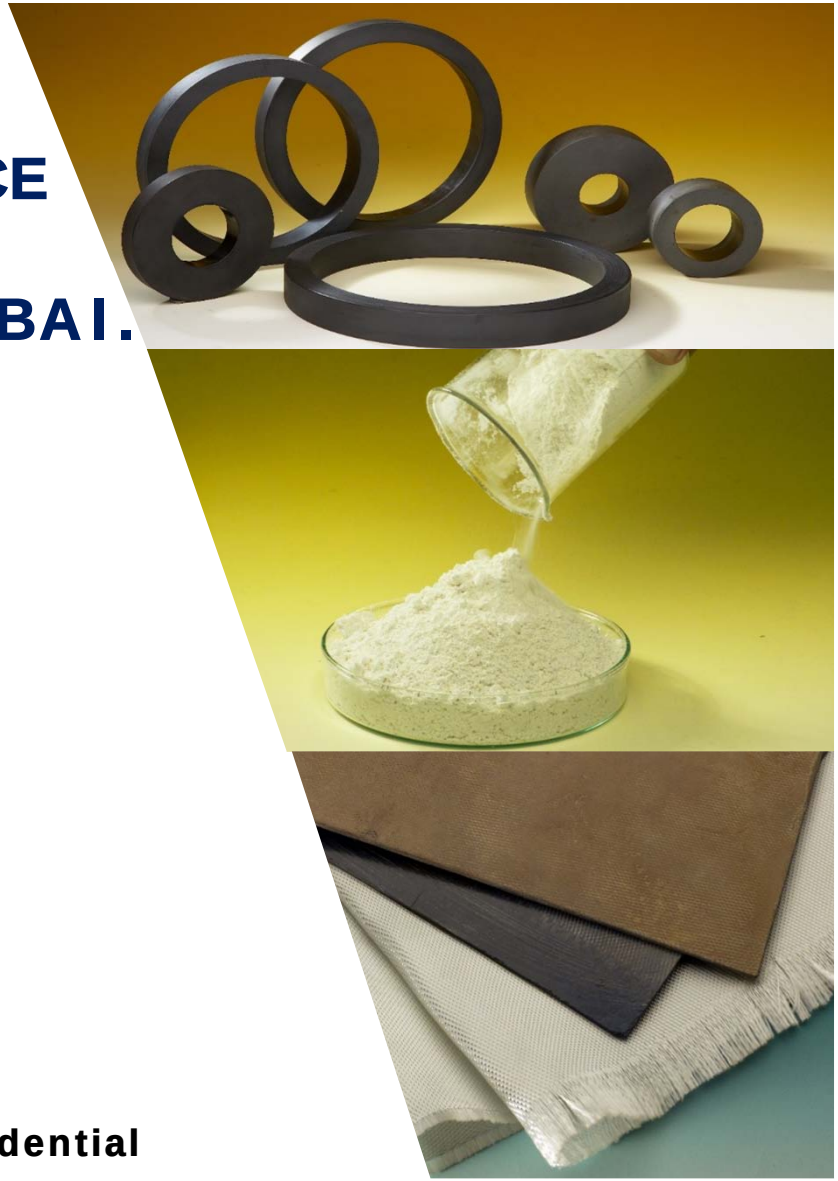
SOCIETY OF POLYMER SCIENCE MUMBAI CHAPTER AT K J SOMAIYA COLLEGE , MUMBAI.



Dr. Prakash Trivedi
&
Dr. Atul Raja

Gharda Chemicals Ltd.
2nd March 2020

GHARDA
Polymer SBU

GHARDA CHEMICALS SPECIALTY PLASTICS

- **1990-2011: Dombivli, Panoli.**
  - Acrylics, PPE & Blends
  - PES, PSU, PPSU, Blocks Copolymers, E-PEEK – at Panoli – 1996 –till 2006 (taken over by Solvay)
  - Fluoro Monomers, Aramides
- **2011-Till Date: Ankleshwar (GIL) , Panoli, Dombivli.**
  - N-PEK, PEKKs : Commercial
  - ABPBI : Pilot Plant
  - PEI : Pilot Plant

GHARDA
Polymer SBU

JOURNEY OF GHARDA POLYMER – 1990 – till date

PEK production started at GIL, ABPBI Fiber lab preparations.

2011 - 2020

GCL Panoli- New plant commissioned in 2019
Products : PEKK all variant and their monomer EKKE

Sulfone and Ketone Polymer with their Monomer Production started and commercialization

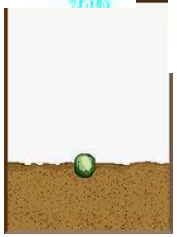
2005 -2006

PSST – Block Polymer production started – Got Patents - 2005
GCL Polymer plant sold to Solvay – in May 2006

