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PROCESSING OF RECYCLED PEKK-CF IN POWDER BED FUSION

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Abstract

Ecological and economical demands are driving developments of sustainable solutions in the AM market, especially in the field of industrial applications. One open key point is the consideration of end-of-life scenarios for AM parts. This research evaluates recyclability of parts made from high temperature PAEK materials manufactured by laser sintering. In a first step, aging mechanisms of commercial PAEK materials in Powder Bed Fusion are evaluated. Secondly, parts made from carbon-fiber reinforced PEKK are micronized into powder and employed as feedstock for powder-based additive manufacturing. Basic part properties of laser sintered specimen produced with different content of recycled material are presented. Overall, technical feasibility of recycling of PAEK parts in powder bed fusion is shown, whilst qualification for serial applications still has to be performed.

Introduction

With Additive Manufacturing (AM) evolving from prototyping to serial production, requirements regarding material and part properties, qualification and certification have augmented. Whilst in Powder Bed Fusion (PBF) polyamides, especially polyamide 12, are the main material class [1], specific applications demand extraordinary properties. Among others, these include mechanical performance, chemical resistance, or intrinsic flame retardancy. Thus, thermoplastic high performance materials have gained an increasing role in AM for industrial applications, and are expected to almost double by 2028 compared to 2023 [2]. Applications range from aerospace and automotive to applications within harsh environments, e.g. chemical industry or deep-sea applications, or regulated markets, e.g. medical applications [3]. Amongst these high performance materials, the polymer family of poly arylene ether ketones (PAEKs), especially poly ether ether ketones (PEEK) and poly ether ketone ketones (PEKK), are used with different AM technologies [4]. Within the field of PBF, particularly materials from the later class are available commercially [5,6].
With specific requirements for materials for proper processing, e.g. alteration in linking of arylic rings [7] or viscosity and coalescence behavior [8,9], several research projects were conducted to develop PEKK suitable for PBF [10].

Synthesis of PAEKs is depending on available monomers and desired structure of the polymer. Whilst for PEEK polymerization is commercially conducted as a nucleophilic substitution reaction of fluorinated diaryl ketones with aromatic diols is employed, PEKK can be synthesized by Friedel-Crafts Acylation of chlorinated aromatic dicarbon acids with aromatic ethers [11].
Arkema is using isophthalic chloride and/or terephthalic chloride and diphenyl ether as monomers for synthesizing their Kepstan PEKK grades with a catalyst at 50°C to 125°C [12]. By controlling

the ratio of terephthalic (T) to isophthalic (I) units, resulting in angled chains, the processing behavior can be controlled. This alteration in chain conformation results in hindered alignment of the chains, influencing the crystallization behavior, i.e. slowing down nucleation and crystallization and thus allowing for a suitable processing window [13]. PEKK Kepstan 6000 series, which is commonly used in Additive Manufacturing, has a 60/40 T/I ratio [14].

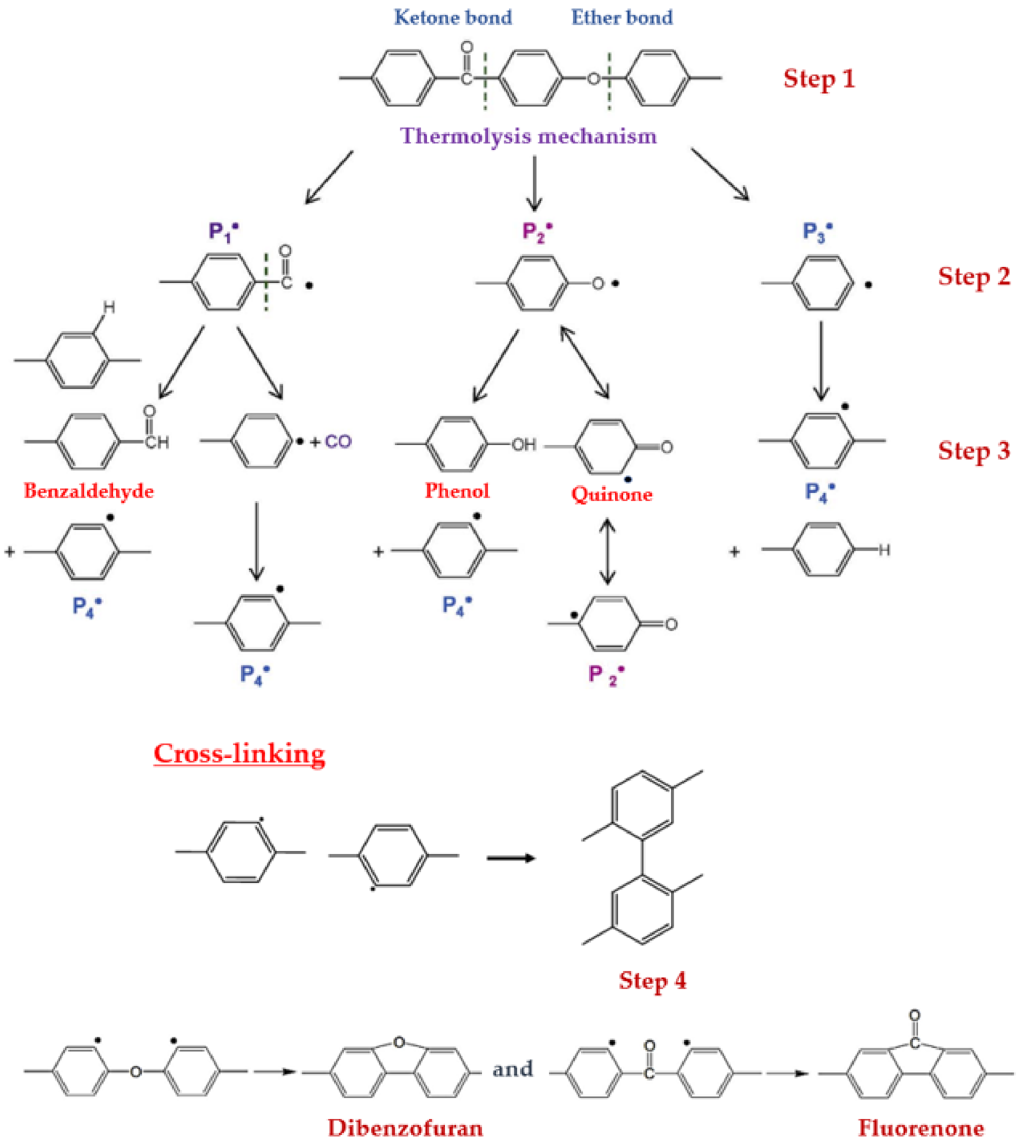

Figure 1: Reaction mechanism for PAEK material aging: radical initiation by chain scission, radical stabilization and termination [15]

PAEKs are often considered for delicate applications due to outstanding stability of the materials at elevated temperatures. Due to the poly aromatic structure they can withstand high temperatures without progressing oxidation reactions, as they can intrinsicly stabilize the radical intermediates. Nonetheless, besides physical aging effects, e.g. crystallization, chemical aging effects are observed with these materials at typical processing conditions [16]. It was found, that at elevated temperatures, e.g. 400°C as a common processing temperature for PAEKs in extrusion processes,

chain scissions at ether or ketone groups result in the formation of radical structures. These radical structures either follow subsequent decomposition reactions breaking down the material or, due to formation of meta-stable aryl radical structures, allow radical termination reactions by either intermolecular or intramolecular crosslinking [17–19] (Figure 1).
Research on aging behavior of PAEK powders for PBF has been applied, with a main focus on evaluating the reusability of unsintered materials [20–24]. Changes in viscosity of the polymer melt and thus issues with particle coalescence behavior are considered the main challenges in re-using thermally aged powder in PBF.

This work aims to extent the understanding of aging mechanism of PEKK materials in PBF beyond the aging of powders and the linked reusability. In order to evaluate analytical methods and significance of results, exaggerated powder aging in a simulation environment is conducted in first place. In a second step, the analytical methods are adapted to PEKK material inside parts manufactured by PBF. Lastly, the PBF processing of carbon fiber reinforced PEKK powder, produced from said parts, is tested to show basic feasibility of closed loop material recycling.

