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A High-performance Material for Aerospace Applications: Development of Carbon Fiber Filled PEKK for Laser Sintering

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Abstract

In a time where rapid prototyping successively transforms to additive manufacturing (AM), nylon 11 and 12 and their composite powders, which have evolved to be the most commonly used materials in laser sintering (LS) due to their easy processability, cannot fulfil all challenging requirements of industrial applications any more. Especially in the aerospace industry, there is a high demand for stiff and lightweight parts for interiors, which currently are fabricated from glass fiber reinforced phenolic and epoxy resins by a lamination process. Due to the strong diversity of the parts, this traditional manufacturing is quite labor-intensive and expensive, which makes it very attractive to manufacture these parts with additive manufacturing, especially laser sintering. Additional part design requirements, such as greater chemical and UV resistance, an elevated softening temperature, higher mechanical strength and better performance in flammability and heat release tests generate opportunities for the use of high performance AM polymers. Promising candidates that have the potential of satisfying these demands can be found among the different Polyaryletherketone thermoplastics.

In this work we present the development of a carbon fiber filled PEKK composite material for laser sintering, optimized especially for the production of interiors, such as air ducts for cabin ventilation in aerospace application.

Based on process tests, powder characterization and test builds, the material and its manufacturing procedure were optimized towards isotropic properties and refreshability. Simulations of building cycles helped to understand the extent of powder ageing, which is directly connected to the ability to recycle the material.

Furthermore the laser sintering hardware of an EOSINT P800 and the building processes were adapted to ensure a stable building process and fulfill the requirements of parts on mechanical properties in x, y and z directions, dimensional stability and surface quality.

Introduction

Even in recent years, nylon powders are still the most commonly used polymers in powder bed fusion processes [Woh2016, p.54]. Looking at the laser sintering powder manufacturers, about 90% of the powders available in their 2015 portfolio are based on nylon 11 and 12 [Schm2015], and probably more than 90% of laser sintered parts worldwide were built from nylon 12 powders and their compounds [Schm2015, Schm2015.1]. Nylon powders are easy to process, are well known and understood. Many studies have focused on the mechanical properties, refreshability and characterization of different nylon powders manufactured for laser sintering [Good2012, Mun2015, VdE2015, Bai2015 and Ver2016]. Now, as additive manufacturing techniques evolve from rapid prototyping to series production, the demand for a more diversified spectrum of materials increases. Asking users of additive manufacturing about their requests for new materials, 60% would like to see high temperature plastics and 52% of the respondents desired carbon fiber reinforced materials, a request especially arising from automotive and aerospace industries [SDM2013].

In 2016, AM equipment and material manufacturers and AM service providers served many different industries; a significant share of AM parts (16.6%) goes to the aerospace industry [Woh2016, p.19f.]. This industry is known to have very demanding requirements on material properties, especially in terms of continuous operating temperature, flammability, smoke development and toxicity as well as chemical resistance. In addition, another

very important property of parts used in aerospace applications is their weight, as it has direct influence on the fuel consumption of an aircraft. So far, many parts are manufactured from glass and carbon fiber reinforced phenolic and epoxy resins by a lamination process. This fabrication method is very labor-intensive and therefore expensive. Replacing these parts by additively manufactured ones has many advantages, including great freedom of design.
Here, we show the approach and first data on the development of carbon-fiber reinforced PEKK polymer, a high-performance polymer optimized for aerospace applications.

Materials and Equipment

Carbon-fiber reinforced PEKK was supplied by ALM Inc., TX. The PEKK resin contains 23% carbon fibers and is sold under the name “HT23”.
All Parts were built on an EOSINT P800, which was slightly modified to process carbon-fiber reinforced PEKK in an optimal way. The modifications include an optimized process, heating parameters and recoating concept as well as the use of a different recoating blade. All parts were built after thoroughly warming up the machine employing an automated heat-up phase (about 3 hours), the building procedure was followed by a regulated cool-down phase [Pfi2009] to ensure uniform cooldown of all parts and avoid warpage.
Melt viscosity was determined according to ISO 1133-1:2011 and recorded as melt volume rate [cm^3/10min]. The lower the MVR value, the higher the melt viscosity of the examined material.
Mechanical data was achieved from standard ASTM D638 tensile bars which were built in 3 spatial directions, i.e. an x-tensile bar was built with its gauge length parallel to the recoating direction (x-direction, cf. figure 1).

