Leading High Heat-resistant Polymers Vie for a Spot in the Top 10

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Introduction

Automotive, business machinery, industrial equipment, chemical industry, aerospace, fiber industry and semiconductor equipment applications are more and more demanding unique balances of thermal, mechanical, electrical, chemical, optical and tribological properties for outstanding performance parts. Some specialty polymers offer peak or long term thermal resistance exceeding 250°C, excellent mechanical strength and toughness, dimensional stability, low outgassing, resistance to hydraulic, automotive, and many industrial fluids and solvents, low coefficient of thermal expansion, creep resistance, and into the bargain flame retardancy, radiation resistance.

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These outperforming polymers are excellent replacements for metals, ceramics, and others allowing to manufacture a broad range of parts such as thrust washers and oil seal rings for automotive and off road vehicle transmissions, thermal insulators and stripper fingers for high-speed copiers, jet engine components, check valve balls, spline couplings, heat-resistant gears, vanes, wear strips, and valve seats, carriers for aluminium hard disks and silicon wafers, journal bearings, and bearing retains, super fibers for bullet-proof fabrics, shields, helmets or micro-asteroid shields etc.

Among the more or less well-known specialty high heat polymers, we can quote PBI, Polyimides and derivatives such as melt processable TPIs and Polyamide-imides (PAI), PEEK (polyetheretherketone), Polybenzoxazole (PBO), some Liquid Crystal Polymers (LCP), Polyphenylene sulfide (PPS), alloys of PBI and PEEK or TPI and PEEK, Perfluorinated polymers (PTFE, FEP PFA), silicones, special versions of Epoxies, Polysulfones, Polycyanates etc.

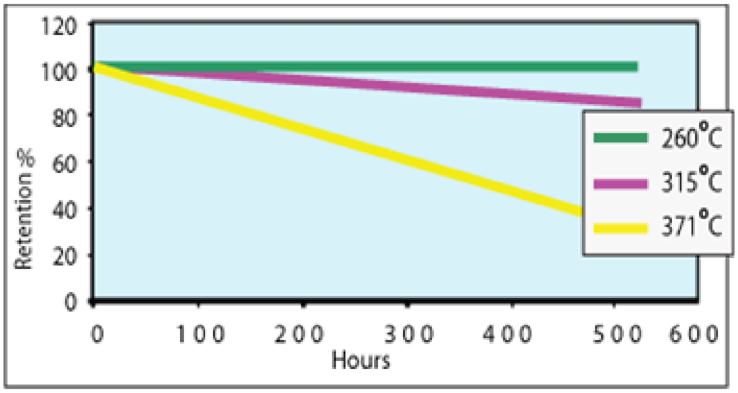
Many other chemical entities are developing for special applications such as, for example Hyflon® MFA resins, Ultrason® E Dimension and EpiSpire® HTS-2620, Araldite® benzoxazine thermoset resins, polyetheramide (PEAR) thermoset resins, Fluorinated poly(imide-ether-amide), polyquinoxalines, Phthalonitrile thermoset resins, poly(phthalazinone ether ketone), poly(phthalazinone ether sulfone), and poly (phthalazinone ether sulfone ketone), Benzocyclobutene (DVS-BCB), derivatives of bisoxazolines and formaldehyde-free phenolic novolacs, Phenolic Triazine (PT), poly-para-phenylene copolymers, polyhydroxyamides (PHA)…

What is the problem?

High temperatures have immediate and delayed effects. Modulus and strengths immediately decrease by softening but in addition the fall speeds up with time. Chemical structure is more or less rapidly damaged leading to a chemical decomposition and a brittle structure.

This time dependent phenomenon can take from a few minutes up to years according to the temperature and the polymer compound. Antioxidants and other heat stabilizers can slow down the degradation.

The following Figure 'PBI compression strength retention' shows the retention of compression strength for a PBI after ageing up to 500 hours in hot air. The half life is about 500h @ 371℃ but the degradation is undetectable after 500h @ 260℃



PBI Compression strength retention

The immediate softening can be more or less hidden by reinforcement with carbon or mineral fibers. Requirements for thermal resistance varying with the applications, it isn't possible to define precisely the properties of 'High Heat Resins'. For example, requirements can be as diversified as:

- High strength and modulus retention during short temperature peaks
- High HDT during short high temperature expositions
- Fair strength and modulus retention after long high temperature expositions
- Moderate heat resistance combined with another functional property such as transparency, fire resistance, electrical behaviour etc.