Materials & Methods

For studying aging mechanisms, different grades of PEKK powders, based on different formulations and viscosity grades from Kepstan 6000 series by Arkema are employed. Details on the grades are described in Table 1. The samples are subjected to artificial aging in a circulating air oven with controlled atmosphere (> 95 % nitrogen) at temperatures representative of typical processing conditions in laser-sintering process, i.e. 275°C, 280°C, 285°C, 290°C and 295°C (the latter two only for PEKK-CF) for different times up to 72 hours. Samples are sieved after heating and then subjected to analyses.

Table 1: material samples employed for aging studies

Sample Name	Modification	Trade Name
PAEK-CF	Carbon fiber-reinforced PEKK (compounded), powder ground from pellets	HT-23, Advanced Laser Materials
PAEK-1	Low viscosity grade, based on Kepstan 6000 series by Arkema, powder ground from flakes	(experimental grade)
PAEK-2	Low viscosity grade with improved refreshing behavior, based on Kepstan 6000 series by Arkema, powder ground from flakes	(experimental grade, similar to PEKK-100, Advanced Laser Materials)

Material for the recycling study is scrap parts made from HT-23 (PEKK-CF), produced on EOS P 810 system, a commercially available laser-sintering system with processing temperatures up to 300°C and a dual head exposure unit, with standard process parameters. As a reference, commercial HT-23 powders are used in different states: virgin, used (from build job) and refreshed powder (60% used powder, 40% virgin powder; standard for HT-23 according to application notes [25]).

Parts are micronized to powders in a two-step process: Firstly, parts were cut to pellets using a cutting mill, with a 4 mm sieve insert. In a second step, these pellets were ground to fine powder using a cryogenic pin mill grinder REKORD 224 by Gebrüder Jehmlich GmbH. For cryogenic grinding, the pellets are frozen in liquid nitrogen and fed into the additionally cooled grinder. The grinder is operated at circumference speed of 185-206 m/s and an outlet temperature of 15 to 30°C. The obtained powder is sieved at 160 µm mesh size to obtain the powder employed for further trials. Coarse powder is returned to the grinding process. Recycled PEKK-CF powder is additionally annealed according to state of the art [10] at 265°C.

Melt viscosity of powder and granule samples is analyzed by means of Melt Volume Rate (MVR) according to ISO 1133-2. Samples are dried in vacuum at 120°C for 30 minutes and afterwards purged with dry nitrogen for five minutes before being transferred to the analytical device. Measuring conditions are 380°C and 5 kg load. Preheating prior to starting the flow is 300 seconds.

All results shown is this report are normalized against the obtained values of respective virgin material for aging study or the value of virgin HT-23 used as reference for the recycling study respectively.

Differential Scanning Calorimetry (DSC) is used to assess melting and crystallization behavior, using a TA Instruments DSC 2500. The analysis is conducted following ISO 11357-1/2/3 in inert atmosphere (nitrogen 5.0), standard aluminum pans, an approximate sample weight of 5 mg and following the method described in Table 2. Slow cooling is used to enable proper observation of crystallization effects, whilst otherwise heating and cooling rates of 20K/min are used to allow proper analysis of glass transition.

Table 2: DSC method for analysis of powders and pellets

Segment	Temperature Range	Heating/Cooling Conditions
1	25°C – 360°C	20 K/min
2	360°C	isothermal, 5min
3	360°C – 300°C	-20 K/min
4	300°C – 180°C	-2 K/min
5	180°C – 100°C	-20 K/min
6	100°C	isothermal, 5min
7	100°C – 360°C	20 K/min

Color and color changes of aged powder samples are analyzed using a BYK-Gardner spectroguide sphere gloss using a d8 observer. Powder is placed in a glass container (optical quartz glass) with sufficient filling level to avoid influence of surrounding light. Results are described within the CIE L*a*b* color range.

For tracing chemical changes, material samples are analyzed by Infrared Spectroscopy using a PerkinElmer Spectrum 3 FTIR spectrometer with Universal Attenuated Total Reflection (UATR) module. Samples are scanned in a range of 4000 to 650 cm^{-1}, with a resolution of 4 cm^{-1} and at least 16 scans to allow comparison of low signal regions with good signal-to-noise ratio. Equipment is operated without inert gas purging, using the software options for compensation of moisture and carbon dioxide in the scanning path. Any obtained spectra are subjected to automized ATR correction algorithm of PerkinElmer SPECTRUM 10 software.

Particle size distribution of powders is evaluated by dynamic image analysis according to ISO 13322-2 using Camsizer XT with X-Jet module. Two grams of powder are added through the vibratory feed and dispersed in air at 80 kPa pressure. Results shown in this report are referring to minimum of maximal chord lengths xc_min, which gives best correlation to particle sizes obtained from sieving analysis. To evaluate particle shape, the average sphericity of all particles, defined as weighted ratio between projected particle area A and projected particle circumference U according to following equation:

$$SPHT=4\pi\frac{A}{U^2}$$

Furthermore, for optical assessment of particle size and shape and to evaluate distribution of carbon fibers, powders are analyzed by SEM imaging.

During recycling study, printing trials are conducted using a modified EOS P 810, which allows to print parts with low material quantity in a reduced build volume. Processing conditions are standard parameters for HT-23 material and 120 µm layer thickness. The build job design of approximately 15 cm (X) x 10 cm (Y) x 10 cm (Z) contains tensile bars according to ISO 527-2, Type 1BA, in X- and Z-orientation, as well as test geometries to evaluate surface roughness. Job design is depicted in Figure 2. In case of little powder quantities, only specimens in X direction at the beginning of the job are printed. Parts are unpacked at ambient conditions and blasted with glass beads prior to analysis to remove adherent powder.

Material selection for building trials includes HT-23 in virgin state, refreshed state (40% virgin powder, 60% used powder) and used powder, as well as PEKK-CF recycled powder and a blend of recycled powder and HT-23 (40% HT-23 virgin powder, 60% recycled powder).

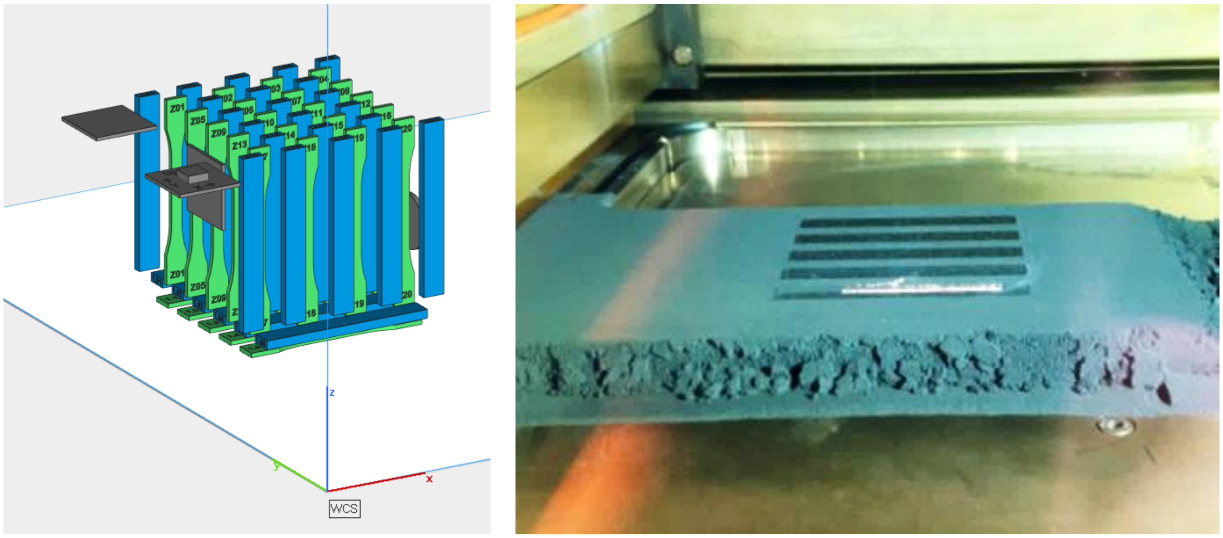

Figure 2: Build Job Design (left) and exemplary build inside modified EOS P 810 (right)

Tensile bars are evaluated according to ISO 527-1/2. Test speed for tensile modulus is 0.5 mm/min, otherwise 2 mm/min. Samples are tested in dry condition. Any results obtained from tensile testing are shown normalized against properties of refreshed HT-23, X orientation. Surface roughness is evaluated according to ISO 4287 using a Keyence VCR-6000 3D profilometer.