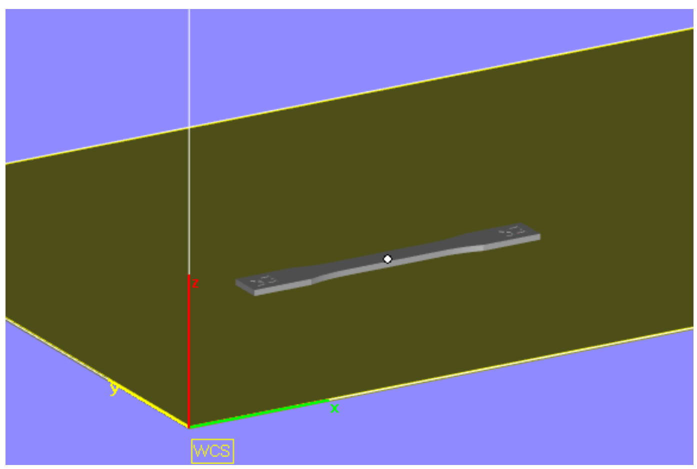

Figure 1: Position of an x-tensile bar on the EOSINT P800 building platform.

Approach and Results

Among the most promising candidates to fulfil the requirements of the aerospace industry are Polyaryletherketone polymers. These semi-crystalline polymers have been shown to be inherently flame retardant, develop minimal toxic gases when burned and have excellent chemical resistance. In addition, the continuous operating temperature is stated in literature to lie above 250°C for most of the polymers [Becker/Braun, p.359ff; Fink p.209ff.]. PEKK was chosen as a base polymer, a polymer which is commercially and readily available. Milled carbon fibers act as reinforcing component.

Isotropy:
The most common way of reinforcing materials for laser sintering with carbon fibers, glass beads or other additives is to simply blend the polymer powder with the reinforcing component [Wan2015, Wan2015.1 and Ath2010]. This method has, especially for the use of carbon fibers, one major drawback: The part properties of the laser sintered parts exhibit high anisotropy. Due to the movement of the recoater, fibers tend to align along the recoating direction. This leads to strongly improved mechanical part properties in direction of the recoater movement (x-direction), but a significant drop in all other lateral dimensions (y and especially z). One method

to counteract this disadvantage is to encapsulate the fibers into the grains of the powder [Lyo2014]. This enables the homogeneous orientation of the fibers in all spatial directions.