The unbeatable but difficult-to-process champions: Polybenzimidazole (PBI) and conventional polyimides

TOP

Polybenzimidazole (PBI) by PBI performance Products is an infusible thermoplastic, perhaps, the most advanced polymer from thermal and mechanical points of view (see Table 1) but on the other hand processing is the monopoly of its producer.

PBI is handicapped by a high cost justified by the performances, unsuitability of conventional processing methods, slow long-term moisture uptake, lack of sources and grades.

Potential applications are in high-tech sectors only: aircraft and aerospace, semiconductor, and vacuum industries, electricity and electronics for high heat bushings, valve seats, ball valve seats, contact seals, insulator bushings…; Thermal isolators, high heat insulator bushings for hot runner plastic injection molds…; Guide rollers…; Semiconductor industry, vacuum chamber applications, clamp rings and wafer retaining rings for gas plasma etching, vacuum tips…, Wafer carriers…; Connectors for aircraft engines…; Filaments and fibers; Vacuum cups, fingers and holders for incandescent and fluorescent light bulbs…

Property	Value
Rockwell hardness, M	>125
Tensile strength, MPa	140-160
Tensile modulus, GPa	5-6
HDT A (1.8 MPa), ℃	427-435
Continuous use temperature, ℃	260
Short term use temperature, ℃	425
Glass transition temperature, ℃	400-425
Oxygen index, %	58

Table 1. PBI: Examples of properties

The polyimide resins are obtained in two ways:

- Condensation polyimides or SP-polyimides: Despite the thermoplastic form they are infusible and generally insoluble. Consequently, the producer can only mold this type. It is particularly convenient for the manufacture of thin parts and films, coatings…

- BMI or aminobismaleimides or addition polyimides are particularly convenient for the manufacture of thick parts.

All these polyimides are thermostable (see Table 2). They do not melt before decomposition at high temperature. In thermogravimetric analysis, the decomposition starts at over 400 °C.

	Condensation polyimides			Thermosets	
	Neat	30% glass fiber reinforced	30% carbon fiber	Neat	Glass fiber reinforced
Density, g/cm^3	1.33 to 1.43	1.56	1.43	1.4 to 1.5	1.5 to 1.9
Rockwell hardness, M	92 to 102	104	105	110 to 120	115 to 126
Tensile strength, MPa	70 to 140	168	233	30 to 160	40 to 160
Elongation at break, %	8 to 9	3	2	1	0.5 to 1
Tensile modulus, GPa	2 to 3	12	21	3 to 10	7 to 32
HDT B (0.46 MPa), °C	>250	>250	>250	>300	>300
HDT A (1.8 MPa), °C	235 to 300	242	247	>300	>300
CUT unstressed, °C	180 to 250	180 to 250	180 to 250	180 to 250	180 to 250
Glass transition, °C	315				300
Oxygen index, %	44 to 53				36 to 44

CUT: Continuous use temperature

Table 2. Polyimides: Examples of properties

The following figure 'Vespel parts' shows very different parts made out of Vespel polyimides by DuPont.

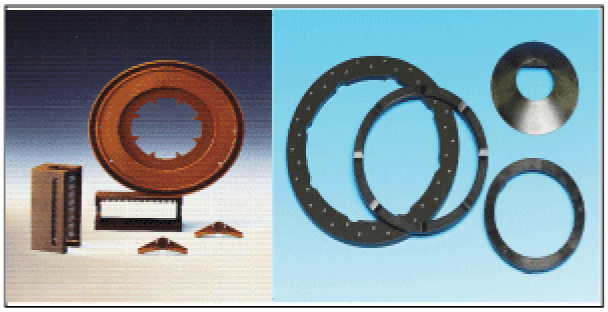


Figure 'Vespel parts' (DuPont gallery)

Polyimides continuously evolve. For example, the DuPont's new family consists of three compositions Vespel® SCP-5000 (unfilled), Vespel® SCP-5050 and SCP-50094 using new filler technologies for lower friction and enhanced wear resistance. All compositions have exceptional high-temperature capabilities, are stronger at ambient and elevated temperature and excel in dimensional stability.

Vespel® SCP-5000 parts have the highest strength retaining 50% of their original strength in ageing tests at 370° to 430° C. They have also outstanding dielectric properties over wide temperature and frequency ranges.

A smart answer to processing difficulties of polyimides: Melt processable TPIs

TOP

Two companies, Mitsui Chemicals and SABIC Innovative Plastics, commercialize TPIs with different balances of properties (see Table 3).