Results & Discussion

To have a proper understanding of challenges in recycling of parts made from PEKK materials to powders for powder bed fusion, the detrimental aging mechanisms of these materials are evaluated, in order to compare the properties of the recycled powder finally. Lastly, processing and part production of said recycled powder is conducted in a feasibility study.

PEKK Aging Behavior

Understanding aging mechanism and the resulting changes in material property are the baseline for evaluating recyclability of the PEKK material. Therefore, powder samples exposed to artificial aging are analyzed by different means to correlate these observations.

As commonly addressed in PBF [26–28], the melt viscosity is a key value in qualifying the powder cycle. Figure 3 is depicting the evolution of MVR along different aging temperature and for aging times up to 72 hours.
For PAEK-CF, at aging temperatures below 280°C only minor variations in MVR can be observed, indicating that there is no significant chemical aging mechanism occurring. A slight increase in MVR can be observed (also for short times at higher temperatures) that could be caused by improved chain mobility due to stress relief inside grains by partly fusing crystalline structures or by initial degradation and chain scission. With increasing temperatures, the MVR values are decreasing over time with increasing intensity. For the highest temperature, MVR value is dropping by almost half at 72 hours of aging.
PAEK-1 is showing similar behavior, but a severe drop of MVR values can already be observed at 275°C. Whilst for PAEK-CF the fibers are significantly influencing flow behavior of the polymer filler compound, unfilled PAEK-1 is showing any changes in polymer viscosity. After 72 hours at 285°C, MVR is even dropping to approximately one fourth of the initial value of virgin powder. Surprisingly, MVR of samples aged at 280°C are showing higher or – at prolonged aging periods – similar values compared to samples aged at 275°C. A possible reason might be chemical changes enhancing flowability, e.g. chain scission reactions initially dominating over crosslinking conditions. Possibly, the thermodynamics and reaction kinetics of melting and radical formation diversify between the ether groups and the ketone groups at 275°C and 285°C respectively, resulting in a transitory state at 280°C.
PAEK-2 shows proper stabilization for up to 48 hours of aging, where MVR values are mostly unchanged, whilst afterwards there is a slight drop to approximately 90 percent of the initial MVR value. This observation is in line with the expected improved refreshing behavior. Also, this material shows higher MVR values for samples aged at 280°C compared to other aging temperatures.
Overall, this behavior proves that chemical changes do occur in the material, even though chain growth reactions (e.g. solid-state condensation reactions as seen in polyamides in PBF) are deemed improbable due to the required halogenated functional groups and catalyst in order to undergo such reaction. Moreover, the polymerization reaction in PEKK manufacturing is taking place at significantly lower temperatures, whereas at elevated temperatures the reaction kinetics would be highly increased, in case the functional compounds are still available, which would be expected to result in much faster increase of viscosity. Additionally, the initially little drop in MVR, which is increasing with prolonged times, is opposing typical step growth reaction mechanism. This reaction

mechanism typically results in a steep increase of viscosity (i.e. drop in MVR) at short times under elevated temperatures, whilst after a while reaction kinetics drops significantly due to highly limited chain mobility of long chains and reduced reaction probability due to reduced number of available functional groups. Thus, analogously to the findings in [18] for chemical aging mechanism in PEKK in molten state, radical-induced intra-molecular crosslinking reactions are expected to be the driving factor of viscosity evolution. The introduction of the extended aromatic structures of benzofuranyl and fluorenone type instead of ether and ketone bonds increase rigidity of the polymer chain, resulting in a limitation of chain mobility. On a macroscopic scale this behavior manifests in decreased flowability of the polymer melt.

Moreover, the modified formulation for refresh-improved PAEK-2 shows effectiveness for a long time. The modification could comprise a radical quenching additive. These typically organic stabilizers are used up at prolonged periods under temperature, which is in line with the drop in MVR values at very long aging times.

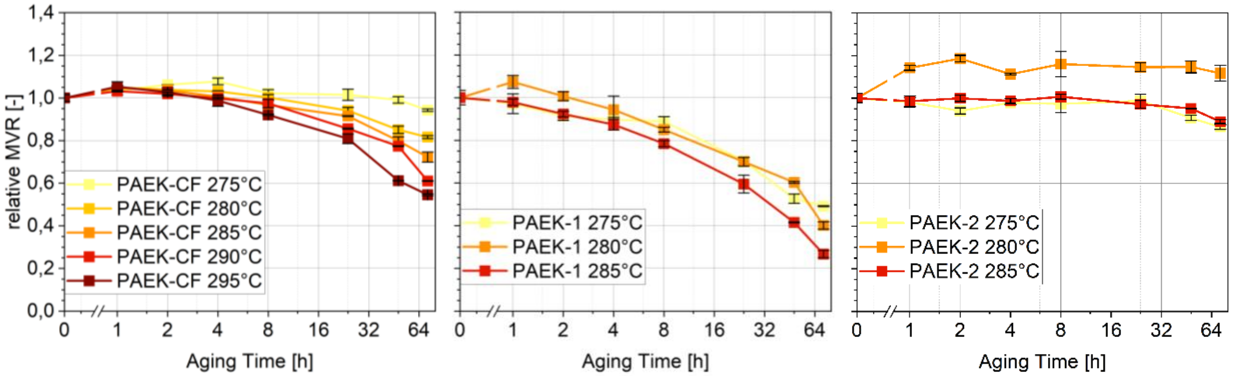

Figure 3: Evolution of MVR along different aging times and temperatures of PAEK-CF (left), PAEK-1 (center) and PAEK-2 (right)

In order to validate the hypothesis of melting thermodynamics vs. reaction kinetics at different temperatures, the melting and crystallization behavior of aged samples is evaluated by DSC analysis. Figure 4 is depicting exemplary curves for first heating run of different aged samples, exhibiting the thermal history applied to the powders by the aging process. Whilst all virgin powder samples show a double peak, the first peak is annealed to higher temperatures with increasing aging temperatures until fully gone.

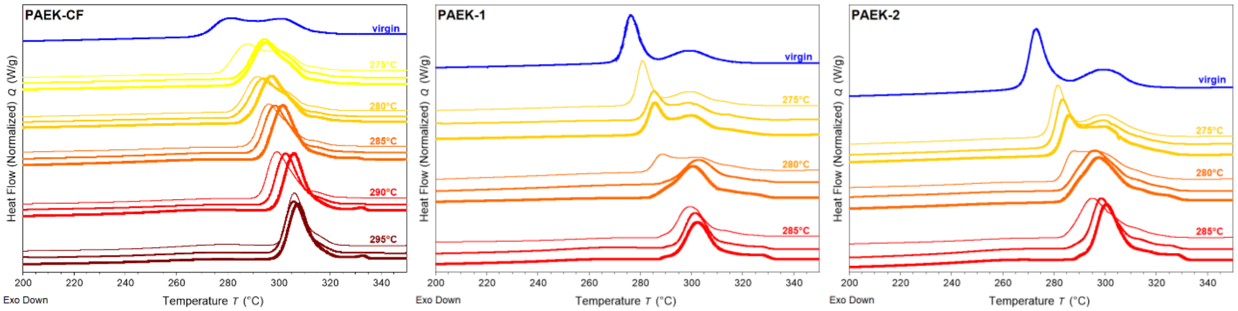

Figure 4: DSC thermograms of first heating runs of aged samples of PAEK-CF (left), PAEK-1 (center) and PAEK-2 (right); different aging temperatures indicated by color, different aging times indicated by line thickness: thin line (top of each group) refers to eight hours, medium line (center of each group) refers to 24 hours and thick line (bottom of each group) refers to 72 hours of aging

For PAEK-CF, shift intensity for all aging temperatures up to 290°C are time dependent, exhibiting the influence of melting and recrystallization kinetics during the aging process. In contrary, any sample of PAEK-CF aged at 295°C is resulting in the same melting peak shape and positioned at 309°C, independent of aging times.