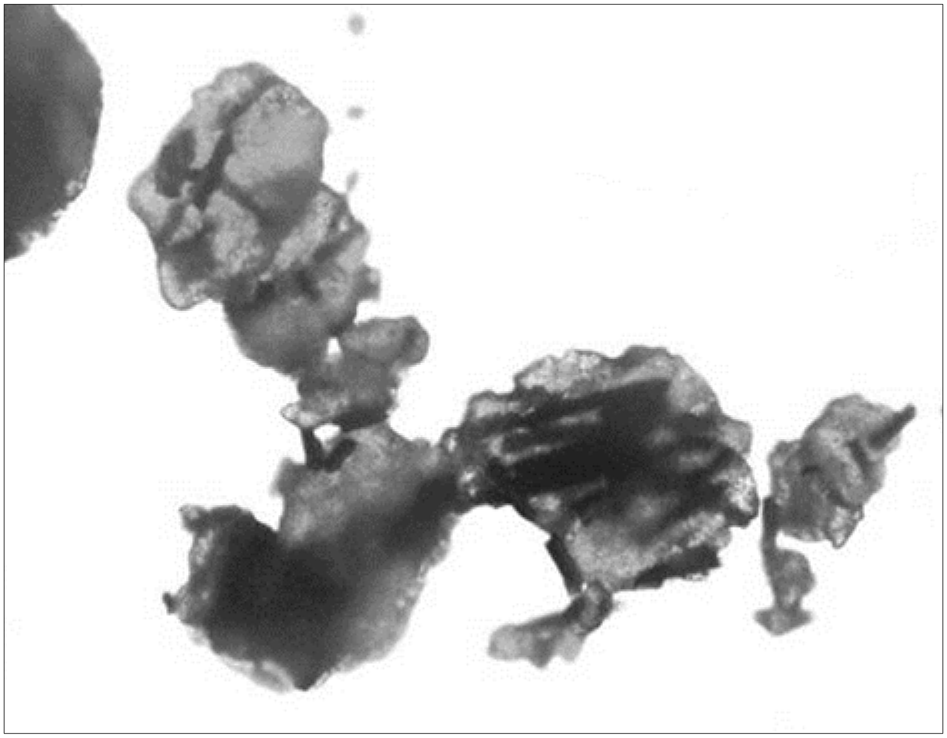

Figure 2: Micrograph of HT23 powder grains with encapsulated carbon fibers.

Table 1 summarizes the relative mechanical part properties in y- and z-direction, compared to x-direction for laser sintered parts from three different LS materials. OXFAB® ESD produced and employed by Oxford Performance Materials (OPM), a blend of PEKK with carbon fibers, shows a drop in mechanical properties of up to 37% [OPM2016] while the two powders HP11-30 (manufactured by ALM Inc.)[Boo2016] and HT23, both having the carbon fibers encapsulated inside the grain (see figure 2), show significantly improved isotropic mechanical properties, which is of great interest for part designers.

UTS [rel] Young's Modulus [rel]	OXFAB® ESD (OPM)	HP11-30 (ALM)	HT23 (ALM) (process not final)
X	1 1	1 1	1 1
Y		1 1	1 1
Z	0.63 0.70	0.82 0.79	0.85 0.90

Table 1: UTS and Young's Modulus for all three spatial directions normalized to x-direction.

Cross sections of laser sintered parts visualize the distribution of carbon fibers throughout the different spatial directions. Figure 3a) shows micrographs of three different cuts through a cuboid part, illustrating the homogeneous distribution of the fibers. In contrary, the micrograph (cut along the xz-plane) of EOS HP3 dry-blended with 10% carbon fibers indicates that most fibers are oriented in-plane, while hardly any fibers are oriented perpendicular to the sintered layers (Figure 3b)