AURUM by Mitsui Chemicals are high-performance polyimides for precision injection molded components and extruded products using most reciprocating screw injection molding machines. Carbon fiber reinforced grades offer a unique balance of mechanical, thermal, and tribological properties for outstanding performance in demanding automotive, business machinery, industrial equipment, aerospace, and semiconductor equipment applications. AURUM components offer mechanical strength and toughness, dimensional stability, high oxygen index, low outgassing, and high radiation resistance. In addition, AURUM exhibits outstanding resistance to hydraulic, automotive, and many industrial fluids and solvents, a low coefficient of thermal expansion, creep resistance, and flame retardancy. AURUM JCF3030 withstands high PV levels and provides a low wear factor and low friction surface over a broad temperature range in lubricated environments.

After Peter Catsman, Global Product Marketing Leader, SABIC Innovative Plastics, High Performance Products "EXTEM resins are not only a major technological accomplishment in themselves, but more importantly, represent a new era in extended-use, high-temperature thermoplastic performance. EXTEM resins give customers a completely new option for replacing metals, ceramics and thermosets which are complicated to process and can add cost and weight. With EXTEM resin technology, SABIC Innovative Plastics is meeting an important market need for a true high-heat continuous use thermoplastic resin technology with a near-perfect balance of properties." EXTEM is an amorphous polymer with similar processability but much greater heat resistance than Ultem polyetherimide with a continuous-use temperature up to 230°C.

EXTEM resins are currently available as unfilled grades; Glass fiber-, mineral- and carbon-fiber-filled versions. The materials can be readily injection molded and extruded. Potential applications include semiconductor parts (seals, pick-up systems), electrical components (connectors, wire and cable), industrial parts (bearings, gears, bushings) and transportation composites and connectors.

A third family will offer up to three times more impact strength with the same flowability and heat resistance as the current materials.

		Unfilled	Carbon fiber reinforced	Glass fiber reinforced
Specific gravity		1.44	1.42-1.44	1.56
Tensile strength	MPa	70-107	170-229	165
Modulus	GPa	3	10-17	9.5
Melt point	°C	388	388	
Glass transition	°C	250	250	250
HDT	°C	238	246-248	

Table 3. Melt-processable thermoplastic polyimides (TPI): Examples of properties

Polyarylketones (PEEK, PAEK, PEK): Easier to process but a little less heat resistant

TOP

Polyarylketone family comprises three main chemical entities:

- Polyetheretherketones - PEEK
- Polyaryletherketones - PAEK
- Polyetherketones - PEK

Polyarylketones (see Table 4) are appreciated for their mechanical, chemical and electrical properties, high service temperatures (250°C), rigidity, good creep behaviour, wear resistance, endurance in fatigue, fair shrinkage and moisture uptake, high purity of special grades, high-energy radiation resistance, possibility of food contact. They are handicapped by light and UV sensitivity requiring an efficient protection for outdoor exposure, the cost justified by the performances, sometimes an insufficient fire resistance but special grades are marketed.

	PEEK 30% GF		PEEK 30% CF		PAEK	
	Mini.	Max.	Mini.	Max.	Mini.	Max.
Rockwell hardness, M	70	100	70	100	55	98
Tensile strength, MPa	150	180	200	220	85	100
Tensile modulus, GPa	9	10	13	30	3.5	4
HDT B (0.46 MPa), °C	>300	>300	323	323	250	300
HDT A (1.8 MPa), °C	290	315	315	320	160	170
Continuous use temperature, °C	250	250	250	250	250	250
Glass transition temperature, °C	143	143	143	143		

Table 4. Polyarylketones: Examples of properties

The following figure 'VICTREX® PEEK™ Parts' shows very different parts made out of Victrex PEEK (Victrex gallery).

Main and targeted applications include:

Figure 'VICTREX®-PEEK™ Parts' (Victrex Gallery)
CMP Retaining Rings (L); Oak Ridge National Laboratory Cooling Jacket (R)

- **Industry:** Impeller wheels for regenerative pumps, pump rotors, multi-pin connectors, glue gun bushings, quick coupling systems, laundry system wheels, conductivity sensors, seals, compressor valve plates, heat exchanger parts…
- **Automotive:** Piston components, seals, washers, bearings, transmission components, transmission thrust washers, braking and air-conditioning systems, ABS brake systems, engine control systems, truck oil screens, starting disks in bus gears, linings…
- **Electrical engineering:** Wire insulation for extremely high temperature applications, cable couplings and connectors, sub-sea connectors, coaxial connector jacks, sub sea controlled environment connectors, wafer wands, wafer transport carriers, surface-mounted trimming potentiometers, appliance handles, cooking equipment…
- **Aircraft:** Airbus interior components, bow-shaped luggage compartment retainers; Cable conduits, cable clips, ventilation wheels inside aviation fans, suction manifold of aviation pumps; Electrical wire harnesses isolated by monofilaments, sleeves; Convoluted tubing, wire insulation, pump casings and impellers…
- **Medicine:** Prosthetics, surgical and dental instruments (up to 3000 autoclave sterilization cycles), haemodialysers, dialysis machine components…
- **Food processing equipment:** Automatic espresso machines, high-tech coffee machines, food pump seals, beverage bottling components…
- **Monofilaments:** woven products for filters, belting and meshes…
- **Films:** Submersible pump insulation, dry transformer insulation, flexible surface heaters, speaker cones and coils, oil field pipe flanges and gaskets, specialty laminates, composite adhesive films, high temperature labels, IC packaging (HDD) trays…