For PAEK-1, a trend similar to PAEK-CF can be observed, with temperature independency already at 280°C aging at times above eight hours. Additionally, an irregularity in peak position can be observed for aging at 280°C: whilst for aging time of 24 hours the peak maximum is located at 305°C, above to the second peak for the virgin powder and other aging conditions, the sample aged at 72 hours shows a drop in peak maximum back to 300°C and a pronounced shoulder below. This irregularity is in line with the observations during rheological analysis, indicating once more a different behavior for 280°C compared to other temperatures. Increased temperatures in melting correlate either with a different crystal structure or the formation of larges crystallites. As no other aging state is ever showing this increased crystal structure, the later factor is assumed to be present. In combination with the experience on melt rheology, it is derived that this larger crystallites are formed due to increased chain mobility at these aging conditions, proposing a change in the molecular structure.

PAEK-2 is also showing the tendency of time-dependent annealing, without the irregularity of increased peak temperature at 280°C. Nonetheless, increased MVR values are observed at 280°C consistently up to long heating times. Therefore, it is assumed that similar reactions might appear compared to PAEK-1 allowing increased chain mobility, but not reflecting in pronounced crystal growth. A possible reason could be the influence of modification of the material.

Besides the beforementioned changes in melting behavior depending on aging conditions, surprisingly a second effect can be observed. At prolonged aging times and high aging temperatures, a shoulder or even a small peak at approximately 330°C is appearing. This crystal growth could correlate with large-range planar, rigid structures of dibenzofuran or fluorenon type caused by intramolecular crosslinking reactions. Especially the planar appearance of the dibenzofuran type is highly deviating from the freely rotating ether group. The evident time dependency is well explained by the requirement of achieving a certain probability of crosslinked structure to meet to form those crystals, which is enhanced with extended aging.

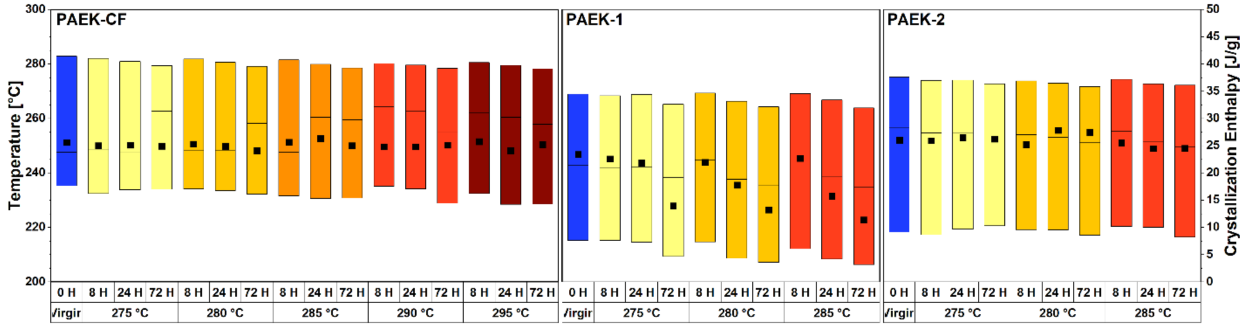

Figure 5: Crystallization behavior of samples aged under different ageing temperatures and durations: PAEK-CF (left), PAEK-1 (center), PAEK-2 (right); depiction of crystallization peak by box chart: onset temperature (top edge), peak maximum (inner line) and endset temperature (bottom edge); Crystallization Enthalpy presented by dots

Altered conformation of chains can also be observed by crystallization behavior (Figure 5).

For PAEK-CF the crystallization peak is tilting towards higher temperatures, i.e. the peak maximum shifting from approximately 245°C to approximately 260°C with increasing aging temperatures: whilst for aging at 275°C only samples aged for 72 hours show the tilting, at 295°C aging times of 8 hours and below already show the same effect. Simultaneously to faster crystallization, crystallization onset temperatures are slightly dropping from 285°C for virgin powder to 275°C for aged samples with decrease depending on aging time primarily and minor influence of aging temperature. Crystallization enthalpy does not show any evolution, which is expected as crystal formation and growth is highly influenced by the carbon fibers.

PAEK-1 shows different behavior. With increasing aging times, onset temperature, peak temperature and endset temperature are shifting evenly to lower levels, with no major influence of the aging temperature. Only the sample aged at 275°C is showing a threshold condition, as only for 72 hours the shift can be observed. In parallel, crystallization enthalpy does drop significantly for these samples. With respect to these observations, it can be stated, that the chemical changes rather decrease nucleation and crystallization kinetics at this cooling rate, which is expected for rigid chain structures. The formation of the high-melting structure as observed with first heating runs can only occur with annealing conditions, i.e. long-lasting high temperatures rather than constant cooling.

PAEK-2 shows the stabilizing effect of modification, compared to PAEK-1. Slight analogous tendencies for studied temperatures can be observed, but to a significantly lower extent. For enthalpy, there is no visual trend at all, indicating the absence of alterations in the crystal structures.

Chemical changes in the polymer composition are expected to influence the color of the material. Therefore, colorimetric data of aged powder samples are shown in Figure 6.

Whilst for PAEK-CF, due to the well expected dark color of the carbon fibers, no significant change of color can be observed visually, the analytical data show a shift of green-red chromaticity a* and blue-yellow chromaticity b* to higher values at aging temperatures above 280°C, whilst the b* shift is even more pronounced at temperatures above 290°C and long aging times.

For PAEK-1 visually a significant change in color is observed, even showing particles with a red-brown shading on optical microscopy imaging (Figure 7). Analytical data is showing significant increases in both a* and b* values with increasing aging times, whilst aging temperatures have only secondary influence on intensity.

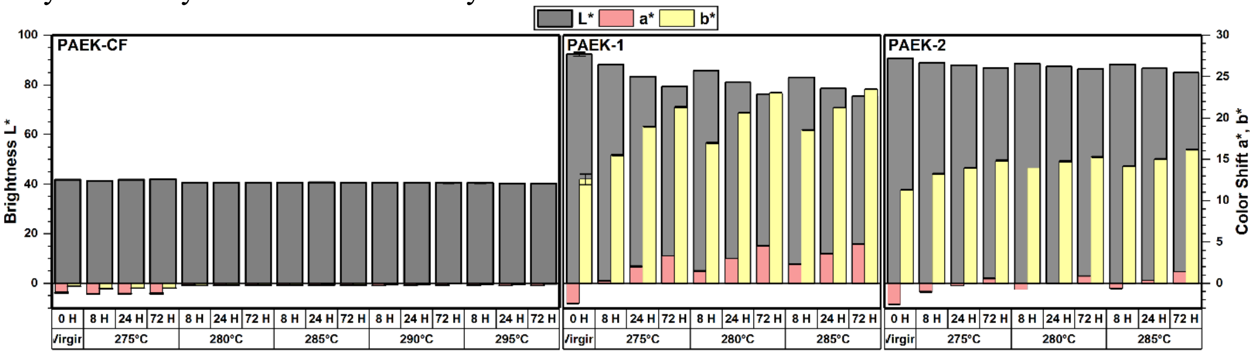

*Figure 6: Evolution of CIE L*a*b* values along aging at different temperatures and times of PAEK-CF (left), PAEK-1 (center) and PAEK-2 (right)*

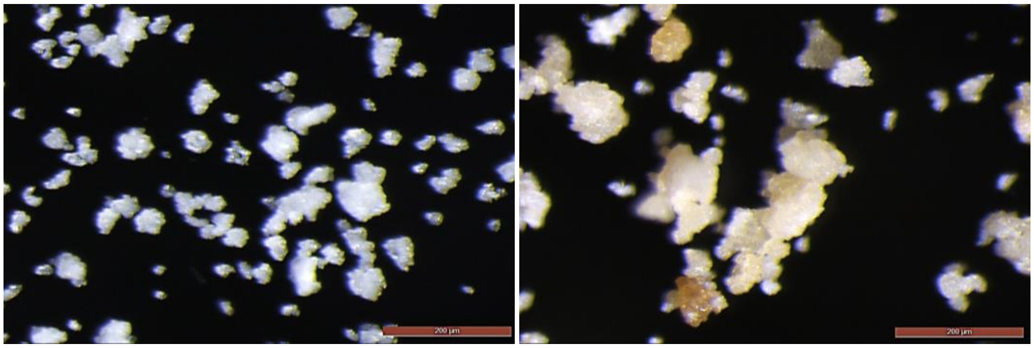

Figure 7: Microscopy images of virgin PAEK-1 (left) and discolored PAEK-1 aged at 285°C for 72 hours (right)

PAEK-2 does not show obvious discoloration. Analytical data reveal, that slight tendencies to increased a* and b* values following both aging times and aging temperatures occur, but significantly lower compared to PAEK-1.