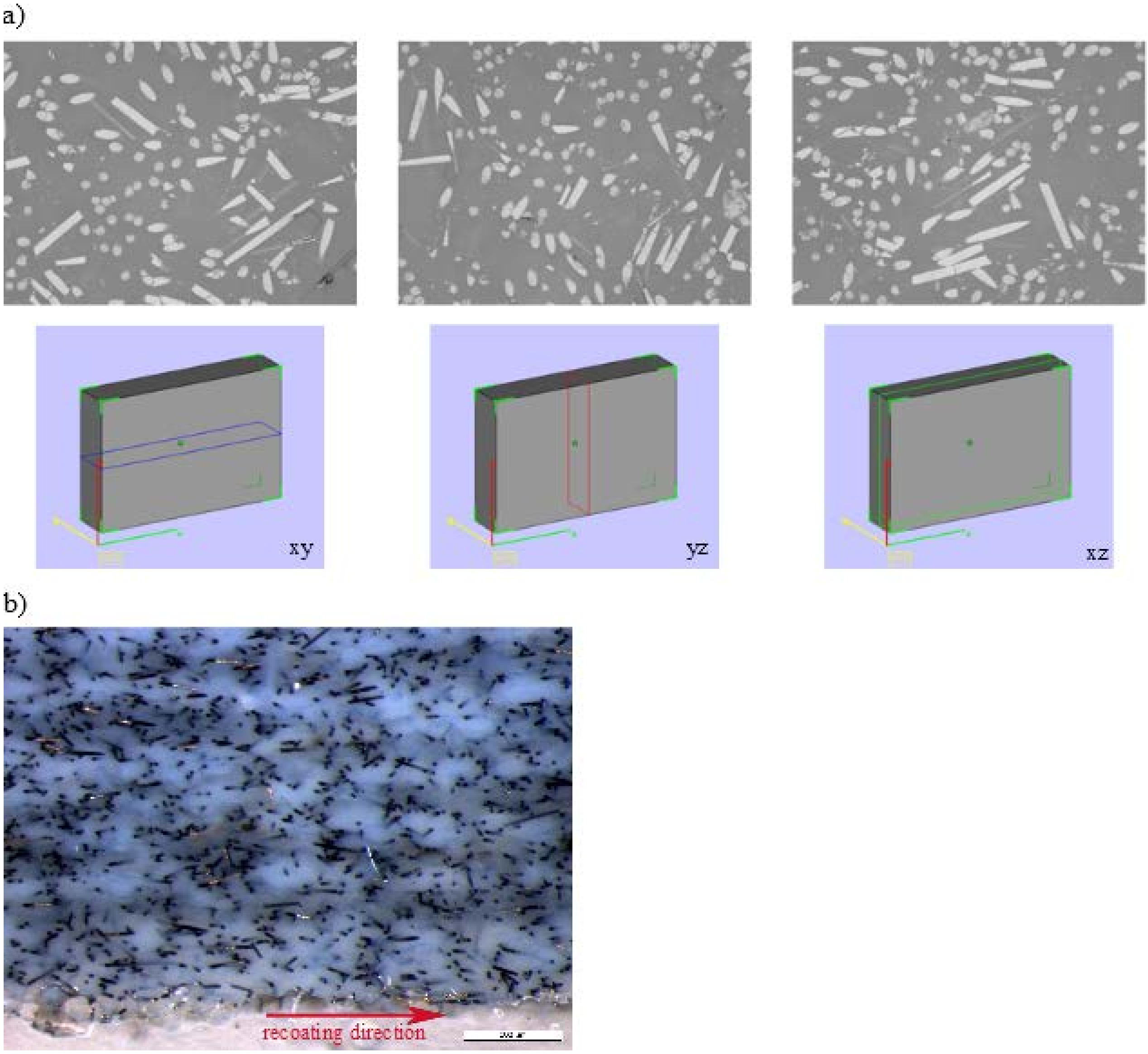

Figure 3: Micrographs of part cross sections. a) Cuts in three directions through a cuboid laser part made from HT23. b) Cross section of a laser sintered part made from a HP3/carbon fiber dry-blend. The recoating direction is indicated in red.

Refreshability:

In the laser sintering process, the powder bed is heated to a temperature close to the melting temperature in order to ensure a secure building process and avoid warpage. After finishing a build, 80-90% of the powder remains unsintered but has been exposed to long heating times which cause physical and chemical changes, generally including an increase of the melt viscosity in the material, that limit it's reusability [Pha2008; Dot2009; Ghi2013]. Therefore, the used powder is usually sieved and blended with a certain fraction of new powder. Especially with regard to cost and sustainability, reuse of the not sintered powder is strongly favored.

The extent of the viscosity decrease is dependent on several material- and processing parameters, such as thermooxidative stabilizing of the polymer or the building temperature. While the former can be influenced by additives or the base polymer itself, the latter is defined or changed in the building process.

In order to get a first idea about the refreshability of HT23, a simulation of nine building cycles with different refresh rates was performed. Small amounts of powder were aged in an oven at a temperature comparable to the usual process chamber temperature and an atmosphere similar to the one in the EOSINT P800. After every oven cycle the oven aged powder was blended with either 60% or 50% of new powder and aged again. A sample of every blend was taken in order to determine the melt volume rate. Both experiments (cf. Figure 4) show an initial drop of the MVR value when comparing new powder (oven cycle "0") with the refreshed ones, indicating an increase of the melt viscosity. Interestingly, there is no further increase of melt viscosity after the first oven cycle; it seems to stay approximately constant during all cycles. Even though the values for oven cycles 1 to 9 vary, they're still within the tolerance of the measurements (cf. error bars in fig. 4a and b).

