

# Radiation resistance and other safety aspects of high-performance plastics by ERTA

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## Abstract:

High-performance plastics, PEEK (polyether-ether-ketone), Ertalon 4.6 (polyamide PA 4.6), PEI (polyether-imide), PES (polyether-sulfone) and PSU (polysulfone), were supplied to CERN by ERTA-EPEC (B) for testing of their radiation resistance. The fire behaviour of pure PEEK and PEI complies with the requirements of the CERN Safety Code and Instructions. PES and PSU could emit toxic and corrosive fumes when involved in a fire; PA 4.6 is not flame retardant in the standard grade. PEEK, PEI, PES and PA 4.6, as well as PSU to a lower extent, are usable at high temperature, but they are often brittle at cryogenic temperature. Mechanical tests have been carried out, prior and after irradiation up to doses as high as 100 MGy, to assess the radiation resistance; flexural strength, deformation at break, limit of elasticity and modulus of elasticity have been measured. The results show that the modulus and the limit of elasticity are usually not affected by radiation. They also allow to sort the materials from the most resistant one to the most sensitive one: PEEK, PEI, PA 4.6, PSU and PES.

## 1. Introduction

The selection of insulating and structural materials is an important part of the CERN Large Hadron Collider (LHC) project. The selected materials have to fulfil the CERN safety requirements which means that in addition to their mechanical, electrical, thermal, and environmental endurance properties, they have to present a good radiation resistance, and a good fire behaviour: they must be flame retardant, and in the event of a fire, the smoke emission must be low and the resultant gases must be non-toxic and non-corrosive, this implies that they be halogen-free.

Numerous mechanical tests have been carried out at CERN and in many other institutes to assess the radiation resistance of various types of materials, and a lot of data is now available [1, 2]. Most of this data concerns glass-fibre reinforced thermosets. Since a few years, high-performance thermoplastics are available on the market. These products present interesting properties on a mechanical point of view, as well as good radiation resistance. They are still often more expensive than common thermosets, but

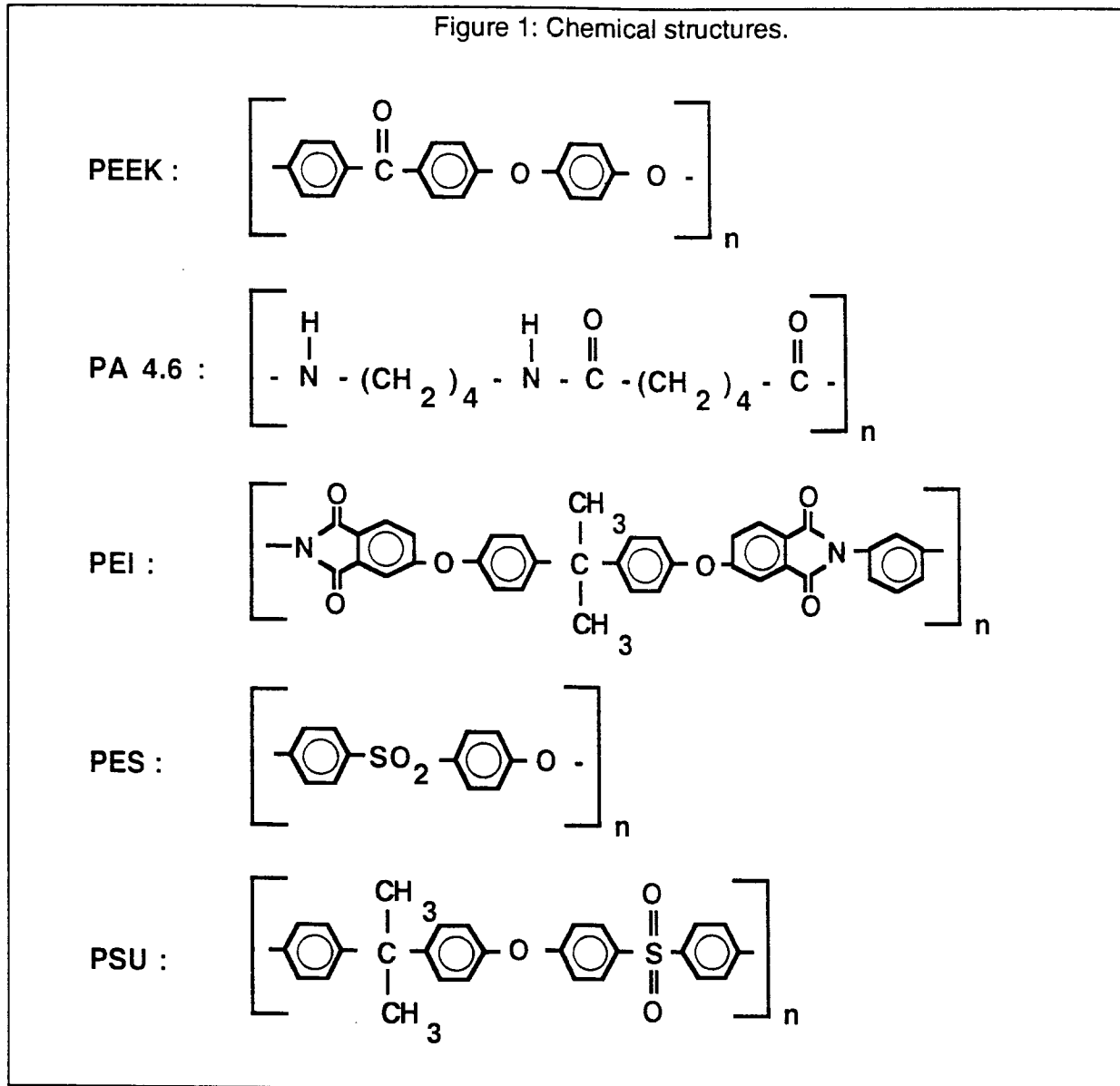
the possibility to mould complicated pieces of equipment makes their process faster and cheaper. The semi-crystalline ones (PEEK and PA 4.6) also present a better wear resistance and a lower friction coefficient. With respect to the standard engineering plastics (PA, POM, PETP and PC) the high-performance thermoplastics also offer a better chemical and hydrolysis resistance especially PEEK which has a chemical resistance almost comparable to PTFE.