Interesting compromises: Alloys of PBI or TPI and PEEK

TOP

Supplied by PBI Performance Products, CELAZOLE® T-series and by Victrex ,VICTREX-T series PBI/PEEK alloys (see Table 5) combine the superior mechanical properties and thermal resistance of PBI with the melt process ability of polyaryletherketones (PEEK). These cost-effective high-performance products are designed for injection molding and extrusion.

	PBI/PEEK	TPI/PEEK
Tensile strength, MPa	98-175	70-147
Tensile modulus, GPa	5-24	3-10
HDT B(0.46 MPa), °C	>305	>220-250
HDT A(1.8 MPa), °C	305	220-250
Continuous use temperature, °C	>250	

Oxygen index	45

Table 5. Alloys: Examples of properties

- The unfilled melt processable PBI/PEEK blend offers excellent mechanical properties, high modulus, thermal and fatigue resistances. This general-purpose high performance product offers the best process ability and is most suitable for complex geometries.
- The carbon reinforced PBI/PEEK blend offers superior strength, high modulus, excellent heat resistance, superior wear resistance and low creep at high temperatures. It is also static dissipative and is highly suited for semiconductor, electronic, and mechanical applications.
- The glass reinforced melt processable PBI/PEEK blend offers thermal and electrical insulation, wear resistance, and very high dimensional stability. It makes an excellent high temperature electrical insulator, and is also an excellent choice for parts requiring minimal thermal expansion.
- A self lubricated melt processable PBI/PEEK blend offers superior wear resistance and low friction, chemical resistance and high load bearing capability. It is particularly well suited for thrust bearings, seals, and washers where a superior low wear rate and a low running temperature maximize equipment lifetime in chemical, petrochemical, and moving part applications.

Figure 'Extem electronics resins'
SABIC Innovative Plastics

By incorporating polyetheretherketone (PEEK) into its proven ultra-performance Extem resin technology, SABIC Innovative Plastics is able to offer customers optimized performance combining the best of both materials (see Table 5 and Figure 'Extem electronics resins' courtesy SABIC Innovative Plastics). New flame-retardant EXTEM UP thermoplastic polyimide (TPI) resins are extreme high-heat materials that recently achieved a UL746B relative temperature index (RTI) rating of 240°C. This unique blend technology opens new opportunities for lower-weight, high-temperature continuous use applications such as semiconductor chip trays, connectors for harsh environments, and metal replacement in high-heat oil and gas, and aerospace environments.

EXTEM UP resins combine the best features of semi-crystalline PEEK, including excellent chemical and wear resistances and high flow, with the advantages of a high glass transition temperature amorphous material, including mechanical strength/stiffness, dimension stability and creep resistance at high temperatures.

These performance properties allow customers to design parts with greater freedom and efficiency, achieve higher strength and stiffness using thinner walls to reduce material weight and costs, and provide tighter dimensional control for high-precision applications.

Targeted applications include semiconductor manufacturing, telecommunications, and electrical/electronics, down-hole oil and gas production equipment, bearings, and gears.

An innovative chemical way for polybenzoxazole (PBO) family (Zylon)

TOP

Toyobo Corporation commercializes a range of polyphenylenebenzobisoxazole under the trademarked ZYLON name for a range of thermoset liquid crystalline polyoxazoles. The following Table 6 displays some properties of fibers and films:

		Fibers	Film
Curing			250°C - 60 min or 285°C - 45 min
Density	g/cm^3	1.55	
Tensile strength	MPa	5800	122
Tensile modulus	GPa	180-270	2
Elongation at break	%	2.5-3.5	10-17
Melting temperature	°C	none	
Decomposition temperature in air	°C	650	
Glass transition	°C		257-280
Limiting oxygen index	%	68	