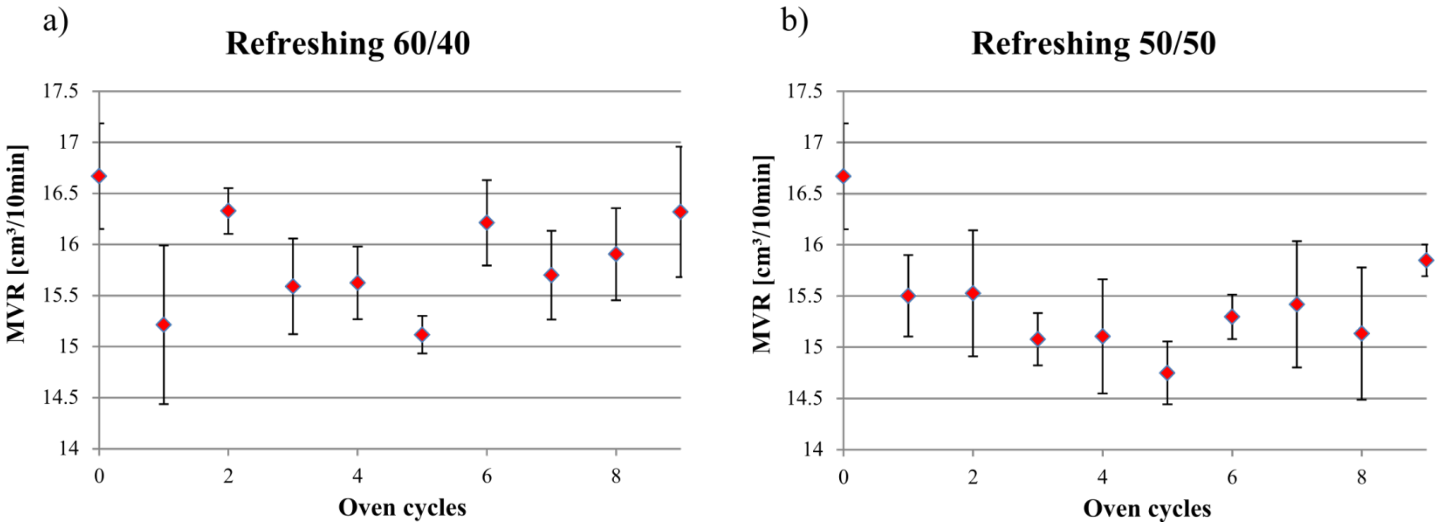

Figure 4: Simulation of 9 cycles of building and refreshing the powder. Cycle "0" indicates the melt volume rate (MVR) of new powder. After every cycle, the powder was blended with 60% (a) or 50% (b) new powder and aged again.

Comparing different refresh rates, it is easily discernable that the initial increase of the melt viscosity is more pronounced when using 50% new powder (Figure 4b) compared to when blending with 60% new powder (Figure 4a). Nevertheless, after the first refreshing cycle, the viscosity stays pretty constant as well.
A similar behavior is seen when comparing the evolution of the melt viscosity with the mechanical data. UTS and Young's Modulus of tensile bars built in x-direction drop by approximately 1% when using refreshed powder (60% new powder) instead of new powder. The decrease in the other spatial directions is within the same range.

Summary and Applications

In this work, we show the approach for the development of a carbon fiber reinforced PEKK high performance polymer for laser sintering. The material is optimized for the demanding requirements of aerospace industry. By encapsulating the carbon fibers into the polymer grain, nearly isotropic part properties could be achieved in contrast to carbon fiber and polymer dry-blends which exhibit significant part property differences over the spatial directions. Cross-sections of laser sintered parts indicate the homogeneous and isotropic distribution of carbon fibers throughout the parts.
Several building and refreshing cycles were simulated by aging the powder in an oven and refreshing it. A sample was taken from every cycle before aging the powder again and the melt viscosity was determined. Two experiments with refreshing rates of 60% and 50% showed that, even if there is a slight increase in viscosity between new powder and refreshed powder, the viscosity is approximately constant from the first refreshing cycle. First laser sintering results confirm this behavior. Mechanical data from parts built with refreshed powder (60% new) are insignificantly lower than the ones from parts built with new powder.
In addition to isotropic part properties and refreshability, the stiff and lightweight material – as known for PAEK polymers – shows a high continuous operating temperature, great chemical resistance and inherent flame retardancy. Facilitated by meeting the FAR 25.853 (requirements on flammability, heat release …) HT23 is perfectly suitable for applications under rough environments with demanding requirements on health and safety. Possible applications include air ducts and exhausts as well as highly customized interior parts for aircrafts and other industries with similar standards.

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