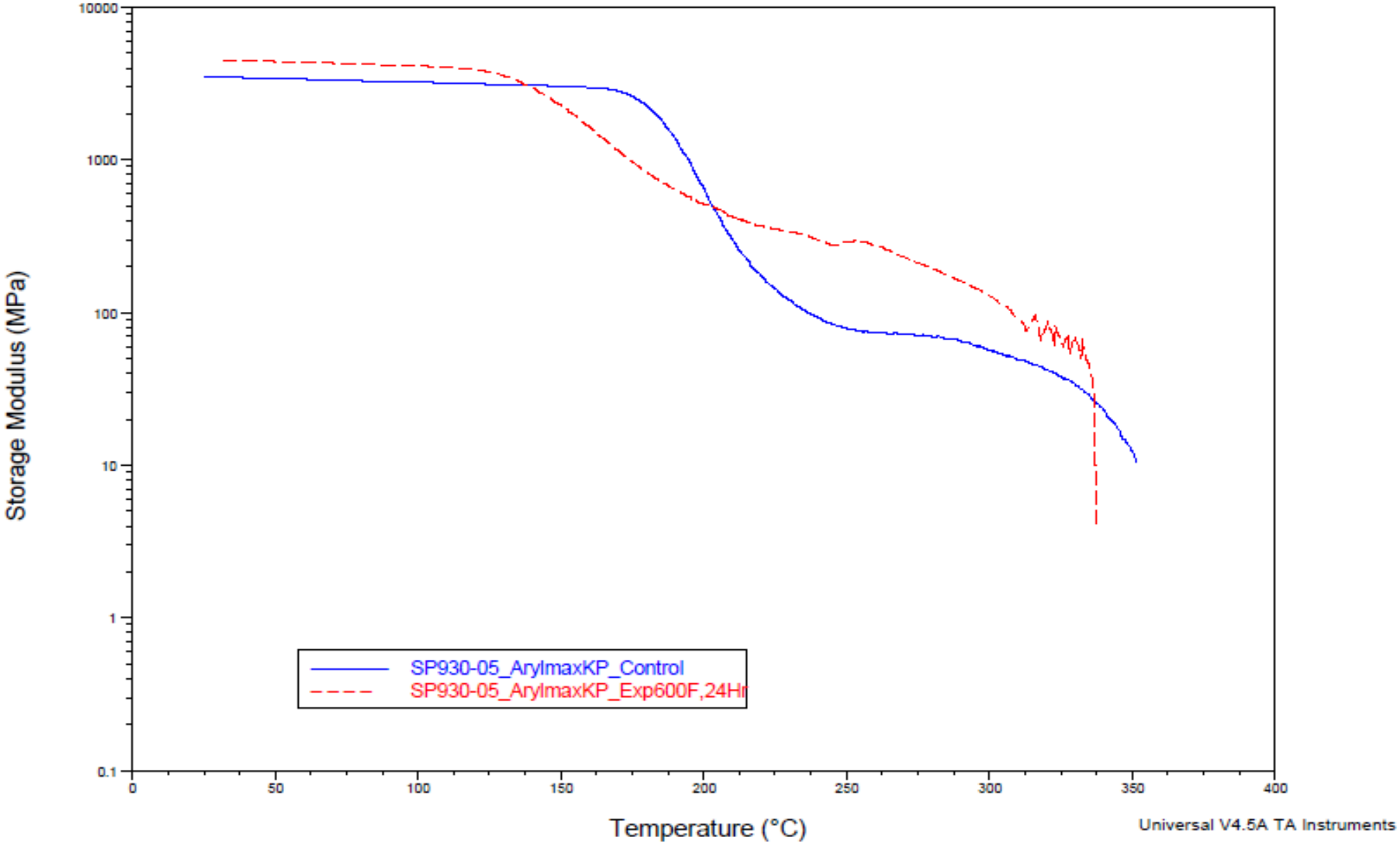
Cross-linked PEEK (Control)