Table 6. Zylon fibers and films: Property examples

Zylon is used in a number of applications that require very high strength with excellent thermal stability such as tennis racquets, table tennis blades, drive belts for snow mobiles, various medical applications, and some of the Martian rovers, webbings, cords, and tapes, crew equipment, space suits, shield applications…

Evelyne Orndoff (Lyndon B. Johnson Space Center Houston, Texas) 'Development and Evaluation of Polybenzoxazole Fibrous Structures' compare PBO and polyamide structures (see Table 7) such as webbings, cords, and tapes. Similar structures have been used extensively for crew equipment, space suits, and many other systems in the space programs. Other structures are being developed and evaluated for debris and micrometeoroid shield applications, as well as blended structures. Like most polymers, PBO and Kevlar are sensitive to light. After 450 hours of exposure to 340nm wavelength, PBO webbing has lost over 98% of its tensile strength.

		PBO	PI	PBO	PI
Weight	oz/yd	0.75	0.77	0.06	0.062
Width	in	1.75	1.75	0.125	0.125
Thickness	in	0.027	0.032	0.125	0.125
Breaking strength	lbs	8995	4173	890.8	469.2
Elongation @ break	%	11.5	7.7	10	4.9
Stress at max. load	250	182773	75710	72590	60050
Abrasion resistance	% change	68.7	85.1	83.9	98.7
Oxygen index	%	74-78	31-35	56-64	30-34

Table 7. PBO and PI structures : Examples of properties

KUROKI T.; TANAKA Y.; HOKUDOH T.; YABUKI K. (*Journal of Applied Polymer Science*, 1997, vol. 65, no5, pp.1031-1036) study the high temperature properties of Poly(p-phenylene-2,6-benzobisoxazole) (PBO) fibers. The PBO fiber has 100℃ higher decomposition temperature than the p-Aramid fiber, and the amount of toxic gases in combustion is smaller. Although the relative strength decreased proportionally in the range of room temperature up to 500℃, the PBO fiber at 500℃ retains 40% of the strength at room temperature. After thermal treatment at 500℃ for 60s, the PBO fiber retains 90% of its original strength.

Polyamide-imide (PAI): A melt processable cousin of polyimides

TOP

Polyamide-imides (see Table 8) are appreciated for their Good mechanical and electrical properties, high service temperatures (up to 220℃ with possible long times at 260℃), rigidity, good creep behaviour, fatigue endurance, low shrinkage and moisture uptake, inherent flame retardancy, chemical resistance, usable down to -196℃. Polyamide-imides can slowly absorb some water in wet environment, which has a plasticizing effect and can lead to a significant linear expansion.

	PAI		PAI 30% glass fiber		PAI carbon fiber	
	Mini.	Max.	Mini.	Max.	Mini.	Max.
Rockwell hardness, M	86	100	95	110		
Tensile strength, MPa	130	195	105	210	203	203
Tensile modulus, GPa	4.2	5	11	15	22	23
HDT B (0.46 MPa), ℃	>280	>280	>280	>280	>280	>280
HDT A (1.8 MPa), ℃	278	278	280	280	282	282
Continuous use temperature, ℃	220	220	220	220	220	220
Glass transition temperature, ℃	275	275	275	275	275	275
Oxygen index, %	45	45	51	51	52	52

Table 8. PBI: Polyamide-imide: Examples of properties

Industrial and targeted applications include non-lubricated bearings, seals, bearing cages, rotating and sliding components for automotive and industry, bushings, seal rings, wear pads, piston rings, balls for bearing for America's cup yachts, hook joints for transmission seal rings, tag axle assembly of cement trucks and heavy vehicles, vanes in air motor, reciprocating compressor parts, gears, valve plates, intake valves, impellers, rotors, material handling components, terminal strips, insulators, ESD for integrated circuits, hard disk drives, circuit boards, parts for high speed electronic printing and reproducing equipment, burn-in sockets; fibers for heat and fire protection, clothing for fighter pilots, army and police forces; smoke filtration…

High heat liquid crystal polymers (LCP): Self-reinforcement into the bargain

Liquid crystal polymers (LCP), aromatic polyesters being the most common type, are crystalline in the molten state and highly crystalline after cooling. These thermotropic (melt-orienting) thermoplastics are subject to a molecular alignment under processing shear stresses, which leads to a self-reinforcing effect, the polymer's rod-like macromolecules acting like reinforcing microfibers. Consequently, mechanical properties (see Table 9) are optimized in the orientation direction.

