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Effects of physical and chemical ageing on 3D printed poly (ether ether ketone)/poly (ether imide) [PEEK/PEI] blend for aerospace applications

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ABSTRACT

During service in outdoor environments, or in some application fields, 3D printed polymer-based materials are exposed to various environmental conditions such as moisture, heat, and chemical solvents that may cause significant degradation in properties. The durability of 3D printed high-performance polymer materials under environmental conditions has become an ongoing concern for the industry and researchers due to their increasing use. This study aims to evaluate the effects of physical and chemical aging on the properties of a 3D printed blend of PEEK/PEI. The structural, morphological and mechanical properties of as-printed and aged samples were studied by multiple methods, including FTIR, SEM and tensile tests. Thermal properties of samples were also evaluated through TGA, DSC and DMA analysis. Except for a slight decrease in elastic properties, the PEEK/PEI blend does not exhibit significant changes in tensile strength, degree of crystallinity and thermal properties after 1000 h of physical and chemical aging. The PEEK/PEI blend remained stable after aging under severe conditions similar to those found in a reactor nacelle, conditions to which parts produced by additive manufacturing could be subjected.

Introduction

High-performance engineering polymers satisfy or exceed requirements in aerospace, energy, and automotive applications when compared to conventional thermoplastics [1–4]. These high-performance thermoplastic polymers exhibit superior thermal resistance, good mechanical performance, thermal and chemical stability even at elevated temperatures and under severe conditions [5, 6]. Poly (ether ether ketone) (PEEK) is an important member of poly (aryletherketone) (PAEK) and one of the most used engineering polymers. Thanks to its linear aromatic

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groups and its semi-crystalline structure, this thermoplastic has a melting temperature (T_m) of ~340 °C, a glass transition temperature (T_g) of 143 °C and a service temperature up to 260 °C. PEEK also exhibits high mechanical properties (tensile strength ≈98 MPa, Young's modulus ≈3.5 GPa) [7, 8]. These outstanding mechanical and thermal properties allow PEEK to be used as a suitable replacement for aluminum or steel in a wide variety of high-temperature applications [9]. Polyetherimide (PEI) is also a special engineering plastic with very good properties. It is an amorphous thermoplastic polymer mainly used to manufacture high-performance parts for multiple industrial purposes. The aromatic imide units of PEI's chain provide higher thermal stability while the flexible ether linkages provide good processability and manufacturability [10]. This yields a T_g of ~215 °C [11, 12], a remarkable strength-to-weight ratio and an excellent heat resistance, as well as flame-retardant capacity, and promising flame-smoke-toxicity (FST) characteristics [13].

The literature points out that PEEK and PEI are molecularly miscible in the whole range of composition [11, 12]. Moreover, blending allows the complementary properties of these polymers to be combined and to obtain excellent broad properties. As known, the processing temperature is derived from the melting temperature (T_m) while the service temperature can be determined from the material's glass temperature (T_g). PEEK exhibits a higher price and lower glass transition temperature than PEI, thus limiting its use in the industry while its operating and service temperatures are limited. On the other hand, PEI exhibits a higher T_g but lower chemical resistance than PEEK, and cannot be used above its T_g [11, 14]. Blending PEI with PEEK allows to, because of their complementary properties, tailor properties such as T_g, solvent resistance, mechanical properties, etc. From previous studies, it was reported that incorporation of PEI in a PEEK matrix increases T_g and facilitates processing [6, 15]. *As* a consequence of the increased T_g, the PEEK/PEI blends are expected to retain their properties at elevated temperatures more effectively than pure PEEK [16]. Chen el al. [17] studied the structures and mechanical Properties of PEEK/PEI/PES after thermal aging at 158 °C (below T_g) and 178 °C (above T_g), respectively, for 168 h. Results showed that PEI, PES and the amorphous plastics could increase T_g of the PEEK alloys and was 20 °C higher than that of pure PEEK. After thermal aging, tensile strength results decreased only slightly, but elongation at break reduced significantly, of which thermal aging above T_g would recede the elongation at break more severely.