In order to verify the chemical changes, FTIR spectroscopy is employed. Figure 8 is showing an exemplary excerpt of the fingerprint and carbonyl region of PAEK-CF virgin material and PAEK-CF aged at 295°C for 72 hours. Additionally, the differential spectrum, i.e. the (weighted) difference between aged and virgin sample is depicted to allow easier identification of changes.

It can be observed, that there are very minor changes at ~1660 cm^{-1} which could either indicate the change of conformation from ketone to fluorenon structures or the introduction of the aromatic C-C bond as a consequence of crosslinking, as well as more significant changes in the range of 1200 cm^{-1} to 1000 cm^{-1}, which correlates with C-O stretching, which is obviously reduced when ether structure is converted into dibenzofuran structure.

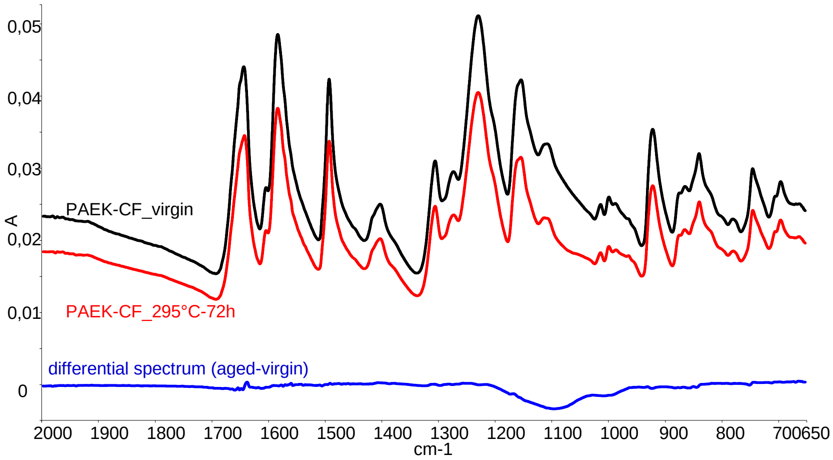

Figure 8: exemplary FTIR spectra of carbonyl (1850 – 1650 cm^{-1}) and fingerprint (below 1500 cm^{-1}) region for virgin PAEK-CF (black) and PAEK-CF aged at 295°C for 72h (red); additionally, differential spectrum (virgin subtracted from aged) is given (blue)

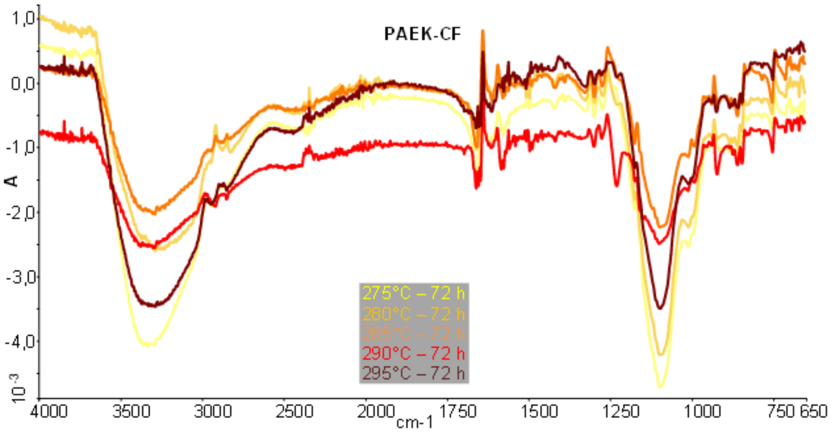

Figure 9: Differential spectrum for PAEK-CF at different temperatures and 72 hours of aging; spectra referenced versus spectrum of virgin powder

Looking at the full MIR spectral range for PAEK-CF at different aging temperatures (Figure 9) additional effects become apparent. Most obviously, a negative peak in the 3500 to 3000 cm^{-1}

region can be determined for all temperatures. This peak typically refers to OH-groups. Possible reasons could be the presence of interaction between hydrogen from aromatic structures with oxygen in the functional groups, i.e. the ketone or ether structures, for virgin material, that does not appear accordingly after the aging, as the crosslinking reduces deformation of the chain and thus hinders the transitionary binding states. Also the influence of thermal degradation during compounding, forming OH-containing degradation products that are consequently present in virgin PAEK-CF powder, can be considered. Alternately, surface chemistry of the carbon fibers could be showing hydroxyl groups for virgin powders, that is altered during aging. Additional changes at 2500 cm^{-1} and at 1100 cm^{-1} support the first two hypotheses, whilst a changing shift within the carbonyl region suggests an influence of the latter hypothesis.

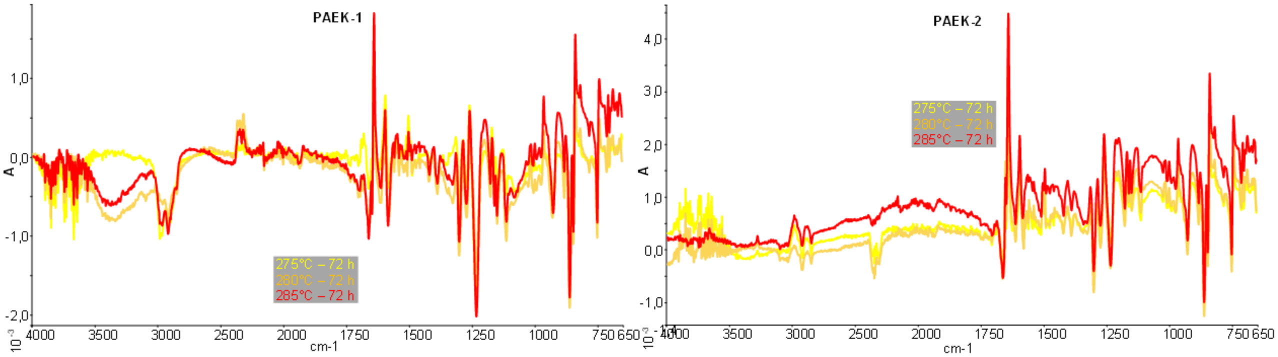

Figure 10: Differential spectra of unfilled PAEK-1 (left) and modified PAEK-2 (right) at different temperatures and 72 hours aging time; spectra referenced versus spectrum of respective virgin powders

The effect of carbon fibers can additionally be estimated by comparison to the differential spectra for unfilled PAEK-1 (Figure 10, left). No difference in the region of OH bonds is observed for 275°C, only slight differences at higher aging temperatures (as relative intensity of the peaks compared to the peak structure at ~3000 cm^{-1}), whilst for PAEK-CF even at 275°C a difference can be observed. In consequence it might be concluded that surface chemistry of the carbon fibers are either changing or at least influencing the aging mechanism.

Comparing PAEK-1 and PAEK-2 (Figure 10), the expected stabilizing effect in terms of chemical changes can be verified. For PAEK-2, neither changes in the OH region nor in the region of 1200 to 1000 cm^{-1}, which is correlated to the ether structure, can be observed. This finally can be addressed as evidence of the intramolecular crosslinking creating the dibenzofuran structure from ether structures as an effect of aging.