	Neat high temperature LCP		30% GF		30% carbon fibers	
Rockwell hardness, M	40	40	<20	40	80	100
Tensile strength, MPa	140	140	117	182	158	241
Tensile sodulus, GPa	10	10	12	15	28	37
HDT B (0.46 MPa), °C	310	310	>250	310	250	310
HDT A (1.8 MPa), °C	275	275	250	284	220	275
Continuous use temperature, °C	200	200	200	240	200	200
Melting temperature, °C	325	325	320	360	280	330
Oxygen index, %			37	48		

Table 9. LCP: Examples of properties

The following figure 'VECTRA LCP parts' shows very different parts made out of Vectra LCP (Ticona gallery).

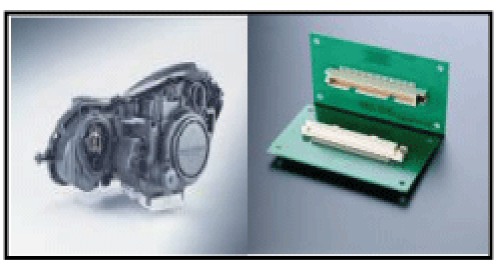


Figure 'VECTRA LCP parts' (Ticona Gallery)
Mercedes-Benz (left); JAE Connectors (right)

Silicones: The most versatile family

Silicone family is the most versatile family including very soft elastomers up to hard resins with a very good stability of the properties (see Table 10) on a broad range of temperatures, long-term heat stability, low-temperature flexibility, good electrical properties, light and weathering behaviour, resistance to various chemicals especially for the fluorosilicones, water repellence, possibility of transparency, physiological inertia of suitable grades. Limitations come from mechanical properties, low rigidity of the majority of the grades, limited resistance to the bases and strong acids, poor behaviour with numerous solvents.

	Silicone resins for electronics	Silicone laminates	Silicone elastomers	Silicone RTV
Density, g/cm^3	1.8 to 1.9	1.8 to 1.9	1.1 to 1.7	1.1 to 1.5
Hardness	40 to 50 Sh D	105 Rw M	30 to 80 Sh A	8 to 70 Sh A
Tensile strength, MPa	25 to 35	140	3 to 12	<1 to 7
CUT unstressed, ° C	<260	220	200 to 300	110 to 260
Peak temperature, °C	350	>250	>250	<260 to 315

Table 10. Silicones: Property examples

The applications are always specific but concern all the industrial sectors for seals, joints, cables, insulators, coated fabrics, profiles, cements used in Building and civil engineering, Electricity & Electronics, Optoelectronics; Electric household appliances, Mechanical industry, Tools for molding and casting, Medical, health, food appliances, Aeronautics, Automobile and Transport, Office Automation…

PPS: A "General Purpose" family of high heat polymers

Polyphenylene sulphides are appreciated (see Table 11) for their good mechanical and electrical properties, rigidity, creep behaviour, endurance in fatigue, low shrinkage and moisture uptake, broad range of service temperatures (-196 up to +200/240°C), weathering resistance, good chemical resistance, fire resistance, suitability for food contact of special grades.

	PPS 20 to 30% GF reinforced		PPS 40% GF reinforced		PPS 20% carbon fibers	
	Mini.	Max.	Mini.	Max.	Mini.	Max.
Rockwell hardness, M	80	103	100	104		
Tensile strength, MPa	130	150	120	150	180	180
Elongation at break, %	1	2	1	4	2	2
Tensile modulus, GPa	6	11	8	14	17	17
HDT B (0.46 MPa), °C	270	278	270	280	>260	>260
HDT A (1.8 MPa), °C	250	260	260	270	260	260
Continuous use temperature, °C	200	240	200	240	200	240
Glass transition temperature, °C	88	93	88	93		
Melting temperature, °C	275	290	275	290		
Oxygen index, %	25	32				

Table 11. PPS: Property examples

The global consumption can be approximately divided into three main sectors: 50% for automotive & transport, 30% for E&E, 15% for industry:

- **Automotive and transportation:** Exhaust gas return valves, carburettor parts, fuel lines, ignition plates, pump rotors, flow control valves for heating systems, heat exchange elements, cases, reflectors…
- **Electrical & Electronics (E&E):** Connectors, terminal blocks, relay components, switch components, coil formers, bobbins, molded bulb sockets for electrical power station, thermostat parts, halogen lamp housings, control panels, plates on terminals, brush holders, motor housings, electrical appliance and PC brackets, components for floppy disk drive, parts for heaters, grids of hair dryers, parts of domestic irons, coffee machines, microwave ovens, cooking appliances…
- **Industry:** Thrusters of pumps, hot water pumps, bearings (PTFE lubricated), precision parts for mechanical and regulation components, sterilizable medical, dental and laboratory equipment, hair dryer grills and components, cutting heads for electric shaves, air outlet grilles for microscopes…

Perfluorinated polymers: PTFE, the most commonly used and PFA, the melt processable

Polytetrafluorethylene or PTFE is the most commonly used, the best known and, perhaps the most performing with an excellent ratio performances/cost. Its main drawback is the impossibility to process it by conventional methods in a molten state.