## 2. Selected engineering thermoplastics

ERTA-EPEC (B) supplies stock shapes in high-performance thermoplastics (EPEC stands for 'Engineering Plastics, Extruded and Cast), five of them have been selected for testing of their radiation resistance: PEEK (polyether-ether-ketone), Ertalon 4.6 (polyamide PA 4.6, also commercialized under the trade-name Stanyl), PEI (polyether-imide), PES (polyether-sulfone) and PSU (polysulfone). All of them are pure plastics, but PEEK is also available in the carbon-black grade, in

a lubricated reinforced bearing grade, or with 30% of glass-fibers.

Their chemical structures appear in Fig.1 below.



Their main physical properties appear in Table 1 [3]. Some of their thermal properties, such as CTE and thermal conductivity are comparable to the best epoxies. They are usually more sensitive to water absorption and moisture, especially PA 4.6 which is very sensitive.

### 3. Fire behaviour criteria and tests

At CERN, the requirements for fire safety are described in the Safety Code E and its appendices, among them, the Safety Instruction IS 23 and the Safety Note NS 11 [4, 5, 6]. The requirements and the

corresponding standards are summarized in another paper of this conference [7].

The UL rating and the limit of oxygen index (OI) appear in Table 1. The data about the toxicity and the corrosiveness of fire gases as well as the smoke density are general data for these types of materials, taken from [8], they are summarized below.

PA 4.6, as other polyamides, burn readily exhibiting dripping. Its use must be restricted in components where fire propagation is impossible because of confinement. Flame retardant grades are sometimes available but their smoke and toxic fume emission should be controlled before selection.

PEEK and PEI present good heat resistance and very good fire retardancy without resort to the use of additives. When involved in a fire, it emits low smoke and toxic and corrosive fume.

PES and PSU also present good heat resistance. PES is rated V-0 in the UL test, PSU is rated V-1 or HB that indicates a rather poor flame-propagation behaviour, even if both types of materials are difficult to ignite. When involved in a fire, they emit sulphur dioxide at high temperature.