1998- 2002

Journey of Polymer synthesis started at GCL Dombivli PPE & Acrylics

1990

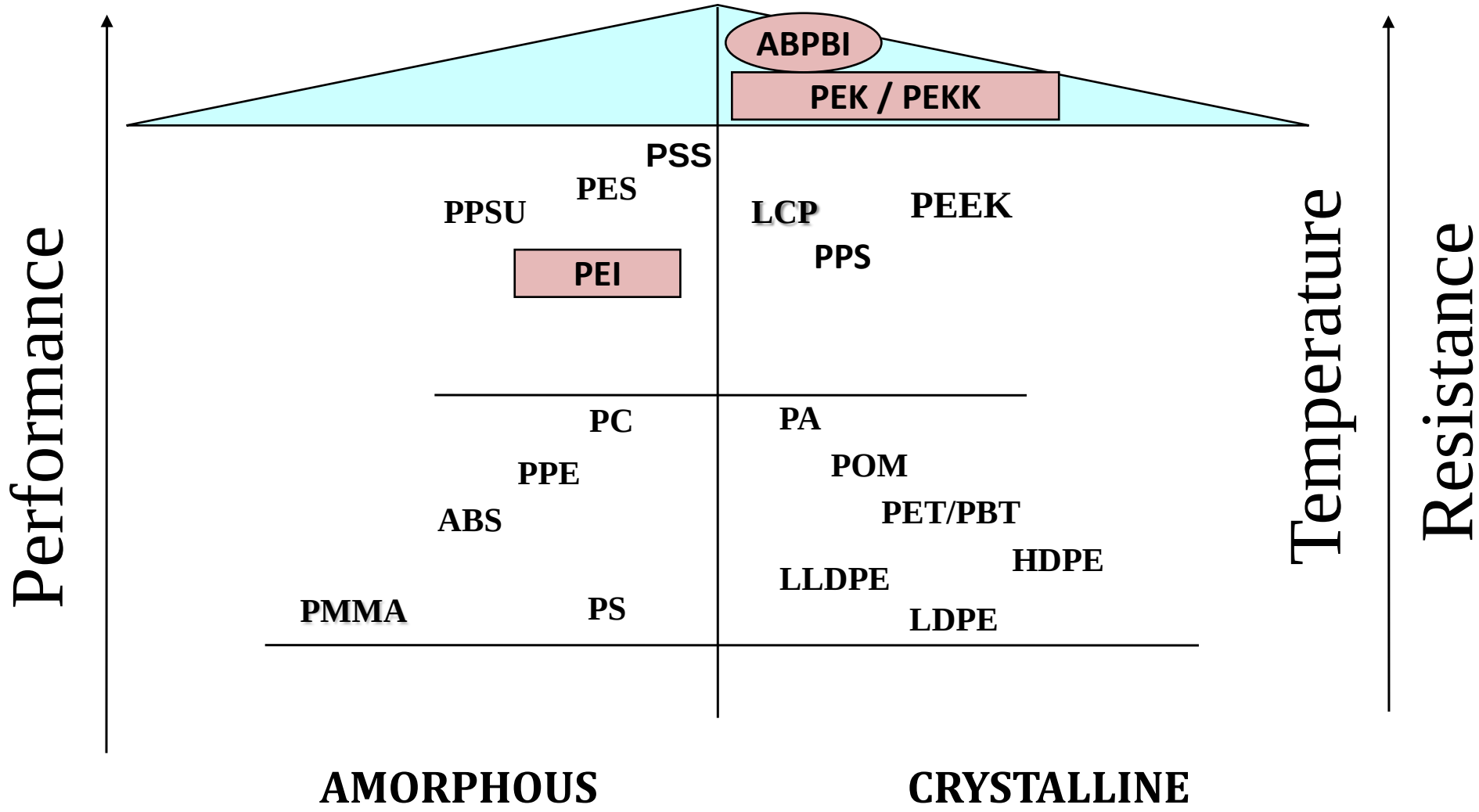


1996

Polymer plant commissioned at Panoli –Gujarat for speciality Polymers

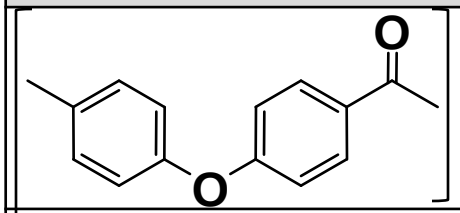
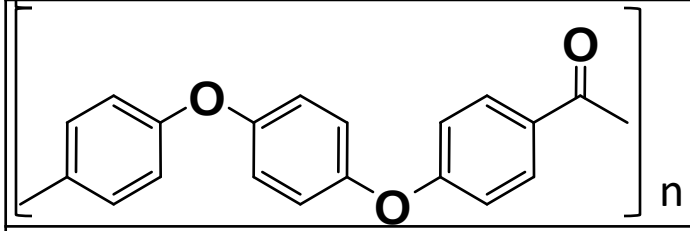
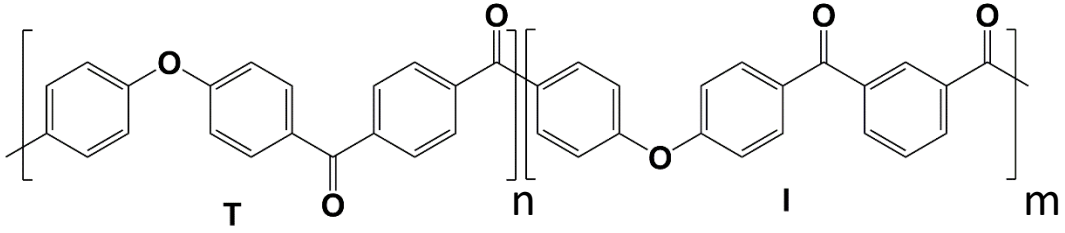
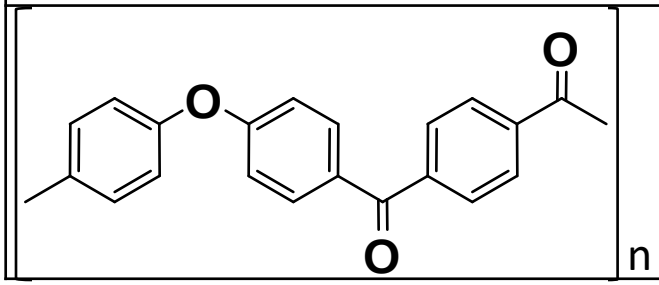
GHARDA
Polymer SBU

THERMOPLASTICS PYRAMID – GHARDA PLASTICS



GHARDA
Polymer SBU

STRUCTURE OF PAEK POLYMERS

Structure	Name	Ketone (%)	Tg (°C)	Tm (°C)
	PEK	50	152	370
	PEEK	33	143	340
	PEKK (T/I) (60/40) (70/30) (80/20)	67	158 163 166	300 335 358
	PEKK (T/I) (100/0)	67	172	395

CURRENT SYNTHESIS OF PAEK.

- **PEKK: T / I : 100:0**

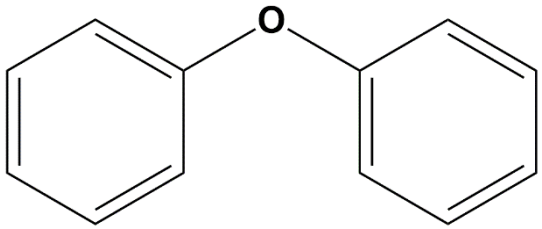
PEKK 100/0

- **100/0 : First & only producer in the world.**
- **Literature indicates – difficult to melt process due to degradation of polymer at 420°C**
- **Gharda developed New process, with Outstanding properties:**
  - **Tm 395^{0}C**
  - **Melt Processable polymer**
  - **Superior flow,**
  - **Improved color,**
  - **good thermal stability.**
- **Available as Powder or Pellet form**
- **As Natural or 30% GF and CF filled.**