Compared to established technologies, 3D printing has attracted much attention in recent years as it offers the possibility to manufacture complex geometries, reduce part count and generate less materials waste. Fused Deposition Modeling (FDM) is an additive manufacturing technology often used for prototyping, physical modeling and end-use production applications. FDM-manufactured components are widely replacing traditionally produced components in many applications in areas such as the automobile, aviation and medical sectors. In contrast to subtractive manufacturing methodologies, the FDM technology can advantageously fabricate complex geometries in a single step without requiring molds, welding, cutting or machining [18]. Thanks to technical development in FDM machines, high-performance polymers (e.g., PEEK, PEKK, PEI) can today be printed easily [19]. With FDM, the thermoplastic filament is fed through a heated extrusion nozzle to be deposited layer by layer onto a build support to form the 3D object. The concept of 3D printed parts properties includes not only the intrinsic properties of the material but also the printing parameters used during the manufacturing process [8]. FDM is considered a complex additive manufacturing technology due to the difficulty in determining optimal printing parameters that influence the final material properties and part quality. The effects of printing parameters have been discussed in many works and researchers found that management and control of these parameters have to be taken into serious consideration as they directly affect the degree of crystallinity, dimensional stability, interlayer bonding, and mechanical properties of manufactured parts [20–23]. In the literature, many researchers found that nozzle temperature, printing speed, raster angle, and layer thickness are the most influencing printing parameters on the tensile properties and degree of crystallinity of FDM-printed PEEK and PEI materials [8, 24]. A review of the available literature shows only one paper on the 3D-printing of PEEK/PEI blend. In this paper, El Magri et al. [25] focused on the preparation and 3D-printing of PEEK/PEI blend. Results showed that adding 30 wt% of PEI to the semi-crystalline PEEK improved

the glass temperature by 20 °C while maintaining the high tensile properties of the PEEK. In the same study, nozzle temperature, layer orientation and layer thickness were selected as printing parameters to evaluate their effect on tensile properties and degree of crystallinity (X_c) of printed PEEK/PEI parts.

As discussed above, the blending of two engineering polymers such as PEEK and PEI has been considered by many scientists to be an interesting approach for balancing their properties and achieving a thermoplastic matrix with high-performance properties. To the best of our knowledge, only one work shows that such a binary PEEK/PEI blend can be processed using the Fused Filament Fabrication (FFF) process [25]. Despite the mentioned advantages of 3D printed PEEK/PEI blend using FFF process, the effect of environmental and chemical aging of this blend on the final properties is still a missing point. To fill this research gap, this study focused on the impact of chemical and physical aging on structural, thermal and mechanical properties of 3D printed PEEK/PEI parts for aeronautical applications.

Materials and methods

Polymers compounding and filament preparation

The poly (ether ether ketone) used in this study was VESTAKEEP 3300G from EVONIK INDUSTRIES (Germany). It is a medium-viscosity grade with a density of 1.30 g cm^{-3}, a melting temperature (T_m) of 340 °C, and a glass temperature (T_g) of 152 °C. Poly (ether imide) (PEI) ULTEM™ 1010 was purchased from SABIC. It has a density of 1.28 g cm^{-3} and a T_g of 217 °C. PEEK/PEI (70/30 wt/wt%) blend was prepared using a co-rotating twin-screw extruder HAAKE Rheomex PTW16/25 coupled to a HAAKE Polylab OS7 system (Thermo Haake, Germany). The extruder has a screw length-to-diameter (L/D) ratio equal to 40, with a screw diameter (D) of 16 mm. Heating along the barrel is divided into nine zones, with the temperature profile displayed in Fig. 1a. The molten PEEK/PEI leaving the extruder was quenched in a water bath, air-dried, and chopped into pellets. These PEEK/PEI pellets were later extruded using a single screw plastic extruder (Next Advanced, 3Devo, Netherland) to produce PEEK/PEI filament. The extruder machine is equipped with four heating zones and a hardened nitride steel extruder screw with a compression zone. In this extrusion process, many variable parameters were adjusted carefully to produce high quality of filaments with a diameter of 1.75 ± 0.05 mm, including barrel temperature, screw speed and fan speed. The processing parameters are given in Fig. 1b.

Thermogravimetric analysis (TGA)

TGA was performed on a Q500 equipment, (TA Instruments, version 20.13), under a 60 mL min^{-1} nitrogen flow in the temperature range of 30 to 1000 °C. Dynamic experiments were carried out at heating rates of 10 °C min^{-1}, using ~20 mg samples.