In respect of the proposed aging mechanism of intramolecular crosslinking reaction, the observations of this study are in line. For PAEK-CF and PAEK-1, which do not contain a reaction stabilizer, the formation of dibenzofuran or fluorenon structures is providing extended aromatic structures, resulting in a color shift to yellow and/or red as well as different crystal structures with progressing aging. The stabilized material PAEK-2 does not show the same changes, which again supports the assumption of the stabilizer being a radical quenching additive, limiting the formation of radical precursors for intramolecular crosslinking reaction. Moreover, it could be shown that the proposed aging mechanism does clearly correlate with material properties, e.g. melt viscosity, also in regard to intensity of chemical aging effects. Still, some additional analytical methods, including in-situ spectroscopy, could be useful to observe the mechanism and discriminate different stages along the reaction mechanism.

<u>Properties of PEKK-CF Powders recycled from Parts</u>

In order to assess the quality of recycled PEKK-CF powder, typical properties are compared to properties of commercial HT-23 grades. Additionally, by comparing to the findings on material aging, an estimation of aging severity is deduced.

An essential property of powders for PBF is a proper particle size distribution (PSD) and powder flow behavior. Figure 11 is presenting the PSD and SEM imaging of recycled PEKK-CF in comparison to a representative batch of HT-23. Whilst in terms of fine fraction d10 and average particle size d50 both powders are very similar, it is obvious that recycled PEKK-CF contains a reasonable coarse fraction, as d90 is increased by approximately 30 µm compared to HT-23. This result can be explained by observations from SEM imaging of these powders: recycled PEKK-CF shows a rather lengthy, almost fibrous particle shape compared to virgin HT-23. Similar observation is obtained when comparing sphericity of the particles, as derived from the PSD analysis: whilst for virgin HT-23 material an average sphericity SPHT of 0.89 was calculated, the value drops to 0.83 for recycled PEKK-CF. In consequence, flowability of recycled PEKK-CF is expected to be reduced compared to virgin HT-23. This was confirmed by bulk density analysis according to ISO 60, where bulk density dropped by approximately 25 percent from 55 g/cm³ for virgin HT-23 to 40 g/cm³ for recycled PEKK-CF.

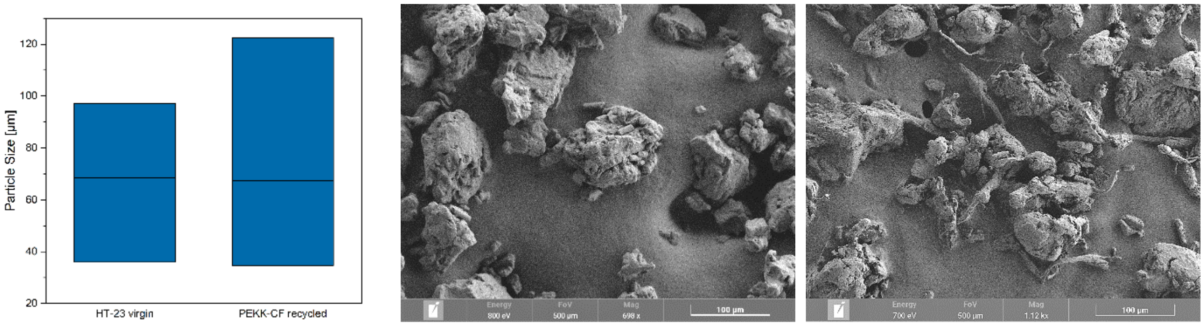

Figure 11: PSD of HT-23 and recycled PEKK-CF (left): D10 (bottom edge), D50 (inner line) and D90 (top edge); SEM imaging of HT-23 (center) and recycled PEKK-CF (right) showing particle shape, where lengthy structures can be observed for PEKK-CF

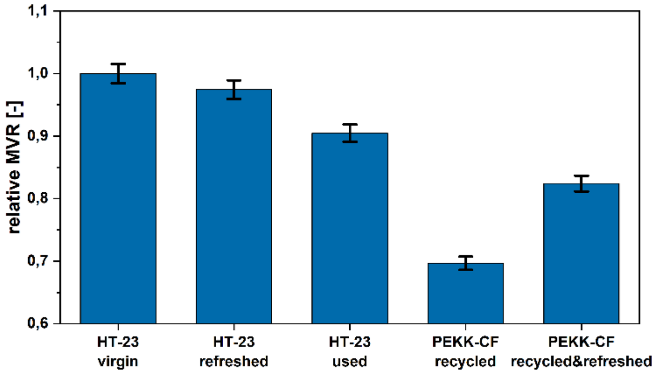

Figure 12: MVR values of different powder samples included for testing processability of recycled PEKK-CF; values normalized against MVR value of virgin HT-23 material

Alongside the flow behavior of the powder, melt rheology is relevant for processing dense parts in PBF process. It can be observed that MVR value of recycled PEKK-CF drops to 70 percent compared to virgin HT-23, which is also significantly lower than MVR value of used powder coming from PBF process. Comparing this value to the findings of the aging study, MVR value is similar to MVR values of samples aged in solid state for 72 hours at 290°C. Even though this temperature is in typical range for processing of HT-23 on EOS P 810, the material is typically not exposed to this temperature for that long period of time, as slow cooling is occurring inside the material after a layer is not exposed to heating radiators in the machine anymore. The intensified increase in viscosity is therefore related to the state of material being molten, which allows intensified chain mobility and could thus enhance the reaction kinetics of intramolecular crosslinking.

As different aging behavior was observed due to a different material state during processing in terms of melt viscosity, thermal behavior is assessed by DSC analysis (Figure 13). For the first heating run, it can be observed, that recycled PEKK-CF prior to annealing shows obvious cold crystallization. Compared to annealing effects during powder aging, the crystalline structures formed during cooling from melt do not yield maximum degree of crystallinity or most stable crystal structures respectively. One might consider influences coming from grinding process, where on impact material could be partly fused and quenched, but comparative DSC analysis on parts show identical behavior.
After annealing, a double peak similar to virgin HT-23 and no cold crystallization can be observed. Compared to HT-23 virgin material, a slight shoulder can be observed at 310°C, but no peak at 330°C, as seen during aging studies (Figure 4), is apparent. Thus, it is assumed that the crystal modification at 330°C can only be achieved during high temperature annealing/aging rather then during cooling from molten state.

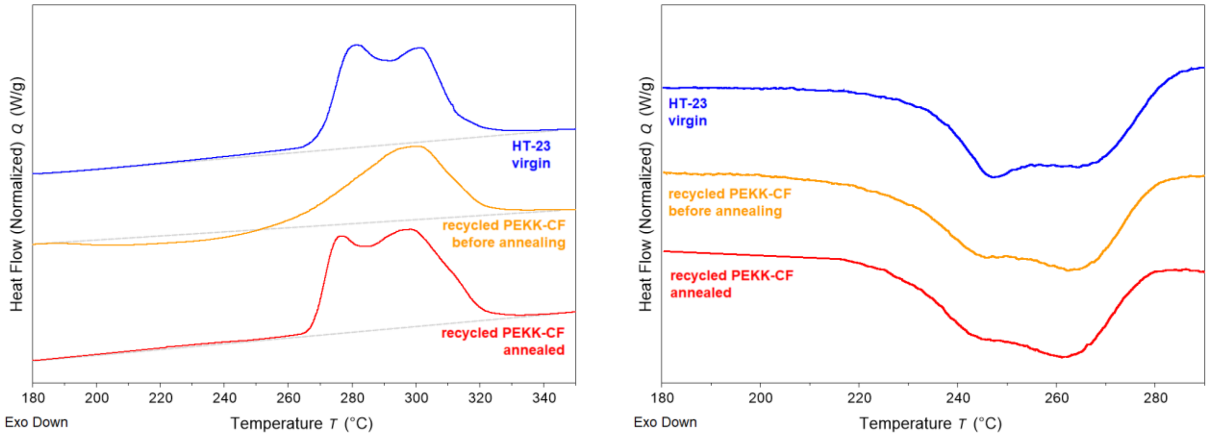

Figure 13: DSC thermograms of recycled PEKK-CF before and after annealing compared to HT-23, depicting first heating run with ideal baselines (left) and cooling run (right)

For cooling run, a shift of peak intensities can be observed. Whilst for virgin HT-23 the dominant peak of the crystallization double peak is at lower temperatures, i.e. 245°C, for recycled PEKK-CF the higher peak at 265°C is more pronounced, but stays unchanged during annealing. It is assumed, that for virgin material the early crystal formation is induced by the influence of the carbon fibers. The fast crystallization behavior is additionally enhanced for recycled material, as the rigid structures due to crosslinking reduce chain mobility, allowing faster formation of large range alignment of the chains, possibly also supported by the adjusting influence along the carbon fibers. In consequence, narrowing of the processing window of recycled material is expected.