## 4. Radiation-test methods

### 4.1. Irradiation conditions

The samples have been irradiated either in a cobalt source ( $^{60}\text{Co}$ ) at a dose rate of the order of 1 Gy/s, up to 1 MGy, or in a nuclear reactor at a dose rate of the order of 50 Gy/s up to 100 MGy. In both cases the irradiations took place in air, at temperatures between 15°C and 60°C which are well below the glass-transition temperatures of the materials.

PEEK and PA 4.6 have also been irradiated in the cobalt source at the same dose rate, but up to 7 MGy, in several times spread over a period of two years.

More details about the irradiation conditions can be found in [9].

### 4.2. IEC 544 Standard

The international recommendations for radiation damage tests are described in the IEC 544 standard, "Guide for determining the effects of ionizing radiation on insulating materials" [10]. As it has been observed that electrical breakdown of insulating materials is usually a consequence of severe mechanical deterioration (see e.g. [2]), the recommended test procedures for permanent effects are testing of mechanical properties, which in the case of structural materials is the only valid method.

The IEC standard recommends that flexible plastics (e.g. cable insulations) be submitted to tensile tests (according to ISO/R527 and ISO/R37) and that rigid plastics, including composites and prepregs, be submitted to flexural tests (ISO 178). IEC 544 recommends that these tests are carried out to rupture of the material: flexural strength and ultimate deformation are measured at the breaking point. This is an appropriate way for assessing the severe mechanical deterioration and the consequent electrical possible failure of an insulator.

In real life, the structural materials are never used up to their breaking point; the strain is usually limited to less than 1% (usually between 0.2% and 0.6%) to minimize long-term creeping (which may never be neglected for plastic materials). If stress and strain are limited, the modulus is often an important property to be considered for the behaviour of the material; the flexural modulus is calculated from the slope of the stress-strain curve at its origin.

IEC 544 recommends that the limit of usability of a material is the absorbed dose at which the critical property (the most sensitive one; often the flexural strength) is reduced to 50% of its initial value, and defines a radiation index (RI) as the logarithm (base 10) of this dose.

### 4.3. Mechanical tests at CERN and criteria

At CERN, the flexural tests are based on a three-point loading system carried out on an Instron 1026 machine, with a crosshead speed of 5 mm/min. It is known that the three-point loading test creates local stresses opposite to the central loading support, but as all samples are tested the same way, the observed reductions of properties are well representative of the degradation of the materials. More details about our test methods can be found in [9].

From the recorded load-displacement curves it is possible to calculate the stress-strain curves, the modulus of elasticity and to determine the limit of the pseudo-elastic region.

The flexural strength at maximum load, the ultimate deformation (at break), the limit of proportional deformation and the flexural modulus of elasticity are given in the results below (Table 2). They are defined as follow :

Flexural strength at maximum load :

$$\sigma_x = (3 \cdot L \cdot P_x) / (2 \cdot B \cdot T^2) \quad (\text{in MPa})$$

Flexural modulus of elasticity :

$$E = (L^3 \cdot F/Y) / (4 \cdot B \cdot T^3) \quad (\text{in MPa})$$

Ultimate deformation (at break) :

$$\epsilon_x = 6 \cdot D_x \cdot T / L^2 \quad (\text{in } \%)$$

Limit of proportional deformation :