Fourier transforms infrared spectroscopy analysis (FTIR)

Fourier transform infrared FTIR analysis was carried out using a NICOLET™ IS50 ATR spectrometer on as-printed and aged PEEK-PEI printed parts. The samples were analyzed in a total of 64 iterations in the wavenumber range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. These analyses aim to identify any macromolecular change in the polymer after aging compared to the as-printed blend.

Differential scanning calorimetry (DSC)

Significant changes in crystallinity and thermal properties can occur in thermally and chemically aged PEEK-PEI parts. This was evaluated using DSC analysis performed on a DSC Q20 (TA Instruments, version 24.11) equipped with a RCS90 cooling system. All measurements were performed under a 50 mL min^{-1} nitrogen flow. Samples (13–15 mg) cut from as-printed and aged specimens were sealed in aluminum pans. Samples were heated from 25 to 400 °C before being cooled back to 25 °C. A heating and cooling rate of 10 °C min^{-1} was used in DSC studies. All characteristic temperatures and associated enthalpies were calculated from the DSC thermograms, using TA-Universal analysis software. To better understand the thermal properties of post-printed and aged PEEK/PEI parts, only the second heating curves were recorded to characterize the thermal properties and the degree of crystallinity X_c(%) experienced after exposition in a harsh environment. The X_c was calculated according to Eq. 1:

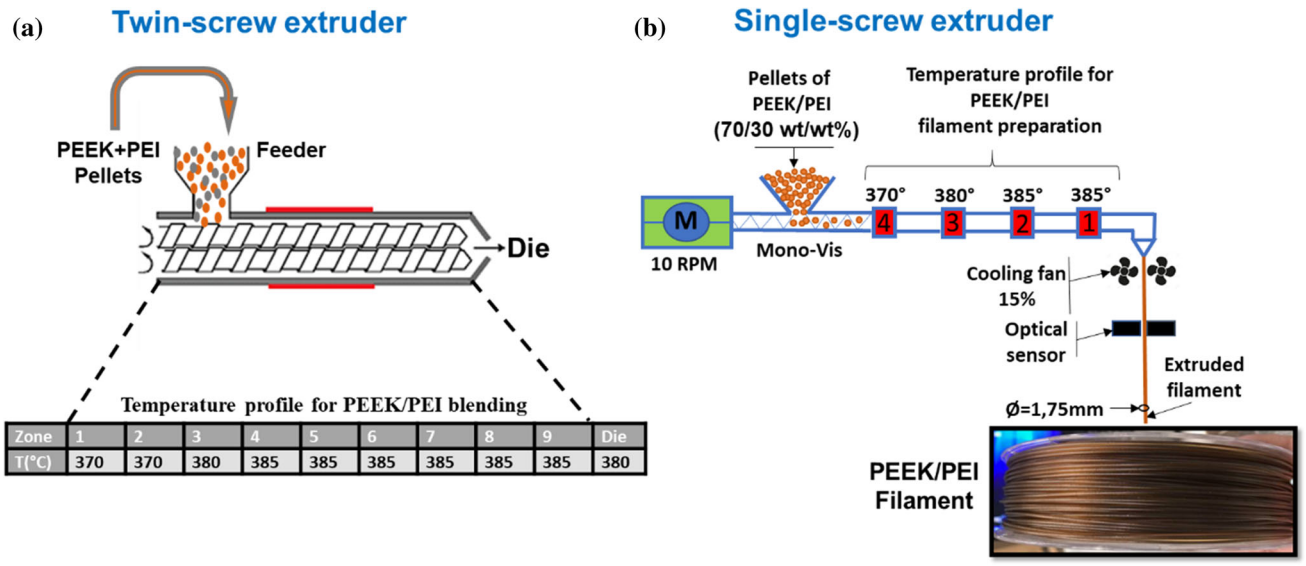

Figure 1 Schematic of extrusion process parameters: **a**: PEEK and PEI blending **b**: PEEK/PEI (70/30) filament extrusion.

$$X_c(\%) = \frac{\Delta H_m - \Delta H_{cc}}{w \times \Delta H_m^0} \times 100 \quad (1)$$

where ΔH_m is the enthalpy of melting (J g^{-1}); ΔH_{cc} is the enthalpy of cold crystallization.