IR Spectroscopy of recycled PEKK-CF compared to virgin HT-23 (Figure 14) reveals some chemical shifts, yet intensity and identification is not as clear as within the aging study. Still, an obvious alteration can be observed in the carbonyl region at around 1650 cm^{-1}, significantly more intense compared aged powders (Figure 8), but the effect at 1200 cm^{-1} to 1000 cm^{-1} is significantly reduced. Possibly, during the rather slow reaction mechanism in solid state for the aging study, the formation of the dibenzofuran and fluorenon structures are in a more transitory state, whilst for materials being molten allow quick reaction of formation of the final structure.

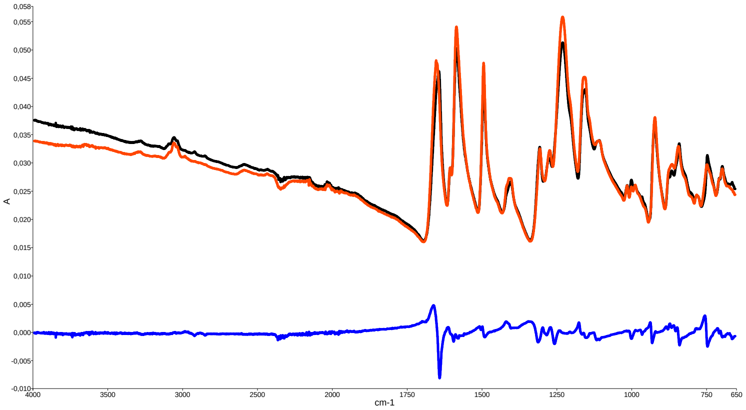

Figure 14: FTIR spectra of recycled PEKK-CF (red) compared to virgin HT-23 material (black) and differential spectrum (blue)

Concluding these observations, it can be stated that aging mechanism of intramolecular crosslinking is also happening for parts produced from HT-23 during PBF. As a matter of increased chain mobility, the effects apparent are more pronounced, similar to 72 hours of aging at very high temperatures. It could be shown, that in general powders can be produced from parts, whilst in terms of particle shape and subsequently powder flow behavior the recycled PEKK-CF powder needs to undergo further improvement. Influence of these deviations from properties of HT-23 on processibility and part properties in PBF are subject of the next study.

Processing and Properties of Parts from Recycled Powders

For processing of the different powders, one temperature settings was fixed. This temperature setting allowed processing of all powders unless recycled PEKK-CF without annealing, which is expected due to cold crystallization which negatively influences processing due to significant changes of powder morphology. As only little amount of recycled PEKK-CF was available, only a very small job design (X oriented specimen only) could be used for processing of this material.

Figure 15 depicts tensile properties of different material variations. In general, an offset in properties between X and Z-oriented specimen is observed, that is well known as an effect of layerwise building process. Thus, X-oriented specimen are typically considered to show differences in material composition, while Z-oriented specimen indicate the influences on the manufacturing process.

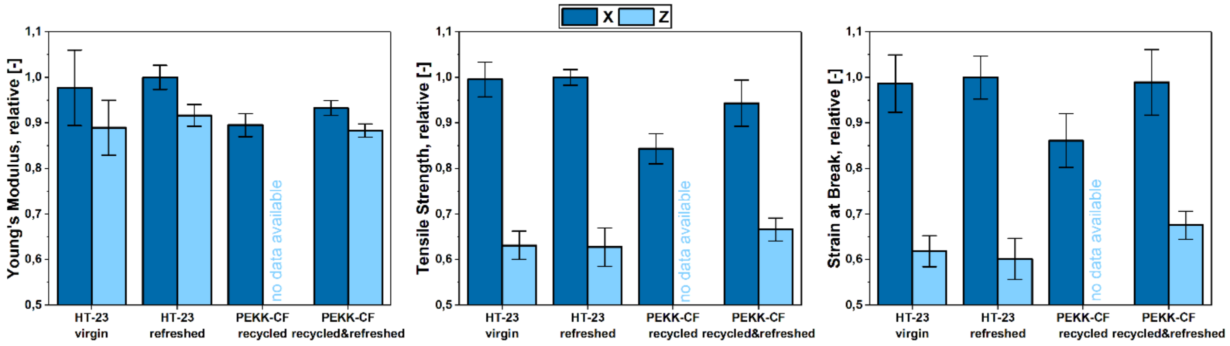

Figure 15: Tensile Properties of HT-23 and recycled PEKK-CF; Young's Modulus (left), Tensile Strength (center) and strain at break (right); values normalized against properties of refreshed HT-23, X oriented

In X orientation, for Young's Modulus a drop of approximately ten percent for recycled PEKK-CF compared to HT-23 is observed, which can be partly recovered when blending recycled PEKK-CF with virgin HT-23 powders. Tensile Strength of PEKK-CF is decreased by almost 20 percent, but also shows touch up when virgin HT-23 is added. Strain at break follows the same pattern.

For Z orientation, no major lowering of properties can be observed, a slight increase in strain at break could be estimated for the blend of recycled PEKK and virgin HT-23.

It is therefore assumed, that applying recycled material does not show negative influence on the processing itself, but material properties might lower the part performance. Reduced strength is expected to be an effect of worse coalescence. Both, increased melt viscosity as well as irregular particle shape resulting in worse powder bed density are considerable root causes. The consequential increased porosity lowers strength while increasing apparent ductility. For investigation of the influences, processing of powders with similar melt viscosity but improved powder flow might be assessed.

The only minor changes in ductility are confirmed by results from Charpy impact testing. Within typical standard deviations, results for parts from virgin HT-23, refreshed HT-23 and recycled PEKK-CF blended with virgin HT-23 show no significant changes for neither notched nor unnotched samples, only a minor increase in ductility for the latter material might be considered.

These observations allow once again to verify the intramolecular crosslinking reactions to be the main aging mechanism, as progressing chain growth or intermolecular crosslinking would be expected to increase ductility and decomposition of chains would decrease ductility.

A secondary influence of PSD and particle shape is observed regarding the surface roughness of parts. Figure 16 shows roughness average R_a and mean peak-to-valley height R_z for surface in XY or Z orientation respectively. Also here, the influence of layer wise manufacturing can be observed, as values for Z oriented surfaces is always influenced by processing conditions, e.g. layer thickness. It can be observed, that samples containing recycled PEKK-CF exhibit increased roughness average R_a and mean roughness height R_z, which are almost double compared to HT-23 samples in XY orientation. Irregular shaped particles and the consequential broader particle size distribution are significantly influencing the surface quality of the parts.

