# PAEK for Additive Manufacturing

## - A Planet Friendly Material




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**About PAEK future growth and potential**

The PAEK polymers are gaining sustain attention from consumers today due to high performance of these polymers and possibility of processing them readily due to superior equipment and techniques, including 3D or Additive Manufacturing. PAEK include PEEK, PEK and various PEKK polymers.

The estimated market of PAEK polymers is expected to be around 6100 million USD by 2025 with 25 % growth rate. It was around 850 million USD in 2015.


*Figure 1 Future demand of PAEK materials in AM*

Out of all polymers used, total PAEK market itself is expected to grow by 1000 million USD by 2025 only just for additive manufacturing, i.e. making granules, filaments, laser sintering powders, printed articles etc.

The total 3D printing market is expected to be 25 billion USD by 2025 (1). The expected growth is 52% in segments like Aerospace, Biomedical, Automotive and Consumer electronics. The major attraction in these segments is demand for light weight structural parts with complex design, wear and heat resistance properties. Today additive manufacturing has become more viable for manufacture such complex parts over even injection molding. Injection molding is much feasible for very high volume parts, generally several thousands. Also, the tooling cost of makining molds plays a major role in deciding about injection molding, where as in additive manufacturing, no major tooling is required. In future high speed printing technology (tool free moulding AM techniques) will overcome this barrier also.

**Advantages with High performance polymers PAEK:**

In PAEK group there is PEEK, PEK and PEKK materials are visible commercially. It has an excellent thermal property over regular engineering plastics. Continuous service temperature of PEEK is 240$^0$C.The major benefits of PAEK over other plastics materials are its outstanding chemical resistance, resistance to fluids, excellent wear resistance at high temperature, excellent thermal properties, excellent mechanical properties and high compressive strength, high gamma-ray radiation resistance. PEEK has large volumes in 3D filament market at the moment as many material manufacturing companies are exist globally in UK, China, India, USA. Typical Tg of PEEK polymer is 140$^0$C and services temp is about 240$^0$C. It has excellent fatigue and creep resistance, good mechanical properties and bio compatibility has made widespread use of this material in medical segments for implants. This material is visible in the 3D filament market as well as famous with FDM printers. PEEK requires printing temperature in range of 370$^0$ to 400$^0$C which is very high and limiting its usage in specified printing machines only. Surprisingly this material PEEK is not visible in SLS (laser sintering applications) due to some technical limitations. Due to this limitation PEEK application are not seen in end component manufacturing by laser sintering. Hence it is not yet in use for actual component manufacturing but only available for rapid prototyping by FDM.

PEK is also semi crystalline polymer like PEEK. The Tg and Tm are slightly superior than PEEK. This material has extra additional advantages on thermal properties compared to conventional PEEK. It can withstand continuous services temp. of 260$^0$C, slightly higher than PEEK. The price of the polymer is little higher than conventional PEEK. Due to its higher melting temperature 365$^0$C to 400$^0$C. it requires

special skills to process into a filament. Like PEEK, this material is also thermally sensitive and need better control of melt temperature in extruder barrel or injection moulding machines. PEK is not yet visible in 3D filament form and hence it is not yet visible in FDM printing market. On the other side, there is great opportunity for 3D printers to explore such materials like PEK for FDM. Also as PEK provides some additional thermal property benefits over conventional PEEK. It requires nozzle temp of 410C to 430C for printing in FDM. This material is considered as one of the best material for SLS application by laser sintering. It is very well visible in High Temperature Laser Sintering applications. There is small challenge of reuse of the PAEK powder in SLS. PEK is used for to make aerospace parts by SLS.

*Figure 2 GAPEKK 6-3200G 3D Filament*

PEKK is one of the amazing novel polymers in PAEK family. Acceptability of PEKK material is becoming very fast in additive manufacturing for bio medical and aerospace segment due to its unique crystalline properties. PEKK is available in 4 different grades with different T/I ratios (2). The most interesting of PEKK grades is 6-3200 (60/40). Which has lowest melting temperature Tm of only 305$^0$C. Which is lowest in PAEK family. The colour is like clear golden. It is suitable for laser sintering, FDM printing & composites printing. The second grade is PEKK 70/30 melt temp is around 330$^0$C which is very moderate melt temperature and excellent crystalline behaviour for FDM printing. It is more visible in FDM filament and printing applications. PEKK 80/20 has melt temp of 365$^0$C. Depending on grade and T/I ratio (60/40, 70/30 & 80/20) the melt temperature Tm and glass transition Tg changes in PEKK. The forth grade (2) having 100:0 T:I ratio has Tm of 395$^0$C, and has yet to be tried for 3D printing.