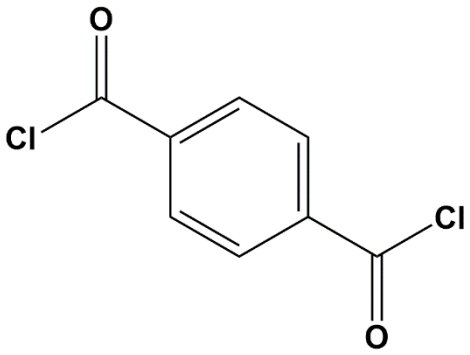
Improved color PEKK 100:0 pellet

CURRENT SYNTHESIS OF PAEKs

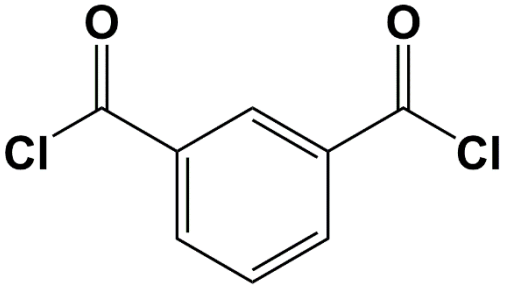
- **PEKK:**



Diphenyl Ether

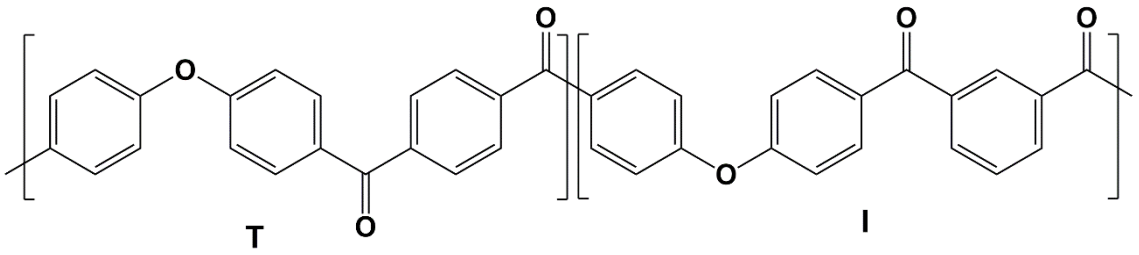


Terephthaloyl Chloride



Isophthaloyl chloride

$ODCB/AlCl_3$/
<100 °C



Polyetherketoneketone

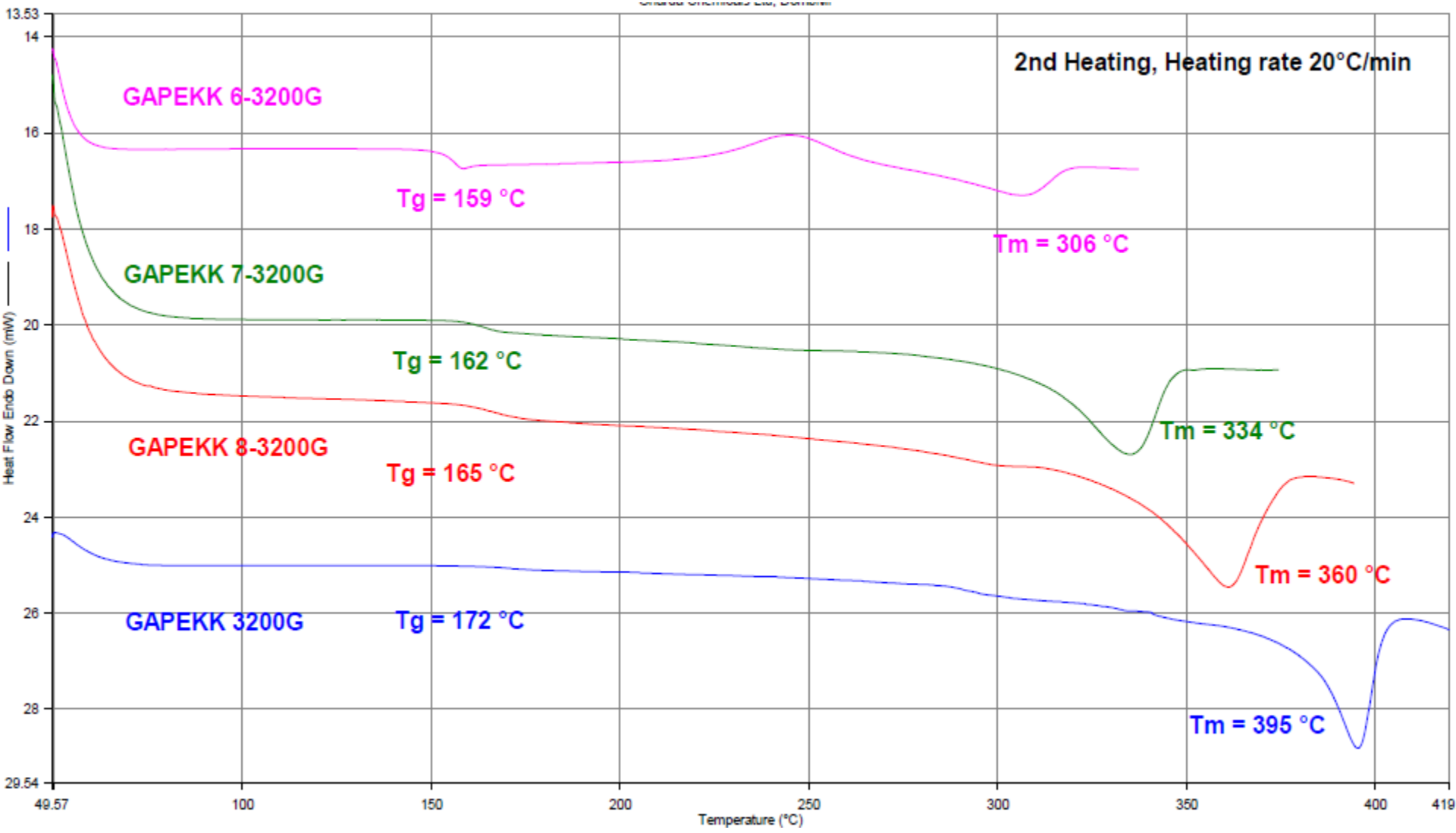
PEKK Advantages

* Outstanding range of thermal properties
* High heat resistance up to 300 °C
* Low Creep and Retention of mechanical properties at elevated temperature
* Outstanding chemical resistance
* Outstanding wear resistance
* Outstanding resistance to hydrolysis
* Outstanding thermal properties
* Excellent mechanical properties
* Very good electrical properties
* Excellent radiation resistance