$$\epsilon_p = 6 \cdot D_p \cdot T / L^2 \quad (\text{in } \%)$$

With, L the span length between the outer supports (= 67.065 mm),

<b>Table 1: Main physical properties of the "High Performance Materials"</b>									
<b>PROPERTIES</b>	<b>STANDARD</b>	<b>UNITS</b>	<b>PEEK</b>	<b>PA 4.6 (1)</b>	<b>PEI</b>	<b>PES</b>	<b>PSU</b>		
Density (ISO)	1183	g/cm <sup>3</sup>	1.32	1.18	1.27	1.37	1.24		
Water absorption (ISO): - after 24/96h immersion in water of 33°C (2)	62	mg	5 / 10	-	20 / 41	43 / 89	23 / 44		
- at saturation in air of 23°C/50% RH	62	%	0.06 / 0.12	1.3 / 2.6	0.26 / 0.54	0.53 / 1.10	0.32 / 0.61		
- at saturation in water of 23°C	-	%	0.20	2.8	0.75	0.9	0.40		
	-	%	0.45	9.5	1.35	2.1	0.85		
<b>THERMAL PROPERTIES</b>	<b>ISO</b>								
Melting point	-	°C	340	295	-	-	-		
Glass transition temperature	-	°C	-	-	215	225	190		
Thermal conductivity at 20°C	-	W/(k.m)	0.25	0.30	0.22	0.18	0.26		
Coefficient of linear thermal expansion:									
- average value between 23 and 100°C	-	m / (m.K)	50 x 10 <sup>-6</sup>	90 x 10 <sup>-6</sup>	60 x 10 <sup>-6</sup>	55 x 10 <sup>-6</sup>	60 x 10 <sup>-6</sup>		
- average value between 23 and 150°C	-	m / (m.K)	50 x 10 <sup>-6</sup>	-	60 x 10 <sup>-6</sup>	55 x 10 <sup>-6</sup>	60 x 10 <sup>-6</sup>		
- average value above 150°C	-	m / (m.K)	110 x 10 <sup>-6</sup>	-	-	55 x 10 <sup>-6</sup>	-		
Deflection temperature under flexural load:									
- method A: 1.8 N/mm <sup>2</sup>	75	°C	160	160	200	200	175		
Max. allowable service temperature in air:									
- for short periods (3)	-	°C	310	200	210	220	180		
- continuously: for min. 20.000 h (4)	-	°C	250	155 / 135	170	180	150		
Min. service temperature (5)	-	°C	-60	-40	-50	-50	-50		
Flammability:									
- according to ASTM ("Limit of Oxygen Index")	4589	%	35	24	47	38	30		
- according to UL 94 (1.5/3 mm thickness)	-	-	V-0 / V-0	V-2	V-0 / V-0	V-0 / V-0	HB / HB		
Note:	<p>1 g / cm<sup>3</sup> = 1'000 kg / m<sup>3</sup></p> <p>(1) if two values are given, the first one corresponds to dry samples, the second one to samples in equilibrium with air at 23°C and 50% RH</p> <p>(2) on discs Ø 50 x 3 mm</p> <p>(3) few hours or very low load</p> <p>(4) for a decrease in tensile strength of 50%</p> <p>(5) if subjected to impact</p>								

Table 1 (continued): Main physical properties of the "High Performance Materials"

PROPERTIES	STANDARD	UNITS	PEEK	PA 4.6 (I)	PEI	PES	PSU
<b>MECHANICAL PROPERTIES at 23°C</b>							
Tensile test (6)	ISO						
- tensile stress at yield	R 527	N / mm <sup>2</sup>	95	100 / 55	105	85	70
- elongation at break (7)	R 527	%	> 25	25 / 100	> 50	> 25	> 50
- modulus of elasticity (8)	R 527	N / mm <sup>2</sup>	3600	3100 / 1500	3000	2700	2500
Flexural test:							
- modulus of elasticity	178	N / mm <sup>2</sup>	4100	-	3300	2800	2700
Compression test (9):	604	N / mm <sup>2</sup>	130	92	130	105	90
- 1%-offset yield strength (8)							
Tensile creep test:							
- stress to produce 1% elongation in 1.000 h							
( $\sigma_1/1.000$ ):- at 23°C	899	N / mm <sup>2</sup>	30	22 / 7.5	30	23	22
- at 60 / 100°C (dry)	899	N / mm <sup>2</sup>	26 / 22	14 / 9	23 / 18	19 / 17	18 / 14
- at 125 / 150°C(dry)	899	N / mm <sup>2</sup>	12 / 5	7 / 6.5	13 / 7	13 / 10	9 / 5
Impact strength - Charpy	179/2D	kJ / m <sup>2</sup>	-	no break	no break	no break	no break
Notched impact strength:- Charpy	179/2C	kJ / m <sup>2</sup>	6	20	4	4	4
- Izod	180/A	kJ/m <sup>2</sup> ; J/m	8 ; 80	25 ; 250	5 ; 50	5 ; 50	4 ; 40
Ball indentation hardness H 358/30 or H 961/30 (10)	2039-1	N / mm <sup>2</sup>	230	165	170	160	155
Rockwell hardness (10)	2039-2	-	M 105	M 92	M 114	M 104	M 91
<b>ELECTRICAL PROPERTIES at 23°C</b>							
Dielectric strength (11)	IEC	kV / mm	30	60 / 25	30	30	30
Volume resistivity	243	Ohm.cm	10 <sup>16</sup>	10 <sup>15</sup> / 10 <sup>13</sup>	10 <sup>16</sup>	10 <sup>16</sup>	10 <sup>16</sup>
Surface resistivity	93	Ohm	10 <sup>14</sup>	10 <sup>14</sup> / 10 <sup>12</sup>	10 <sup>14</sup>	10 <sup>14</sup>	10 <sup>14</sup>
Dielectric constant:- at 10 <sup>3</sup> Hz	250	-	3.3	4 / 10	3.2	3.6	3.1
- at 10 <sup>6</sup> Hz	250	-	3.3	3.8 / 4.3	3.1	3.6	3.1
Dissipation factor tan $\delta$ :- at 10 <sup>3</sup> Hz	250	-	0.003	0.013 / 0.3	0.001	0.002	0.001
- at 10 <sup>6</sup> Hz	250	-	0.003	0.012 / 0.15	0.006	0.011	0.005
Resistance to tracking	112	-	CTI 150	CTI 425	CTI 150	CTI 150	CTI 150
Note:							
1 N / mm <sup>2</sup> = 1 MPa	(6) test samples of type 1 (ISO)						(9) test samples: cylindres Ø 12 x 30 mm
1 kV / mm = 1 MV / m	(7) test speed = 5 mm / min						(10) test samples 10 mm thick
	(8) test speed = 1 mm / min						(11) electrodes P25/P75 on 1 mm thick samples