(J g^{-1});w is the weight fraction of the PEEK in the blend; and ΔH_m^0 is the standard enthalpy of fusion for 100% crystalline PEEK (J g^{-1}).

Specimens fabrication and aging conditions

An INTAMSYS FUNMAT HT Enhanced equipped with a build volume of 260 × 260 × 260 mm was used for 3D-printing PEEK/PEI blend. This FFF system is specifically designed to 3D print high-performance functional materials as it is equipped with a heated build platform and chamber. Test specimens were printed directly on the heated glass bed, using a brim to hold down the edges of test specimens to improve bed adhesion and avoid peeling off during printing. The infill parameter was set to 100% to obtain solid-like samples. Based on our published research work [25], the nozzle temperature was maintained at 400 and 380 °C for PEEK and PEEK/PEI, respectively. Maximum tensile properties values were recorded at these temperatures. The layer thickness was fixed at 0.15 mm to favor strong cohesion, adhesion, and surface contact as reported in [25]. Table 1 summarizes the other selected significant parameters. All specimens were printed flat on the build platform (XY surface). Slicing of the 3D-model into individual layers was performed using the INTAM-suite software (Version 3.5.2). The printed PEEK/PEI samples were annealed for two hours at 200 °C to erase residual thermal stress generated during printing. The annealing condition was chosen according to our last study [25].

Physical aging of polymers is considered as a gradual change of their properties with time at a temperature below their glass transitions (T_g). For this type of aging, the printed samples were exposed to a dry heat environment at 120 °C and to a moist heat environment at 70 °C and 85% relative humidity (RH) for 1000 h. Material performance tests under different conditions (heat and moisture) were performed in a temperature humidity chamber (Guangdong Yuanyao Test Equipment-model: YTHG-072 YTHG-162-China). The characterization of the aged specimens was carried out directly on leaving the climatic chamber without any drying or prior treatment. The chemical aging was realized according to ISO 175:2010 standard which specifies a method of exposing test specimens of polymeric materials, free from all external restraint, to liquid chemicals, and methods for determining the changes in properties resulting from such immersion. This aging test only considers testing by immersion of the entire surface of the test specimen. In this work, the aging protocol consisted of placing in an oven a glass beaker containing the 3D printed test bars immersed in SKYDROL® LD-4 at 70 °C for 1000 h. Skydrol, an advanced fire-resistant aviation hydraulic fluid based

Table 1 Fused filament fabrication printing parameters

Printing parameters	Value	Unit
Print speed	30	(mm s^{-1})
Build platform temperature	100	(°C)
Chamber temperature	30	(°C)
Infill line directions [relative to the long axis of the test bar]	[0/15/−15]	(°)
Layer thickness	0.15	(mm)
Infill pattern	Lines	
Line width	0.4	(mm)
Infill density	100	%
Number of bottom / top layers	2/2	Layer
Number of contours	2	wall

on tributyl phosphate, has low-density, excellent lubricating properties, erosion resistance and high thermal stability. The frequency of the fluid replacement was 7 days to maintain the same aging conditions. After sampling of test bars, the Skydrol excess is wiped off using a lint-free cloth, no prior drying of the specimens was carried out before testing.

Tensile testing and dynamic mechanical analysis

Tensile testing was performed using a universal testing machine (Criterion C45.105 electromechanical universal testing machine, MTS, USA) equipped with a 10-kN load cell. The test speed was set as 5 mm min^{-1} according to ASTM D638–14 "Standard Test Method for tensile Properties of Plastics. Six samples of the D638 type IV geometry (Fig. 2a) were tested at ambient temperature (20 °C) for each batch. Sample displacement (mm) and force (N) were collected and processed by the MTS TestSuite software to draw tensile strain–stress curves and establish Young's modulus, tensile strength and strain at break. All reported values are the averages of the six specimens.

Dynamic mechanical analysis (DMA) is used to characterize the response and measure the glass transition temperature of as-printed and aged PEEK/PEI samples. In this study, a DMA Q800 Dynamic Mechanical Analyzer (TA Instruments) was employed for thermal scans from 25 to 300 °C at a heating rate of 10 °C min^{-1}. All printed samples were tested in dual cantilever bending mode with a frequency of 1 Hz and an oscillation amplitude of 10 μm. Rectangular specimens (Fig. 2b) with a dimension of 59 mm in length, 12 mm in width and 3.2 mm thick were 3D printed based on the standard test method for plastics ASTM D5418-2007. The peak of the storage (E') and loss modulus (E'') were plotted to identify the glass transition temperature (T_g) of *as-printed* and chemically aged PEEK/PEI samples. The T_g was determined to be the intersection of two tangent lines from E' or from the maximum value of the E″ peak. Values for E' and E'' are the average of three tested specimens.