The most unique properties of PEKK are their crystallization Kinetics, moderate crystallinity, excellent thermal stability, better sintering window, easy processing behaviour, which have made them suitable for both FDM and SLS technologies. PEKK is widely accepted by Aerospace companies due to its lightweight and high performance over metals for structural parts by additive manufacturing of SLS and FDM process. PEKK is also becoming very popular material in medical segment. It has excellent bone grafting properties, fatigue and creep/compressive strength, bio-compatibility hence its perfect material for bio-implants. It can be easily modified with bio-active additives to make suitable for Dental and other Orthopaedic implants. The only material in PEAK family which is suitable and visible in both FDM and SLS process world wide is PEKK. PEKK is also easy to injection mould, extrude for films, stock shapes, filaments, compression moulding & thermoforming. The best thing about PEKK, particularly 60:40 grade, is it can be printed in both amorphous and crystalline phase. Due to its low melting temperature and high heat resistance, this material will have lot of opportunities in advance application. The biggest advantage of PEKK in laser sintering is re-usage of powder. It is found possibly easily refresh-able without any loss, which is the biggest advantage of PEKK over other PAEK materials. The filament extrusion of PEKK is much easier than PEEK and PEK. It can be easily printed by FDM in most of the machines with lowest printing temp in range of 310$^0$C to 350$^0$C depending on grade of PEKK. The performance of PEKK part with different infill ratio is found excellent with more aesthetic looking.

**Glass Transition temperature of PAEK materials:**

Glass Transition temperature Tg and Melting Temperature Tm are the most important thermal properties. In PAEK family, the combination of Tg and Tm are very much balanced in PEKK. It has highest Tg and lowest melt temperature Tm. The Tg of PEKK grades for 3D printing starts from 160$^0$C to 167$^0$C and melt temperature Tm in the range of 310$^0$C to 360$^0$C. The highest Tg is found with PEKK 100/0 grades Tg 173C and Tm 396C (Gharda Chemicals is the only successful producer in the world for PEKK 100/0 grade). PEKK 100/0 grades are very much suitable for injection moulding applications of Oil & Gas, Aerospace, Industrial, Automotive break pad components. PEKK 100/0 now widely available with 30% carbon fibre filled and glass fibre filled compounds for critical applications to replace metal. It is yet to explore in AM applications. PEK has Tg of 152$^0$C and melt temp Tm is 374$^0$C. Whereas PEEK has lowest Tg 140$^0$C and moderate to higher melt temp Tm 343$^0$C.

Figure 3 GAPEKK 6-3200G Printed articles by FDM

*Figure 4 GAPEKK 6-3200G Industrial parts by 3D printing*

**PEKK vs PEEK**

PEKK and PEEK has two differences in the basic chemical structure. PEKK has additional rigid ketone group instead off ether linkage in PEEK. Due to Ketone group, it has higher glass transition temperature Tg, where the material first begins to soften by about 25$^0$C over PEEK.

The second ketone group is selectively Ortho or Para substituted. So it is possible to control the melting point by crystallization rate. Hence PEKK 6-3200 (60/40) melts at 305$^0$C and crystallizes slowly, which is also called Pseudo–amorphous. The term is very important to understand while one is extruding PEKK Filament and annealing of PEKK 60/40 printed parts. Whereas PEKK 8-3200 (80/20) will have melting point of about 360C and crystallization rate is almost near to PEEK.

The moderate crystallization rate of PEKK has made it more favourite for FDM/FFF processor due to its dual advantage of extreme performance and easier processing. In short, PEKK is very easy to 3D print than PEEK with lower extrusion temp in printing and super adhesion of layers. It offers superior strength and properties. The PEKK 6-3200G and 7-3200G are found successful even in the very first printing attempt in printing articles.

**Role printing machine/raw material companies – Past and current situation**

3 years back, there were only few companies offering printing machine which can go upto 220$^0$C. There was a challenge of availability of suitable raw materials for filament extrusion. The initial demand started with PLA, ABS, PC, PETG, PA11 and PA12. The highest performing materials then were PA11 & PA12. Due to the limitation of freedom of sourcing material from any material supplier has created dependability on machine supplier (locking system) and very high prices has restricted the growth. Now more and more printing companies are coming forward with open system. This allows printing companies freedom of choosing and buying materials from open platforms. Another revolution is many big polymer raw material companies have also entered in the market with creative solutions and support to AM customers value chains. Now a days, most of the 3D printing companies have started offering high temperature range of machines up to 400$^0$-500$^0$C. These have opened up market for high temperature polymers like PEEK, PEKK, PEI, etc. for industrial product manufacturing. In future, the demand for high performance material is expected to grow rapidly due to demand of composites (Carbon fiber filled), which can offer extraordinary performance over unfilled materials. It is also assumed that in future,advance technology will come soon, which can replace the use of filaments with direct powder or granules for extrusion.