GHARDA

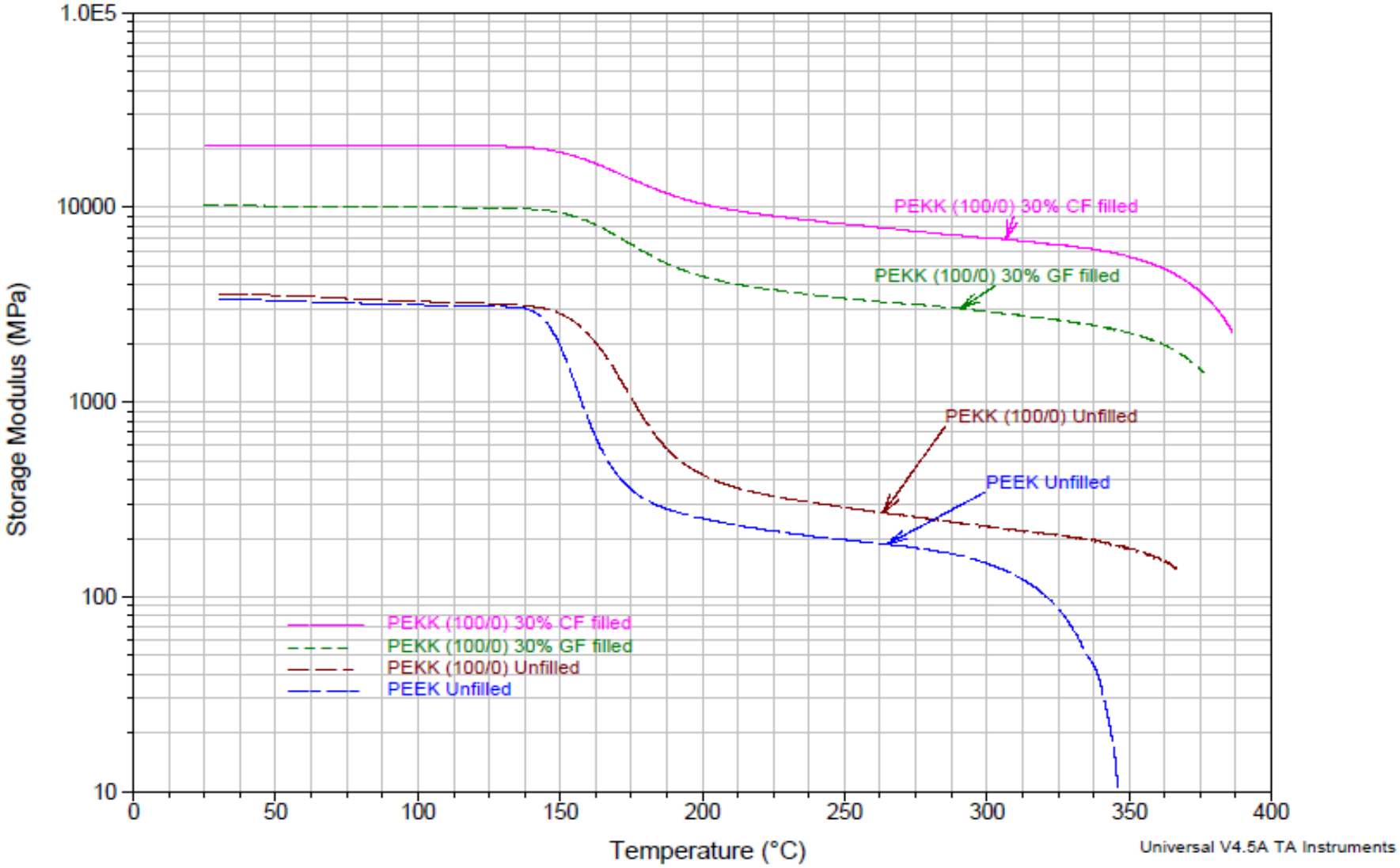
Polymer SBU

Melting behavior of PEKK Homopolymer and Copolymers

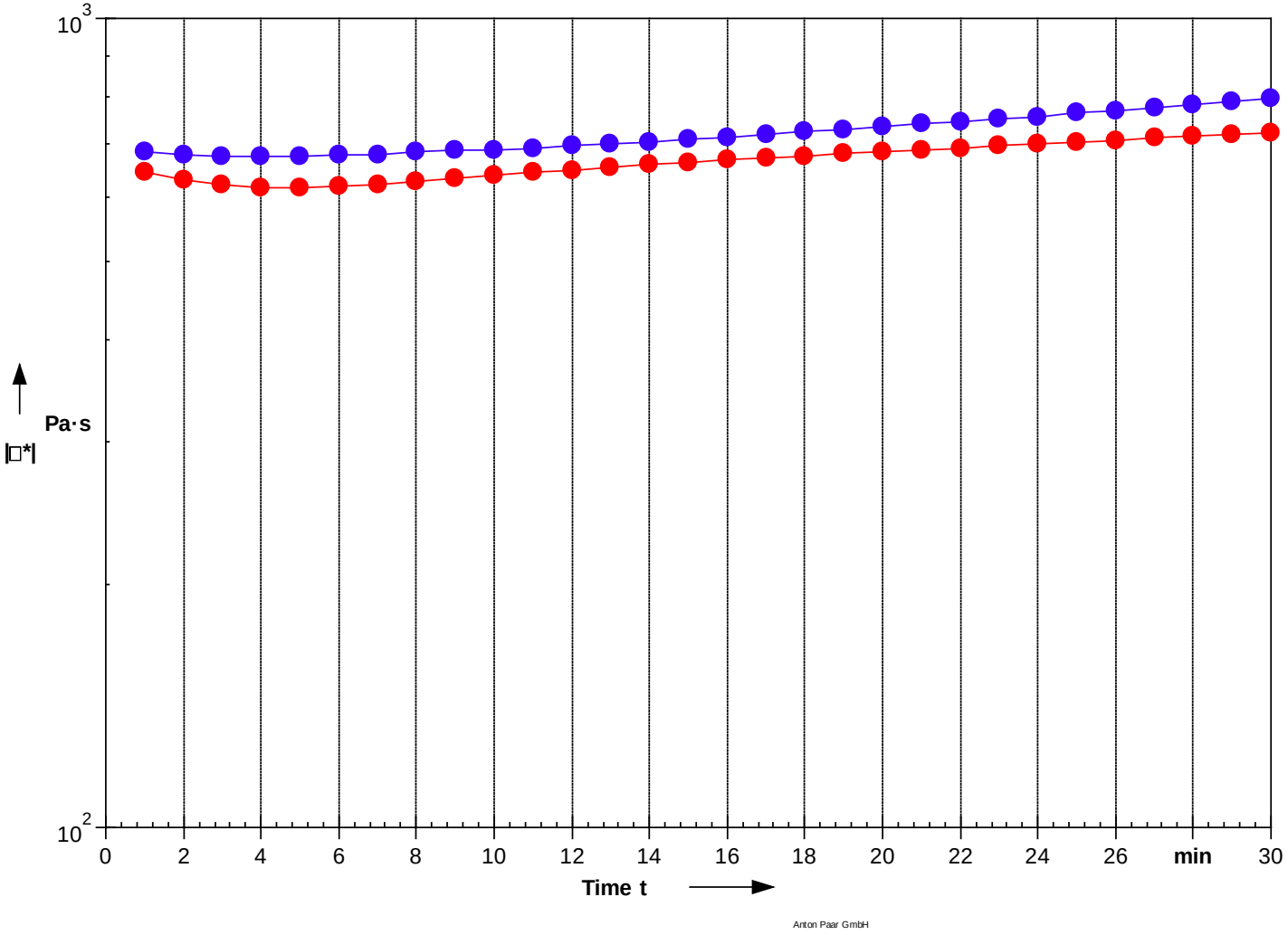


GHARDA
Polymer SBU

DMA of PEKK 100/0 Vs. PEEK



THERMAL STABILITY OF GAPEKK 6-3200P BY PARALLEL PLATE RHEOMETER



ASTM D 4440
Fixture : Parallel Plate, 25 mm
Frequency : 10 rad/s
Temperature : 380 °C
Atmosphere : Nitrogen
Mode: Oscillation

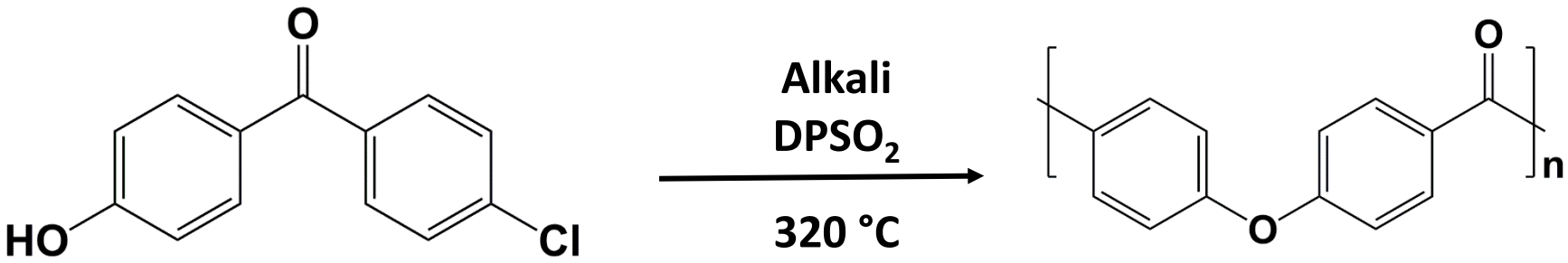
GAPEKK 6-3200P Lot.No.F17/171

Competitor PEKK (60/40)