- B the width of the test piece (= 10 mm),  
 T the thickness of the test piece  
 (=  $5.04 \pm 0.05$  mm),  
 P<sub>x</sub> the maximum load (N),  
 F/Y the slope of the load–displacement  
 curve in its early linear region,  
 D<sub>x</sub> the deflexion at break (mm),  
 D<sub>p</sub> the limit of proportional deflexion (mm),

Note that for technical reasons, the maximum deflexion, in the flexural cage, is 23 mm, the corresponding ultimate deformation is 15 %. The radiation indices will be calculated on the base of the reduction of the flexural strength at break and of the reduction of the deformation at break; the value to be taken for the limit of usability is the most restrictive one.

## 5. Radiation test results

### 5.1. Flexural test results

The variation of the mechanical properties with dose appears in the tables and graphs in appendix, they are summarized in Table 2 for the five selected materials. Two values of the radiation index are given for each material: one based on the reduction of the ultimate flexural strength, the other one based on the reduction of the ultimate deformation; the latter is the lowest one (based on the most sensitive property), it is the value to be considered for the limit of usability of the materials.

### 5.2. Tensile tests on PEEK film

Insulating films made of PEEK (not supplied by ERTA), of 130 and 25 micrometre thicknesses, have been submitted to tensile tests (according to ISO R37, which is not the appropriate standard for films, but which can be used to observe the radiation degradation). After irradiation in the nuclear reactor, it appears that the films are more degraded than the bulk material; the degradation is even more pronounced for the 25 micrometre film which suggest an oxidative effect; RI = 6.8 (see in appendix).

### 5.3. Long-term irradiation

After the long-term irradiations up to 7 MGy, one sample of PEEK has been tested and show no degradation. The four samples of PA 4.6 have been

tested; the results show that it is heavily degraded (see the results with an asterisk in Table 2).

### 5.4. Mechanical tests at low temperature

It is known that the flexibility of the polymers is reduced at cryogenic temperature; their modulus as well as their strength increase slightly or significantly, their ultimate strain as well as their impact resistance decrease. A literature survey has shown that the reduction of the mechanical properties with irradiation is about the same whether the material has been irradiated at room temperature or at cryogenic [11]. For example, Spindel et al. found that the strength and modulus of PEEK and PEI increase sensibly at cryogenic temperature (4 K), and that the irradiation up to 10 MGy still increases these values [12]. ERTA materials, PEI, PES and PSU have been included in a radiation test programme carried out at low temperature (77 K) at the Atominstitut der Österreichischen Universitäten [13]; the same behaviour has been observed, their ultimate deformation prior to irradiation is of the order of 5%. Regarding their ultimate deformation, PES and PSU have an RI of 6.3 which is higher than after a room-temperature irradiation.