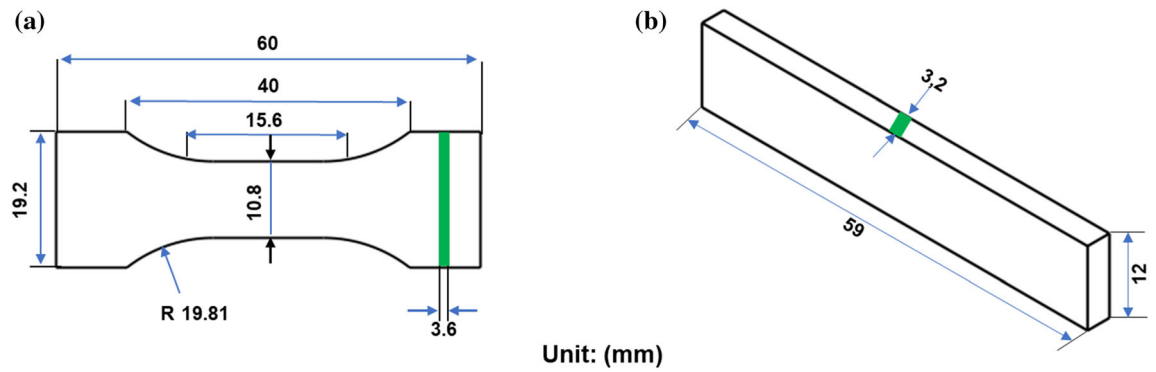

Figure 2 **a** Tensile test sample geometry according to ASTM D638 Type IV **b** DMA sample geometry according to ASTM D5418.

Results and discussion

Effects of physical aging on thermal, structural and tensile properties

Thermogravimetric analysis (TGA)

Thermogravimetry analysis (TGA) was used to characterize the thermal stability of the material before and after the aging process. Figure 3a depicts the typical TGA curves of normalized mass and derivative thermogravimetry (DTG) data of the derivative mass of as-printed and physically aged PEEK/PEI blend in different aging conditions (dry heat and moist heat) between ambient temperature and 1000 °C, collected with at a heating rate of 10 °C.min^{-1} in nitrogen medium. For both aging types, the TGA plots revealed that these samples undergo a two-step decomposition. The onset temperature (T_{onset}), maximum degradation temperature (T_{max}) and residue at 1000 °C were measured by TGA for as-printed and aged samples. As shown in Fig. 3a, the first degradation step begins at 532 °C, with a T_{max} at 552 °C. The second degradation occurs between 730 and 740 °C. The DTG curves show clearly a mild rate for this second degradation. During the final phase of degradation, the mass loss incurred led to a thermostable residue of 46 and 48% for the as-printed and aged samples, respectively. The similarity in thermal profile indicates the insensitivity of the PEEK/PEI blend to aging in dry and moist heat environments. We can refer to studies on