Anton Paar

PEK

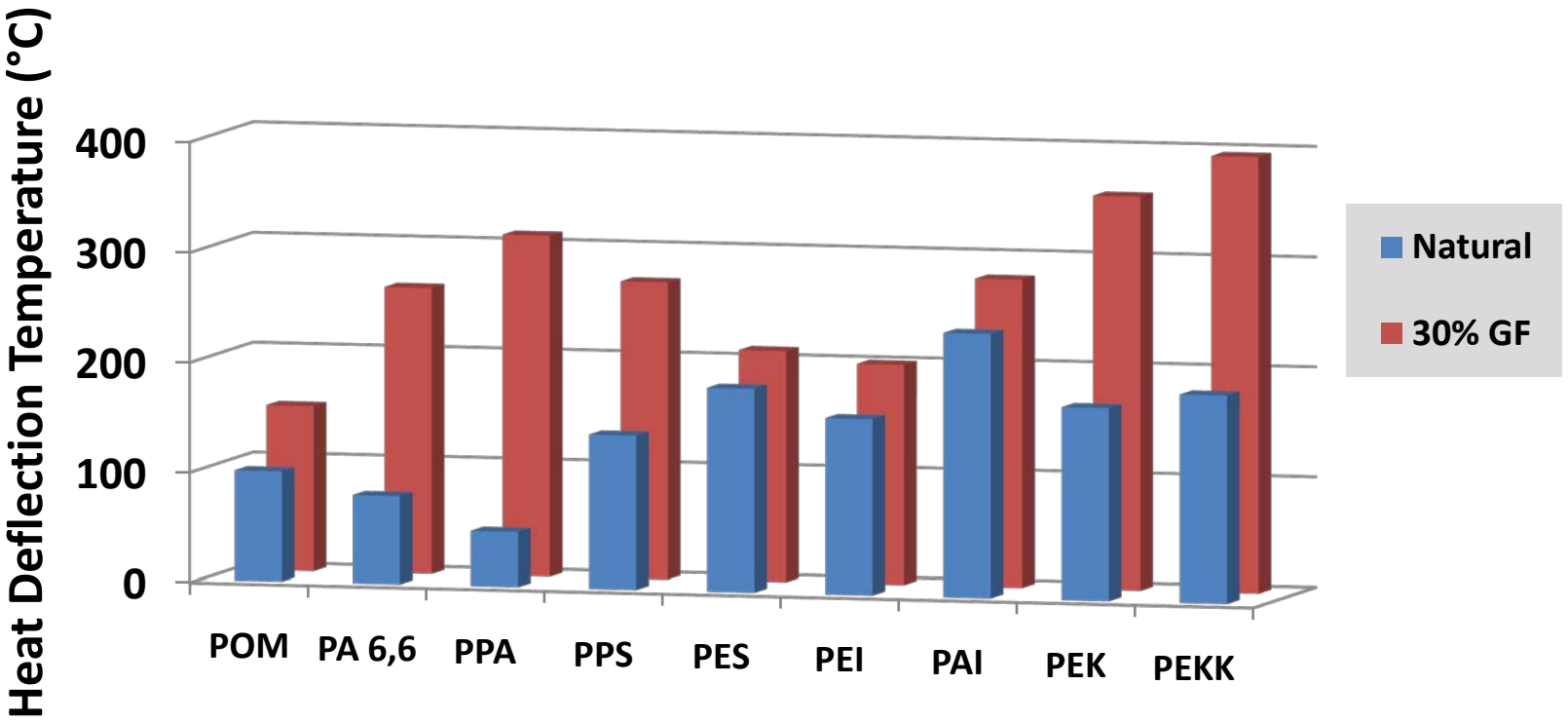
- PEK is made using nucleophilic PZN:



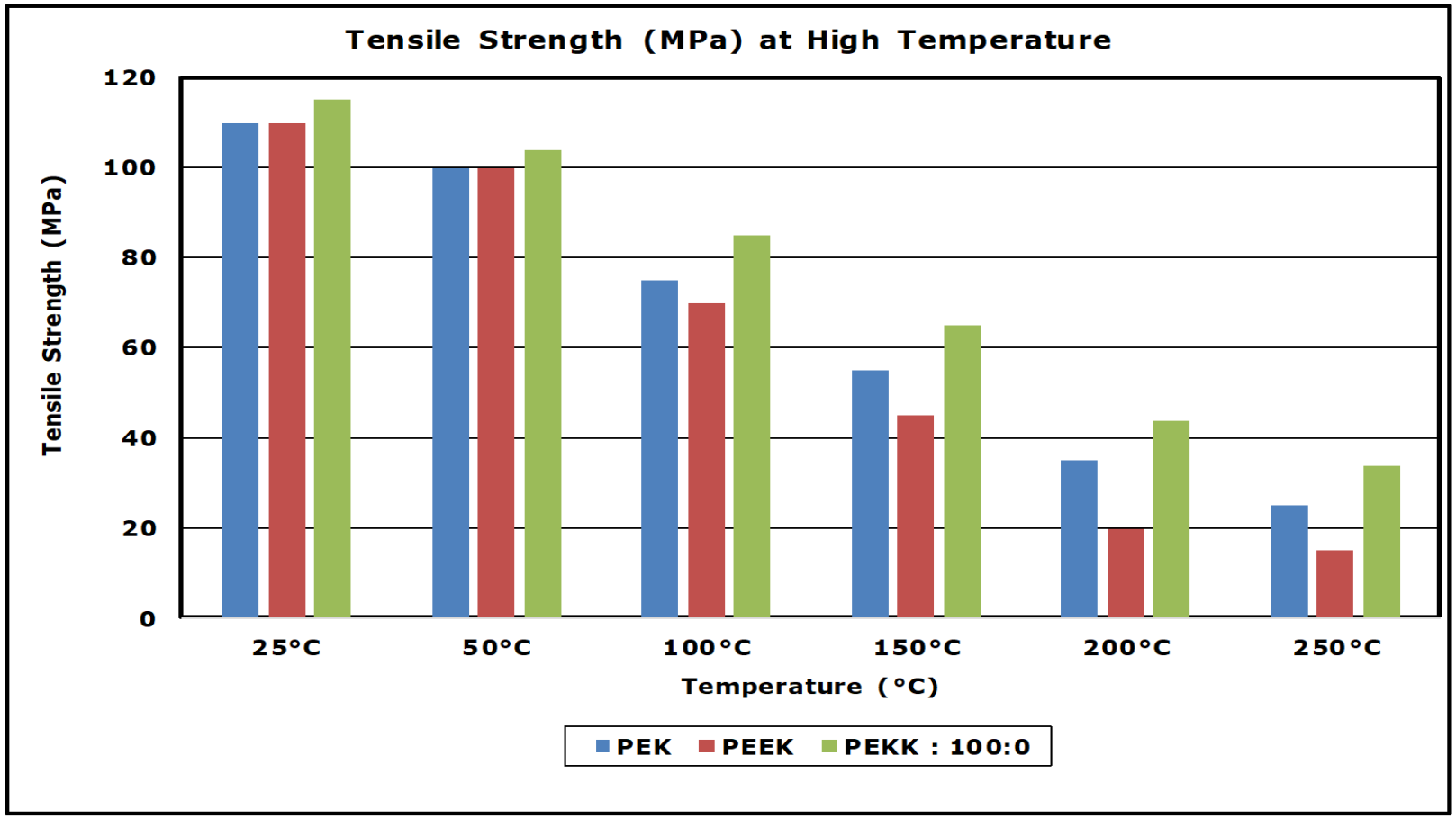
4-Chloro-4'-Hydroxybenzophenone

Polyetherketone

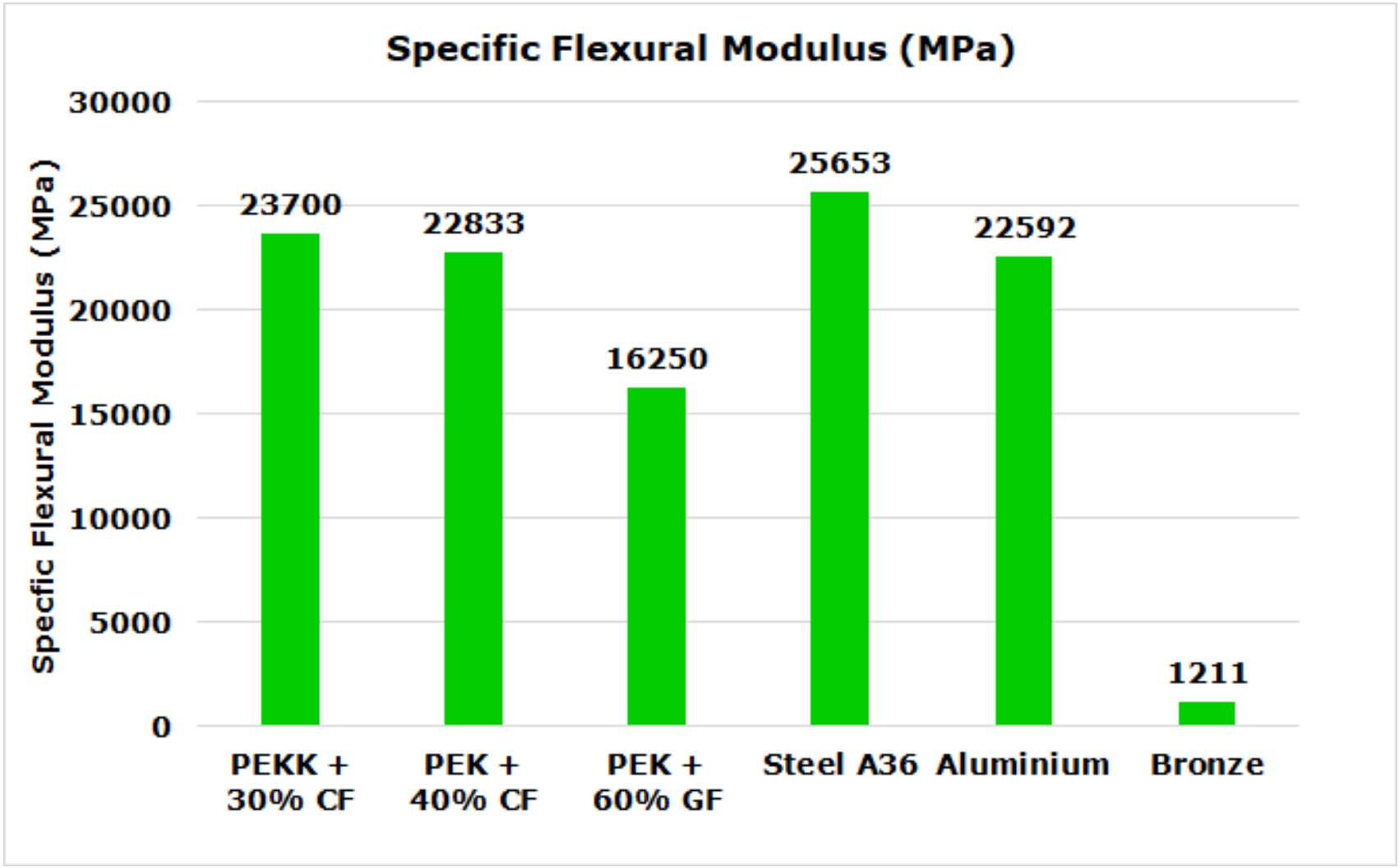
HDT OF PLASTICS



Mechanical Properties at High Temperature



Specific Flexural Modulus



ABPBI Synthesis

3,4-Diamino Benzoic Acid

ABPBI

Gharda Chemicals Ltd has developed and patented synthesis processes to produce high molecular weight ABPBI required for fiber spinning and film casting.

<u>Properties of High Molecular weight polymer:</u>

1. **High Inherent Viscosity (4.5 – 5.0 dl/gm)**
2. **Brookfield Viscosity is 45,000 cP to 55,000cP (at 4.5 % Conc. and 85^{0}C)**
3. **Tg 485^{0}C (of compression molded sample)**

GHARDA
Polymer SBU

Fiber Property Comparison

Property	Unit	ABPBI	PBI	Nomex	Kevlar	Dyneema
Denier	--	1.5	1.5	1.5	1.5	1.5
Tenacity	gm/denier	3.5	2.7	2.9	23	35 -45
Breaking Elongation	%	15	27	21	3	3-4
Specific Gravity	--	1.29	1.4	1.37	1.44	0.97
Moisture Regain	%	20	15	8.2	4	<1.0
Limiting Oxygen Index (LOI)	%	90	41	29	29	<20
Thermal Conductivity	W/m.K	0.05	0.04	0.25	0.04	20
Colour	--	Red-brown	Golden	Raw white	Yellow	White

Application:

- Fire Fighting Suit
- Temperature Resistant Hand Gloves
- Thermal Blanketing

GHARDA
Polymer SBU

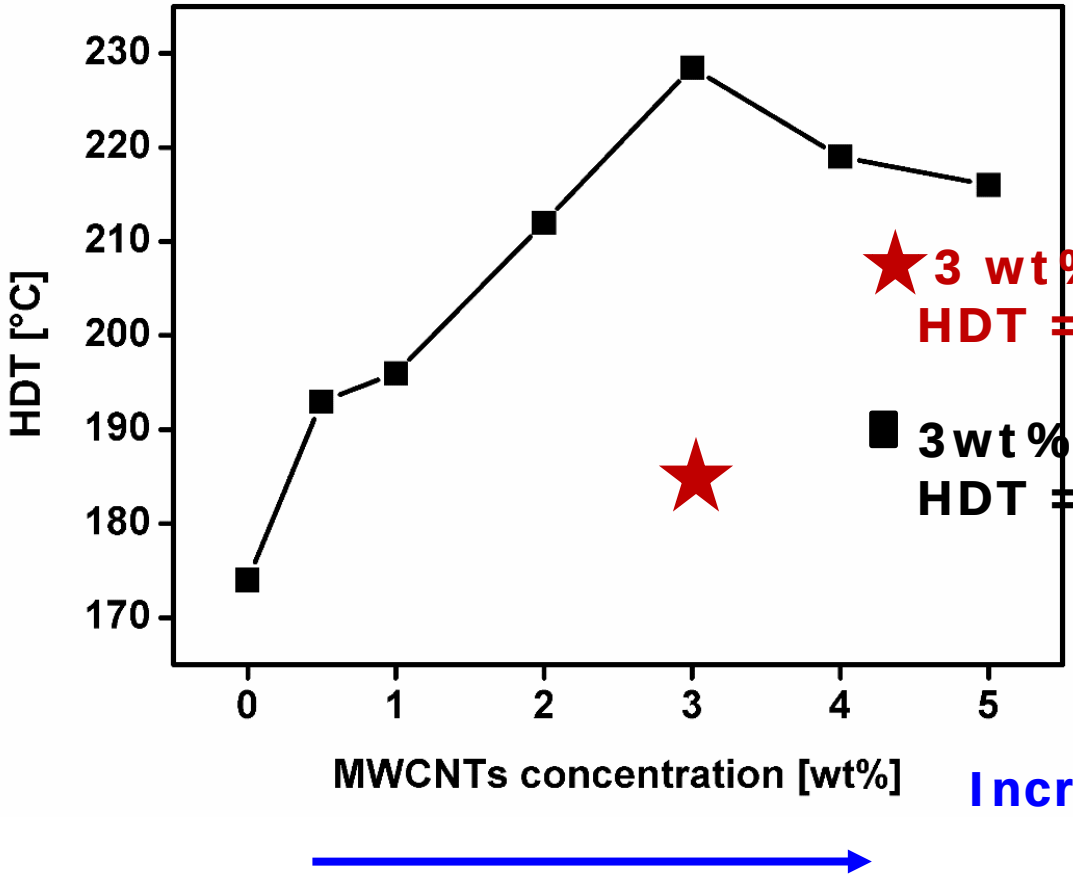
Wear Study- COF at PV Limits

PV (MPa.m/s)	GAZOLE 6430FC (PEK/ABPBI)	CELAZOLE TL 60 (PEEK/PBI)	G-PAEK 1230FCT	TORLON 4435	TORLON 4275	VESPEL SP21
Coefficient of friction μ at 1.5- 2.5 m/s						
18.64	0.08	0.12	0.10	0.12	0.14	Failed
23.30	0.08	0.14	NA	0.09	-	-
27.97	0.07	0.11	0.08	0.07	-	-
32.62	0.06	0.12	0.08	-	-	-
37.29	0.06	0.11	0.07	-	-	-
41.94	0.06	0.10	0.10	-	-	-
55.93	0.05	0.11	-	-	-	-
62.91	0.05	-	-	-	-	-

Heat Deflection Temperature of composites

Method :ASTM D 648

PEK/ABPBI blend+ 3 wt% MWCNTs (Arkema Graphistrength) composites showed 31% increase in HDT over pure blend



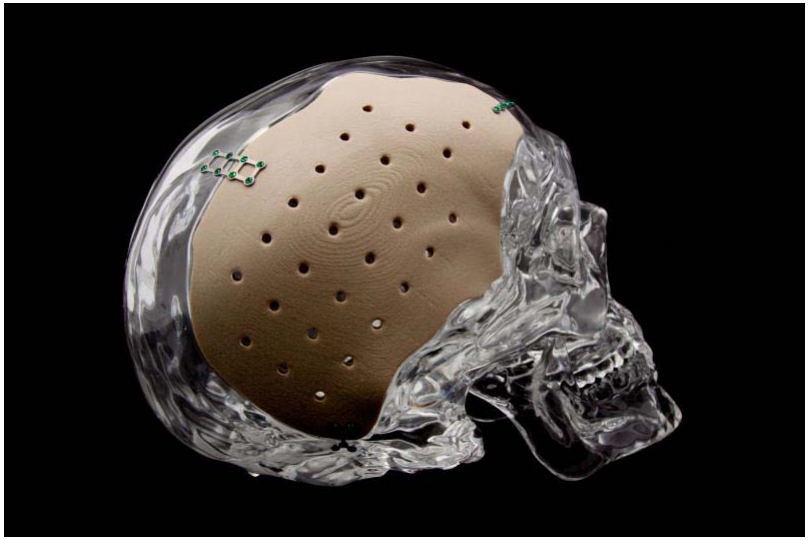
Increase in HDT by 24-31%

Indian Patent has been filed in 2018

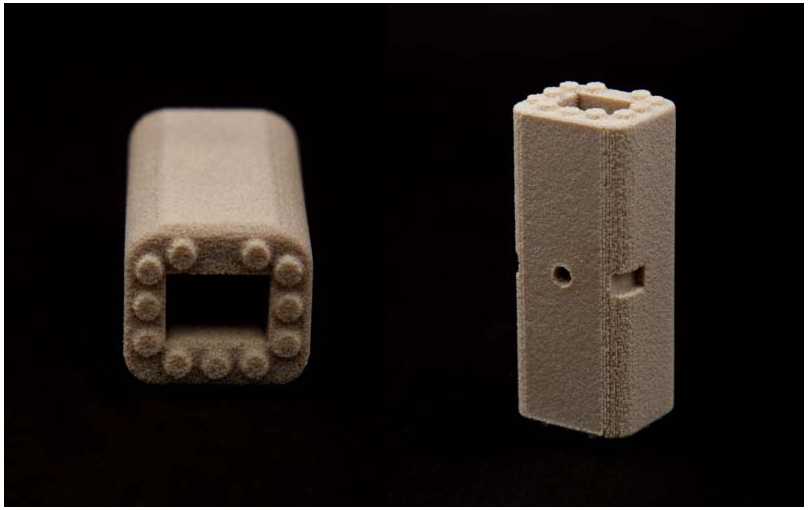
PEKK & PEK APPLICATIONS

- **Off-Shore Application**
  - **Refining**
  - **Cracking**
  - **Oil Drilling**
- **Submersible Pumps**
  - **Dewatering/ mining/ high depth pumps**
- **Friction & Wear parts**
- **Automotive**
- **Nuclear**
- **Food Industries**
- **Semicon**
- **Textiles**
- **Medical Implants & Devices.**

3 D PRINTING APPLICATIONS OF PEKK - 60:40 IMAGES OF IMPLANT & AEROSPACE APPLICATIONS

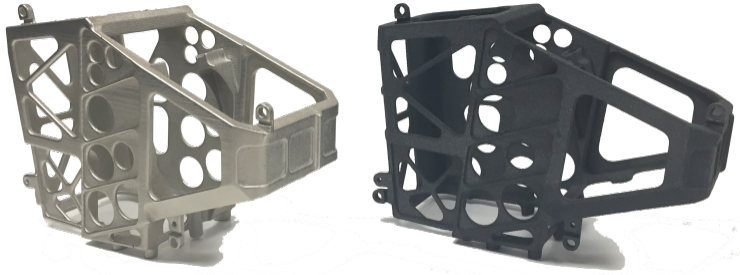


PEKK Patient-Matched Cranial Implant



3D printed spinal implants

Ni Plated Fan Exit Guide Vane

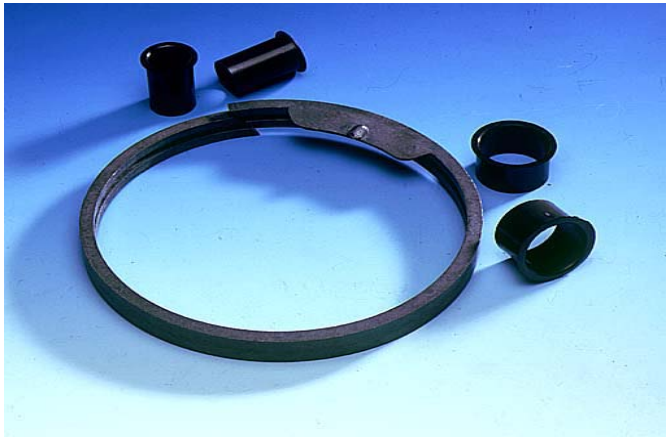


Aerospace Components

Complex Structural Component for Boeing CST-100 Starliner

PEKK & PEK
OFF-SHORE APPLICATIONS

- **Piston Rings & Bushings**
  - **High pressure, High temperature, corrosive gases and chemicals**
  - **Lubricated and wear grades of PEKK / PEK used.**