The 130 micrometre film has also been included in the same programme. Its ultimate elongation prior to irradiation is of the order of 6%, and is unchanged up to 60 MGy. This confirms that PEEK is prevented from radio-oxidative degradation when irradiated in liquid nitrogen.

## 6. Discussion and conclusion

### 6.1. Validity of the tests

As said in 4.2., if stress and strain are limited, the modulus of elasticity and the limit of the pseudo-elastic region (quasi-proportional) are important properties to be considered for the behaviour of the material. The radiation test results show that these properties are almost not affected by radiation.

On the other hand, the decrease of the flexural strength and of the ultimate deformation are representative of the degradation of the material), the ultimate flexibility is always the critical parameter.

Ageing of polymers, due to time–temperature degradation as well as other environmental factors such as radiation combined with fatigue, appears as a change in the fracture mode, from ductile to fragile.

TIS No	Trade name	Dose (MGy)	Strength (MPa)	Deformation (%) at break	Deformation (%) prop.	Modulus (GPa)
520	<b>Erta PEEK</b>	0.0	177	> 15	2.4	4.3
		5.0	179	> 15	2.9	4.1
		7.0*	187	> 15	1.6	3.0
		10.	161	11.6	2.7	4.2
		50.	111	3.8	1.5	4.3
		100.	143	5.8	1.9	4.2
		<b>RI</b>		<b>&gt; 8.0</b>	<b>7.0</b>	
526	<b>Ertalon 4.6</b>	0.0	126	3.7	1.2	5.8
		3.0	133	3.4	1.6	5.9
		7.0*	50	1.2	1.0	3.0
		10.	64	1.4	1.5	3.7
		50.	33	1.5	1.0	1.9
		<b>RI</b>		<b>7.0</b>	<b>6.8</b>	
533	<b>Erta PEI</b>	0.0	171	> 15	2.1	3.1
		1.0	174	> 15	2.0	3.2
		3.0	179	> 15	2.1	3.3
		10.0	158	10.9	1.2	3.2
		50.0	102	3.3	2.2	3.3
		<b>RI</b>		<b>&gt; 7.7</b>	<b>7.0</b>	
534	<b>Erta PES</b>	0.0	141	> 15	2.9	2.7
		0.5	134	> 15	1.9	2.8
		1.0	132	11.7	2.0	2.9
		3.2	47	1.7	1.6	3.1
		10.0	14	0.5	0.4	3.3
		<b>RI</b>		<b>6.3</b>	<b>6.0</b>	
535	<b>Erta PSU</b>	0.0	120	> 15	2.1	2.6
		0.5	114	> 15	1.9	2.7
		1.0	102	9.6	1.8	2.8
		3.2	58	2.1	2.0	3.0
		10.0	19	0.7	0.6	3.0
		<b>RI</b>		<b>6.4</b>	<b>5.9</b>	

\* long-term irradiations

The measurement of the ultimate properties as done in the tests recommended by the IEC 544 standard is representative of the transition in this rupture mode

and hence of real ageing of the material. Therefore, the reduction of one of these properties is a valid base for the limit of usability.

### 6.2. Cryogenic behaviour under radiation

At cryogenic temperature, polymers are not ductile and their fracture always occurs in the fragile mode. Irradiation at constant low temperature does not increase the degradation compared to a room temperature irradiation, the presence of the cryogenic fluid even impedes the radio-oxidative degradation.

### 6.3. Long-term behaviour under radiation

As other polyamides, PA 4.6 is sensitive to radio-oxidative degradation and to moisture. Its fire behaviour characteristics prohibit its use in places where fire propagation presents a danger. All of this restricts the use of this high-performance thermoplastic in confined vessels without oxygen and where the atmosphere is controlled.

### 6.4. Ranking

The results show that the modulus and the limit of elasticity are usually not affected by radiation, the flexural strength is slightly affected, the deformation at break is the critical property.

The results also allow to sort the materials from the most resistant one to the most sensitive one: PEEK, PEI, PA 4.6, PSU and PES.

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