PFA is very near PTFE with very similar properties but is melt processable and more expensive. FEP is also melt processable but is not so performing.

Perfluorinated polymers are appreciated (see Table 12) for their exceptional chemical resistance, very good resistance to heat and low temperature; very good electrical insulating properties even in hot and wet environment, good resistance to light, UV and weathering; low coefficients of friction, strong anti-adhesion properties; flexibility, good fatigue resistance under low stresses, fire resistance but beware of toxic fumes; food, medical and high purity grades, very low water absorption. PFA can be processed by injection and extrusion and offers the same advantages as PTFE.

FEP can also be processed by injection and extrusion and offers the same advantages as PTFE but with a lesser degree. The upper service temperature is not so good, roughly inferior by 50°C.

	PFA		PTFE		PTFE glass fibers	
	Mini.	Max.	Mini.	Max.	Mini.	Max.
Rockwell hardness, M	< 20	< 20	< 20	< 20	< 20	< 20
Tensile strength, MPa	27	30	19	21	7	20
Elongation at break, %	300	300	250	300	250	260
Tensile modulus, GPa	0.6	0.8	0.3	0.7	1	1.7
HDT B (0.46 MPa), °C	70	75	70	70	125	125
HDT A (1.8 MPa), °C					110	110
Continuous use temperature, °C	240	260	205	205	180	260
Melting temperature, °C	305	305	275	275		
Oxygen index, %	95	95	95	95	95	95

Table 12. Perfluorinated thermoplastics: Examples of properties

The following figure 'Teflon Hoses' shows hi-tech hoses made out of a perfluorinated polymer, Teflon® TE 9810 by DuPont.

Perfluorinated thermoplastics are used for high-performance applications related to high heat, low temperature, chemical inertness, high purity, non-stick and self-lubricating properties. High purity grades are appreciated by semiconductor, pharmaceutical and other similar sectors. Among other applications let us quote for example:

- **Industry:** Washers, flanges, baffles, gaskets, seals, rings, encapsulation and liners, self lubricating components, bellows, valve and pump components, bearings, bushings, woven-glass composites…
- **Electricity and Electronics:** Coaxial cable connectors, terminal and high voltage insulators; transformer, relay, antenna, power amplifier components, laminates for critical microwave components, antennas and subassemblies, telecommunications…
- Films, sheets, pressure sensitive tapes and other bonding films…
- Expanded, microporous PTFE

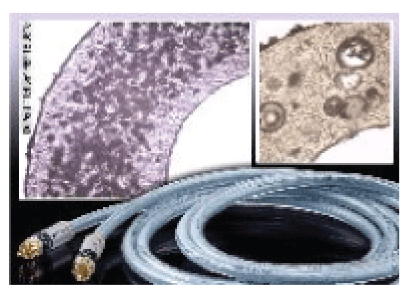


Figure 'Teflon hoses' (DuPont gallery)

Challenging polymers for the coming years

Depending on the actual requirements, a broad range of developing or emerging products can be considered. For example, without claiming to be exhaustive:

- Solvay has launched a new family of MFA resins, the Hyflon® F-Series, designed as a replacement for fluorinated ethylene propylene (FEP), with higher clarity, improved electrical properties and higher service temperature.
- New High-Temperature amorphous polysulfone (PSU) and polyethersulfone (PESU) are launched by Solvay Advanced Polymers and BASF.
  - Ultrason® E Dimension by BASF is a high-temperature resistant thermoplastic exhibiting not only very high stiffness at temperatures between 120 and 220°C, but also exceptional dimensional stability.
  - EpiSpire® HTS-2620 by Solvay Advanced Polymers is an innovative high performance grade reinforced with 20% glass fiber. It has a glass transition temperature of 265°C and a heat deflection temperature of 260°C.
- Huntsman Advanced Materials presents Araldite® benzoxazine thermoset resins with a unique combination of flame retardancy, dimensional stability, low water absorption, low dielectric constant and high temperature resistance. The products are used in composites, coatings, adhesives and encapsulants.
- Commercially available polyetheramide (PEAR) thermoset resins is derived from bisoxazolines and formaldehyde-free phenolic novolacs. The inherently tough thermoset formulations developed by Ashland Specialty Chemical Co. offer superior thermo-oxidative stability and tensile strengths.
- Fluorinated polyimide-ether-amides exhibit decomposition temperatures above 360°C and glass transition temperatures in the range of 221-246°C. The polymer films have a low dielectric constant, tough mechanical properties and are readily soluble in organic solvents like dimethylformamide (DMF), methylpyrrolidinone (NMP), pyridine or tetrahydrofuran (THF). They give flexible films by casting of such solutions.
- Certain polyquinoxalines are thermo-stable with high glass transition temperatures up to 435°C, high decomposition temperatures (510-560°C), notable oxidative resistance in air but on the other hand, they form highly viscous solutions which don't wet reinforcing fibers easily.
- Phthalonitrile thermoset resins are said to exhibit excellent oxidative and thermal stability and show no signs of glass transition at temperatures of 450°C. In addition, composite materials may be fabricated by short-term processing, either through autoclave layup, casting, resin infusion, or resin transfer molding. The mechanical properties of phthalonitrile are said to be comparable or superior to other organic polymers. For example, tensile strength of the neat resin is 80MPa.
- Under the brand name ChemphySteel, New Chemphy, a company from China, is planning to launch three materials: poly(phthalazinone ether ketone), poly(phthalazinone ether sulfone), and poly(phthalazinone ether sulfone ketone). They are claimed to exhibit high performance at temperatures of up to 250°C. Along with the associated high heat resistance, the polymers are also light and robust. Priced lower than other engineering polymers already in the market, New Chemphy aims to target markets including aerospace (jet engine fan blades), automotive (engine parts) and electronics (Liquid Crystal Displays, where it can serve as an ideal glass-replacement). The main competitive polymer it will have to push back on is PEEK in these high-end markets.
- Benzocyclobutene (DVS-BCB) polymer is proposed by Dow as an interlayer dielectric (ILD) material. CYCLOTENE advanced electronics resins are specifically engineered to meet the microelectronics industry need for extendible, integratable dielectrics. Currently, the acceptance of DS-BBC is challenged by today's thermal requirements of greater than 400°C for CD-W via/plug and post device/contact anneals.

Conclusion

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State-of-the-art industries as well as mass production markets, from aerospace up to automotive or electronics require more and more outstanding balances of thermal, mechanical, electrical, chemical, optical and tribological properties for high-performance parts. Some specialty polymers offer peak or long term thermal resistance exceeding 250°C, excellent mechanical strength and toughness, dimensional stability, low outgassing, resistance to hydraulic, automotive, and industrial fluids and solvents; low coefficient of thermal expansion, creep resistance, and into the bargain electrical property stability, flame retardancy, radiation resistance.

To offer smarter answers to application and processing issues, new polymer versions are based on existing specialty high heat polymer families such as PBI, Polyimides and derivatives such as melt processable TPIs and Polyamide-imides (PAI); PEEK (polyetheretherketone), Polybenzoxazole (PBO), High Heat Liquid Crystal Polymers (LCP), Polyphenylene sulfide (PPS), alloys of PBI and PEEK or TPI and PEEK, Perfluorinated polymers (PTFE, FEP PFA), silicones, special versions of Epoxies, Polysulfones, Polycyanates etc.

Many other chemical entities are developing for special applications such as, for example Hyflon® MFA resins, Ultrason® E Dimension and EpiSpire® HTS-2620, Araldite® benzoxazine thermoset resins, polyetheramide (PEAR) thermoset resins, Fluorinated poly(imide-ether-amide), polyquinoxalines, phthalonitrile thermoset resins, poly(phthalazinone ether ketone), poly(phthalazinone ether sulfone), and poly(phthalazinone ether sulfone ketone); Benzocyclobutene (DVS-BCB), derivatives of bisoxazolines and formaldehyde-free phenolic novolacs, Phenolic Triazine (PT), poly-para-phenylene copolymers, polyhydroxyamides (PHA)…

References

Technical books and guides, papers, websites: Arkema, Ashland Specialty Chemical, Ausimont, BASF, Bayer, Chevron Phillips, Daikin, Degussa, Dow, DSM, Dupont, Dyneon, Evonik, GE, Huntsman Advanced Materials, Kuraray, Lanxess, Mitsui Chemicals, New Chemphy, Omnexus, PBI Performance Products, PRW, Sabic Innovative Plastics, Shin-Etsu, Solvay, SpecialChem, Ticona, Toyobo Corp, Victrex, Wacker, Wikipedia… Thermoplastics and Thermoplastic Composites, M. BIRON, Elsevier, 2007 Thermosets and Composites, M. BIRON, Elsevier, 2004

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