PEKK Stock Shapes
Rods & Plates

PEKK 70:30 BASED COMPOSITES

Glass fiber composites using PEKK 70:30

Thick fuselage airplane parts

PEK – MEDICAL DEVICES

Key Benefits of PEK Laparoscopic Grasper:

- Outstanding stability upon exposure to radiation
- Design freedom.
- The resistance most chemicals and gasses
- Light in weight
- Very high heat resistance
- Low water absorption
- High dimensional stability
- Good electrical characteristics
- Excellent hydrolytic stability

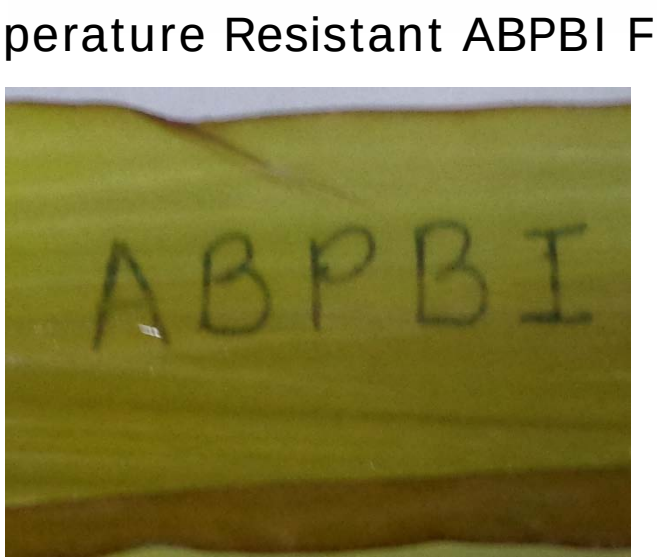
- Orthopedic tools
- Inhaler housing
- Laproscopy tool handles
- Twizer insulation coatings

GHARDA
Polymer SBU

ABPBI Fiber

ABPBI Fiber

Temperature Resistant ABPBI Fiber Gloves



ABPBI Film

12 NATIONAL AWARDS FOR GCL POLYMER

- Sir P. C. Ray Awards for Technology Development: 1998, 2001, 2005, **2012**, **2019.**
- Plasticon Awards for New product Development:1999, 2002, 2005, **2012, 2015**.
- FICCI Award for Novel Product Development: 2005.
- Ministry of Chemical of Chemical & Fertilizer Innovative Product Award: **2012.**

Research & Application Development Centre

Gharda Institute of Science and Technology (GIST), Mumbai, Maharashtra, INDIA

Authors acknowledge and thank
Dr. K. H. Gharda, Chairman &
MD of Gharda Chemicals Ltd. for
permission to present this work.

THANK YOU!

FIRST 3D PRINTED PART : PEKK

GHARDA
Polymer SBU

GAPEKK UNFILLED GRADES

PROPERTIES	UNIT	TEST METHOD / CONDITIONS	PEKK (100/0)	PEKK (80/20)	PEKK (70/30)	PEKK (60/40)
Tm	^{0}C	DSC	395	365	335	305
Specific Gravity	-	ASTM D 792	1.30	1.29	1.29	1.27
Tensile Strength	MPa	ASTM D 638	110	112	110	88
%Elongation at break	%	ASTM D 638	10	20	20	80
Tensile Modulus	MPa	ASTM D 638	4200	3800	3800	2900
Flexural Strength	MPa	ASTM D 790	200	171	168	128
Flexural Modulus	MPa	ASTM D 790	4200	3900	3900	3000
Compressive Strength	MPa	ASTM D 695	160	152	149	108
Compressive Modulus	MPa	ASTM D 695	NA	3800	3800	3000
Impact Strength (Notched)	J/m	ASTM D 256	50	50	45	45

Mechanical Properties at High Temperature - GAPEKK UNFILLED GRADES

(PEKK T/I Ratio 100/0)

PROPERTY	UNIT	TEST TEMPERATURE (°C)					
		25	100	150	200	250	300
Tensile Strength	MPa	100	83	60	37	28	22
Elongation at Break	%	4	4	38	60	60	60
Flexural Strength	MPa	193	143	84	26	19	11
Flexural Modulus	MPa	3900	3470	2690	340	267	125
Compressive Strength at 10% Strain	MPa	130	98	81	30	20	14
Compressive Strength highest value	MPa	130	104	85	40	32	25
Compressive Modulus	MPa	1900	1730	1390	360	240	165

G-PAEK™ PEK Vs. PEEK

Properties	Conditions/ Test Method	Unit	G-PAEK 1200G	Victrex PEEK 450G
Glass Transition Temperature (Tg)	Onset, ASTM D 3418	°C	**157**	143
Melting Point (Tm)	ASTM D 3418	°C	**374**	343
Tensile Strength	ASTM D 638	MPa	110	95
Tensile Modulus	ASTM D 638	GPa	4.3	3.5
Elongation at Break	ASTM D 638, 23°C	%	20-25	30
Flexural Strength	ASTM D 790	MPa	**190**	156
Flexural Modulus	ASTM D 790	GPa	4.2	4.1
Izod Impact Strength	ASTM D 256	J/m	50	55
Rockwell Hardness	ASTM D 785	M Scale	103	99
HDT	ASTM D 648, 1.8 MPa	°C	**167**	152

Mechanical Properties at 23°C- PEK Glass Filled Grades

PROPERTIES	UNIT	TEST METHOD	G-PAEK 1220GF	G-PAEK 1230GF	G-PAEK 1460GF
Specific Gravity	-	ASTM D 792	1.45	1.54	1.85
Tensile Strength	MPa	ASTM D 638	140	180	190
%Elongation at break	%	ASTM D 638	4	4	3
Tensile Modulus	MPa	ASTM D 638	10000	13000	27000
Flexural Strength	MPa	ASTM D 790	220	280	220
Flexural Modulus	MPa	ASTM D 790	10000	14000	27000
Compressive Strength	MPa	ASTM D 695	-	150	-
Impact Strength (Notched)	J/m	ASTM D 256	40	60	70
Rockwell Hardness (M scale)	-	ASTM D 785	-	90	-

GHARDA
Polymer SBU

ABPBI Fiber Spinning

- **ABPBI can be produced as powder for alloying and molding, as fiber or film by wet spinning process.**

Properties of ABPBI:

1. **Glass Transition Temperature (Tg) is 485ºC (molded sample).**
2. **Insoluble in most solvents.**
3. **Highest LOI (>90%)**
4. **High moisture regain (20%), making the clothing comfortable to wear.**
5. **Very high abrasion resistance.**
6. **Very High Initial Decomposition Temperature (IDT) 550°C in air**
7. **Low Density of 1.29 gm /cc**
8. **Low smoke density.**