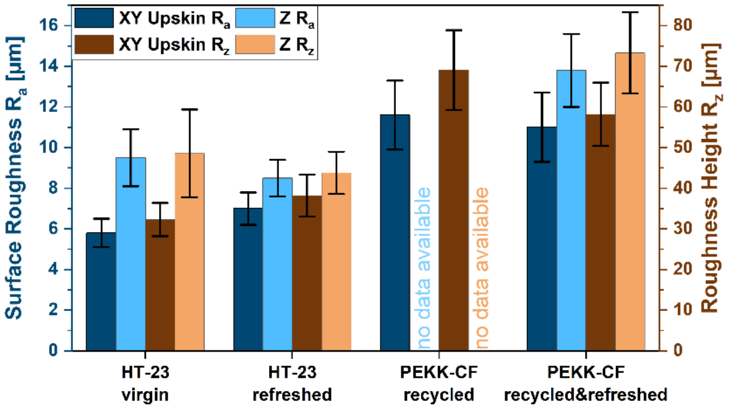

Figure 16: Surface roughness of parts produced from different variations of HT-23 and recycled PEKK-CF

Conclusion & Outlook

The study confirms, that intramolecular crosslinking is the major effect of material aging of PEKK materials based on Arkema's Kepstan 6000 series. Moreover, the effective usage of stabilizers, which are expected to act as radical quenching agents to prevent the crosslinking, is demonstrated. The physical and chemical aging effects revealed by high temperature exposure of powders below melting point are not fully applicable to aging effects that occur within the parts produced from PEKK material by Powder Bed Fusion. Whilst the increase in melt viscosity is equaling the behavior of harshest conditions at sold state aging, assumingly due to faster reaction due to increased chain mobility in molten state, the crystal structure within parts is significantly different. Additional analyses, e.g. solid state NMR or spectroscopy at elevated temperatures (in-situ spectroscopic observation during aging, e.g. high temperature IR or NMR spectroscopy) could help to further understand these aging mechanisms. Moreover, the formation of alternate crystal structures in aged samples could be revealed by WAXS (wide angle X-ray scattering).

Feasibility of recycling of parts made from HT-23 is demonstrated with lab scale trials. Powders produces from parts by grinding process yield properties that are suitable for processing in PBF, while optimization is still required. Especially the formation of lengthy particle structures needs to be addressed, e.g. by polishing the particles according to methods that are already used for improving powder flow properties [10], or by applying different powder production methods. Parts produced from recycled material show partly reduced mechanical properties, which is assumed to be an effect of powder compaction behavior and/or changed melt flow behavior due to chemical aging. The influence of grinding process on the fiber length distribution needs to be addressed, especially when considering repeated recycling. Shortening of fibers is expected to result in loss of mechanical strength.

Within further studies, improvements to powder quality, PBF processing parameters and potential regeneration methods for reduction of aging effects shall be considered. Additionally, comparative analyses on parts made from other PAEK materials, especially with respect to the variations employed in the aging study, shall be considered. Finally, beyond the singular recycling of parts, repeated reuse of material in the PBF process and related aging has to be addressed, with special remark to additives, fillers and contaminants.

References

1. Manfred Schmid, Antonio Amado, and Konrad Wegener, "Polymer powders for selective laser sintering (SLS)" (Paper presented at the PROCEEDINGS OF PPS-30: The 30th International Conference of the Polymer Processing Society – Conference Papers, Cleveland, Ohio, USA, 6–12 June 2014).
2. Maximilian Munsch et al., "AMPOWER Report 2024: Additive Manufacturing Market Report" .
3. Stephanie Hendrixson, Understanding PEKK and PEEK for 3D Printing: The Cool Parts Show Bonus. https://www.additivemanufacturing.media/articles/understanding-pekk-and-peek-for-3d-printing-the-cool-parts-show-bonus (accessed 9 June 2024).
4. V. Carlota, All You Need to Know About PEKK for 3D Printing. https://www.3dnatives.com/en/pekk-3d-printing-material-130520204/ (accessed 9 June 2024).
5. Sybille Fischer et al., "A High-Performance Material for Aerospace Applications: Development of Carbon Fiber Filled PEKK for Laser Sintering,".
6. Andreas Pfister, Novel high performance polymer PEKK for Laser Sintering (3D-printing) fulfills your needs for cost efficient and demanding small series production | LinkedIn. https://www.linkedin.com/pulse/novel-high-performance-polymer-pekk-laser-sintering-fulfills-pfister/ (accessed 9 June 2024).
7. Frank Müller, Andreas Pfister, and Martin Leuterer, *PAEK-Pulver, insbesondere zur Verwendung in einem Verfahren zum schichtweisen Herstellen eines dreidimensionalen Objektes, sowie Verfahren zu dessen Herstellung*, 15 pp., 2007 (accessed 7 June 2024).
8. L. Benedetti et al., "Evaluation of particle coalescence and its implications in laser sintering," *Powder Technology,* 342 (2019), 917–928.
9. Patrice Peyre et al., "Experimental and numerical analysis of the selective laser sintering (SLS) of PA12 and PEKK semi-crystalline polymers," *Journal of Materials Processing Technology,* 225 (2015), 326–336.
10. Benoît Brule et al., *Improved Powder for Additive Manufacturing*, 64 pp., 2020 (accessed 8 June 2024).
11. Gerhard W. Becker et al., eds., *Kunststoff-Handbuch,* Kunststoff-Handbuch Technische Thermoplaste, / hrsg. von Ludwig Bottenbruch … ; 3 (München: Hanser, 1994).
12. Guillaume Le, Julien Jouanneaum, and Jérome Amstutz, *Method for Synthesizing Polyaryletherketones*, 6 pp., 2015.
13. Andreas Pfister, Frank Müller, and Martin Leuterer, *Selective sintering of structurally modified polymers*, 17 pp., 2009 (accessed 7 June 2024).
14. Arkema France, "Kepstan-PEKK" (2022).
15. Aarif Shaik, "Processing of ground PEKK-CF from Laser-Sintering Parts" (Master Thesis, Hochschule Kaiserslautern, 2023).
16. C. J. Tsai, L. H. Perng, and Y. C. Ling, "A study of thermal degradation of poly(aryl-ether-ether-ketone) using stepwise pyrolysis/gas chromatography/mass spectrometry," *Rapid Communications in Mass Spectrometry,* 11 (18) (1997), 1987–1995.
17. Parina Patel et al., "Mechanism of thermal decomposition of poly(ether ether ketone) (PEEK) from a review of decomposition studies," *Polymer Degradation and Stability,* 95 (5) (2010), 709–718.

18. T. Choupin et al., "Macromolecular modifications of poly(etherketoneketone) (PEKK) copolymer at the melting state," *Polymer Degradation and Stability,* 155 (2018), 103–110.
19. Oana Ghita et al., "Physico-chemical behaviour of Poly (Ether Ketone) (PEK) in High Temperature Laser Sintering (HT-LS)," *Journal of Materials Processing Technology,* 214 (4) (2014), 969–978.
20. Peng Chen et al., "Aging mechanism of polyetheretherketone powder during layer-wise infrared radiation of high-temperature laser powder bed fusion," *Materials & Design,* 213 (2022), 110348.
21. S. Berretta et al., "Polymer viscosity, particle coalescence and mechanical performance in high-temperature laser sintering," *Journal of Materials Science,* 51 (10) (2016), 4778–4794.
22. A. R. McLauchlin, O. R. Ghita, and L. Savage, "Studies on the reprocessability of poly(ether ether ketone) (PEEK)," *Journal of Materials Processing Technology,* 214 (1) (2014), 75–80.
23. Mengxue Yan et al., "High temperature rheological behavior and sintering kinetics of CF/PEEK composites during selective laser sintering," *Composites Science and Technology,* 165 (2018), 140–147.
24. Akanksha Patel et al., "Evaluating poly(ether ether ketone) powder recyclability for selective laser sintering applications," *Polymer Degradation and Stability,* 185 (2021), 109502.
25. EOS GmbH Electro Optical Systems, "HT-23 for EOS P 810: Application notes" (2018).
26. Dietmar Drummer, Katrin Wudy, and Maximilian Drexler, "Modelling of the aging behavior of polyamide 12 powder during laser melting process" (Paper presented at the PROCEEDINGS OF PPS-30: The 30th International Conference of the Polymer Processing Society – Conference Papers, Cleveland, Ohio, USA, 6–12 June 2014).
27. S. Cholewa, Andreas Jaksch, and Dietmar Drummer, "Coalescence Behavior of Polyamide 12 as Function of Zero-Shear Viscosity and Influence on Mechanical Performance" (Paper presented at the Solid Freeform Fabrication Symposium, Austin).
28. Pengfei Tan et al., "Multiphysics modelling of powder bed fusion for polymers," *Virtual and Physical Prototyping,* 18 (1) (2023).

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