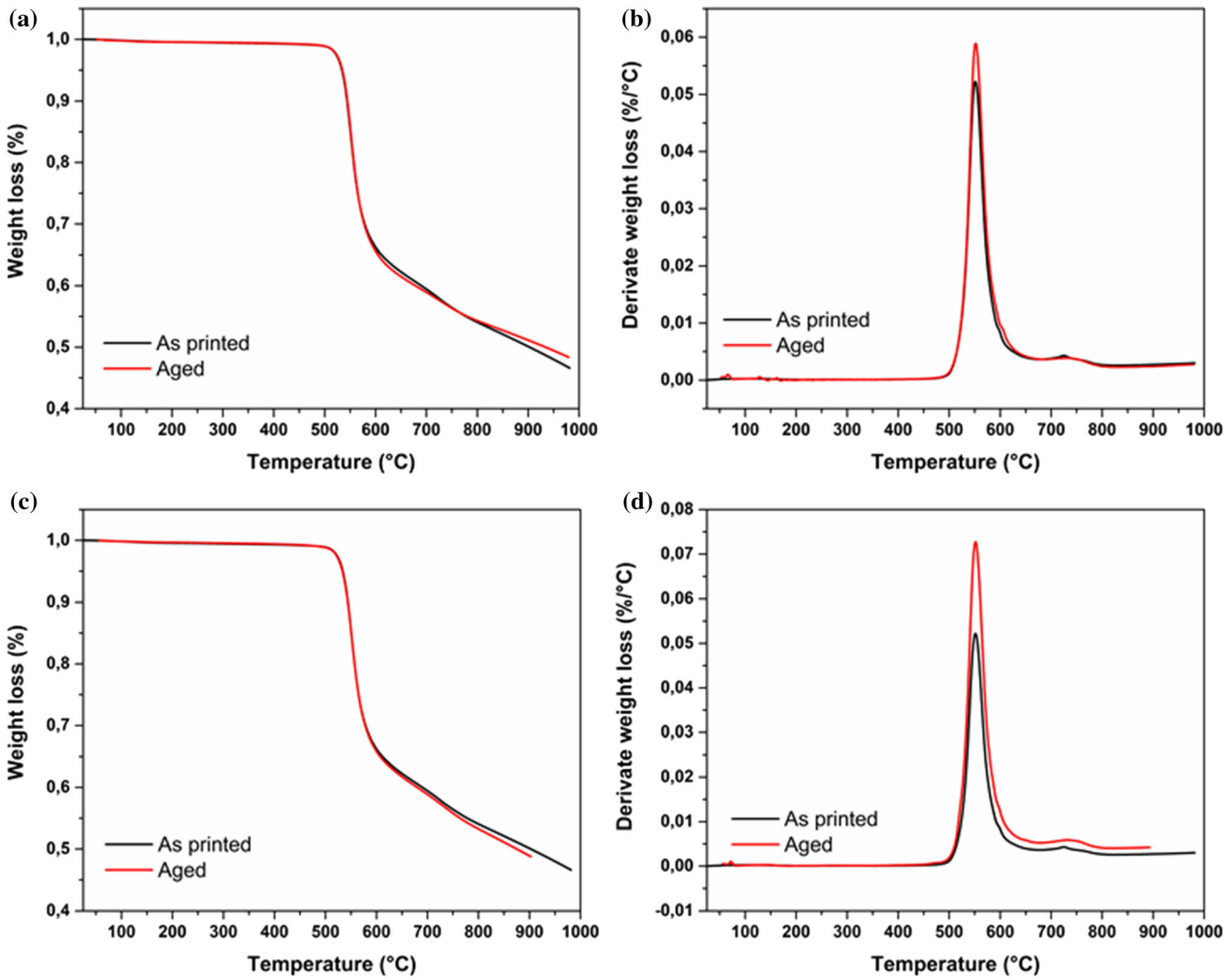

Figure 3 Thermal gravimetric analysis (TGA)-Derivative thermogravimetric (DTG) curves of as-printed and aged PEEK-PEI samples. Results of **a** ATG, **b** DTG at moist heat treatment at 70 °C-85% RH/1000 h; **c** ATG, **d** DTG at dry heat treatment at 120 °C/1000 h.

PEEK and PEI [26, 27] to better understand the decomposition of PEEK/PEI blends. In a study on the pyrolysis of PEEK by TGA/MS in nitrogen a medium [28], the first major pyrolysis step observed at 570 °C was attributed by the authors to the main chain-scission of the ether and ketonic groups. The cleavage of these latter groups mainly yielded phenol and CO_2, respectively. The second step pyrolysis was mild and observed at 800 °C due to the cleavage of ketone group formed in the first step [28, 29]. A pyrolysis study of PEI in inert atmosphere [26] reported the scission of the imide group in two-stage pyrolysis process. The first step at 540 °C was related to the formation of CO_2, benzene, phenol and aniline [26]. The partially carbonized structure undergoes further pyrolysis in a second step above 560 °C, where the remaining imide group produced CO_2 as the major product along with benzene and benzonitrile as pyrolysates.

Our results are in agreement with the two-step decomposition process discussed above for PEEK [46, 47] and PEI [20]. The two-step decomposition observed in the blends and the expected end-products could be a combination of what has been reported for PEEK and PEI depending on their composition in the blend.