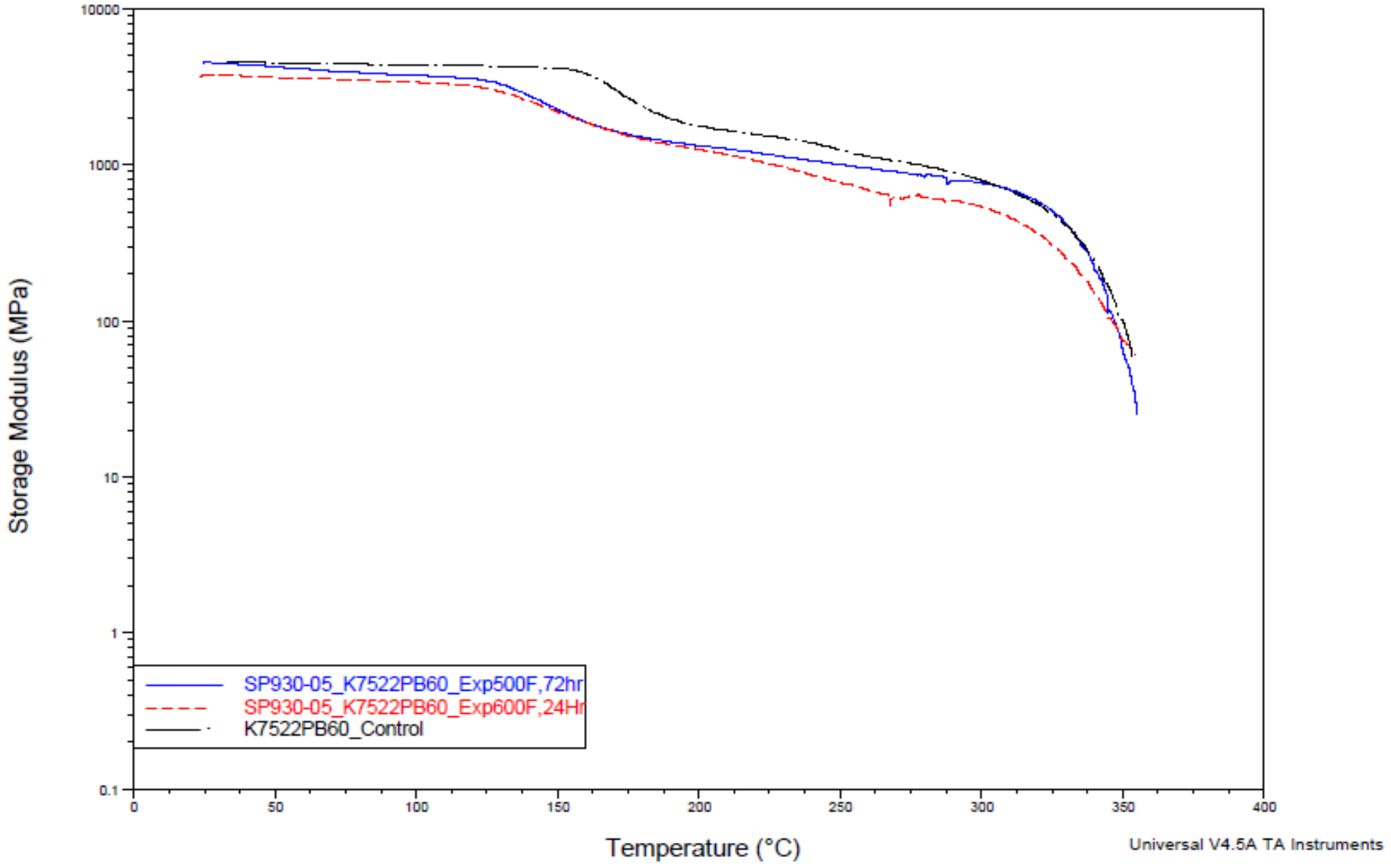


PEKK/PAEK

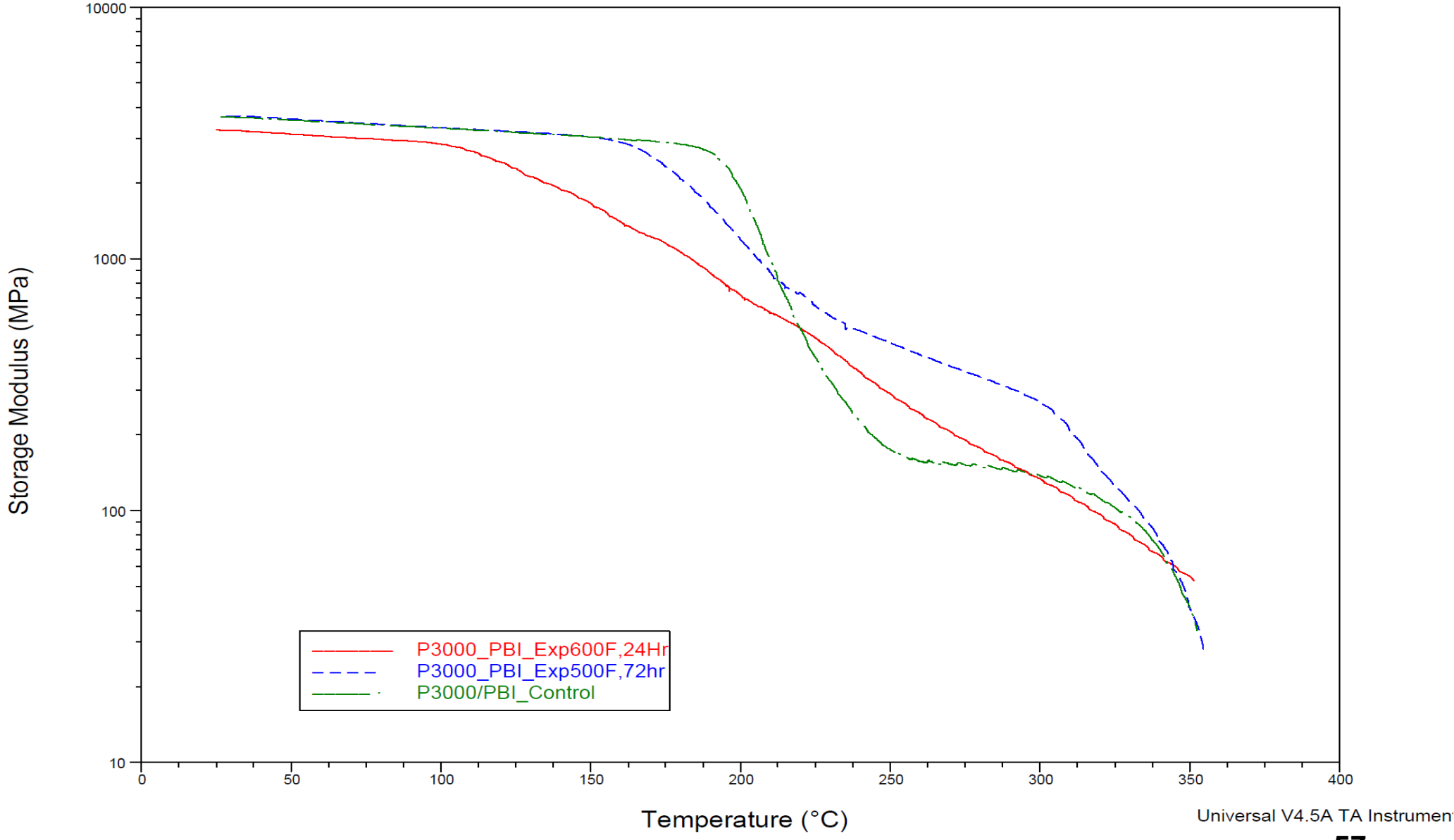
(Arylmax® KP)



PEKK/PBI
(Arylmax K7522PB60)



PAEK/PBI
(Arylmax P3000PB20)



Summary & Conclusions

- It's possible to further enhance PAEK thermal and mechanical properties by blending with high Tg polymers such as PBI.
- Arylmax® P can be potential high heat modifier for other PAEK to enhance performance by forming miscible blends (Alloys).
- Miscibility may play an important role in the proper design of high Tg polymer alloys with improved plateau moduli, and enhanced environmental resistance for corrosive HPHT conditions.
- While most PAEK & it's blends or alloys survives 500 °F/72 hrs steam treatment, further optimization may depend on actual application requirements.
- Only very limited family of PAEK alloys survive 600 °F/24 hrs steam treatment. Additional modification will be needed to further optimize performance as potential candidates for application in similar environment.

ACKNOWLEDGEMENT

- Department of Chemical Engineering, The Pennsylvania State University,
  - Equipment Support
- PBI Performance Products Inc.
- Polymics® Development Team
  - Mike Logsdon
  - Jeremy Johnson
  - Marcus Lancaster
  - Blanca Cruz

Polymics
Concept to Solution