Differential scanning calorimetry (DSC)

DSC analysis was performed for PEEK/PEI samples in the as-printed and physically aged conditions. Thermal events and crystallization ability of neat and aged blend were established from the second heating and cooling DSC scans (Fig. 4). After first scanning to eliminate the thermos-stress history, the second scanning is recorded for the thermal properties measurements.

Table 2 summarizes values found for the glass transition (T_g), melting (T_m), crystallization (T_c) temperatures, as well as the melting (ΔH_m) and crystallization (ΔH_c) enthalpies. The degree of crystallinity (X_c) was calculated for each sample. All samples exhibited the same T_g, T_m and T_c regardless of aging condition, confirming that printed PEEK/PEI parts are not affected by the thermal history experienced during aging cycles. In addition, the stability of T_g proves the absence of alteration of the molecular chains of PEEK/PEI caused by aging. Crystallinity is another critical property that requires consideration in 3D printed parts. The crystallinity degree of aged

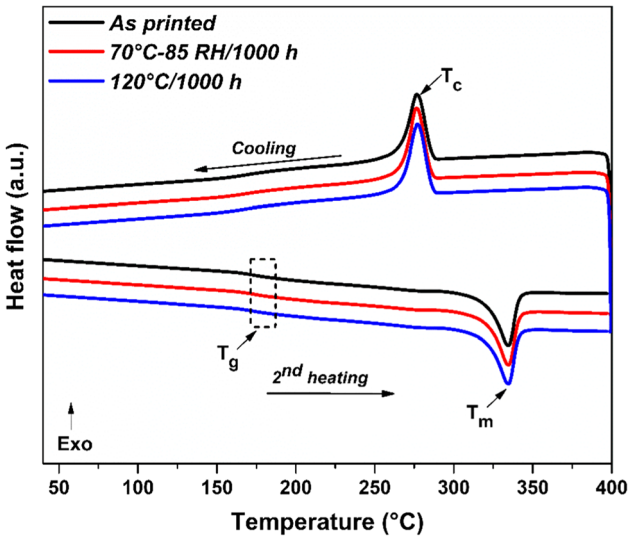

Figure 4 Differential scanning calorimetry scans of as-printed and aged PEEK/PEI blend.

samples was found at ~31% (Table 2), a level similar to that of as-printed PEEK/PEI samples. The results revealed that the structural order of the molecules in the PEEK/PEI blend was not significantly altered during physical aging. All these results confirmed the thermal and structural stability of 3D printed PEEK/PEI parts after aging.

Fourier transforms infrared spectroscopy (FTIR) analysis

The ATR-FTIR spectra of as-printed and aged PEEK/PEI samples were recorded to provide information about polymer–polymer interactions before and after aging (Fig. 5). As expected, the FTIR spectrum of as-printed and aged PEEK/PEI blend exhibits the same chemical characteristic. In this case, the blend displays a peak typically associated with the ketone ring (C = O) stretching at 1650 cm^{-1}, while peaks at 1488 cm^{-1} and 1594 are the C–C stretching of the aromatic rings of PEEK [30]. The band situated at 1220 cm^{-1} is the C–O–C stretching vibrations of the aromatic ether bond, while the 832 and 765 cm^{-1} bands are linked to wagging vibrations. Absorption peaks of PEEK's ether, having less intensity, appear at 1100 and 1184 cm^{-1} [31]. The three noticeable bands in the 500 to 700 cm^{-1} region are associated to aromatic groups, while three less intense peaks in the 2840–3100 cm^{-1} range are the C-H stretch vibrations for the PEEK [32]. The spectrum exhibits also two bands at 1780 and 1718 cm^{-1} arising, respectively, from ketone asymmetrical stretching vibration and

Table 2 Transitions temperatures, enthalpies, and degree of crystallinity of as-printed and aged samples

	T_g (°C)	T_m (°C)	T_c (°C)	ΔH_{cc} (J·g^{-1})	ΔH_m (J·g^{-1})	ΔH_c (J·g^{-1})	X_c(%)
As-printed	172.3	334.9	276.5	–	28.76	29.97	31.60
70 °C/85RH-1000 h	172.5	334.8	276.3	–	28.01	30.60	30.78
120 °C/1000 h	172.2	334.8	276.7	–	28.94	32.24	31.80

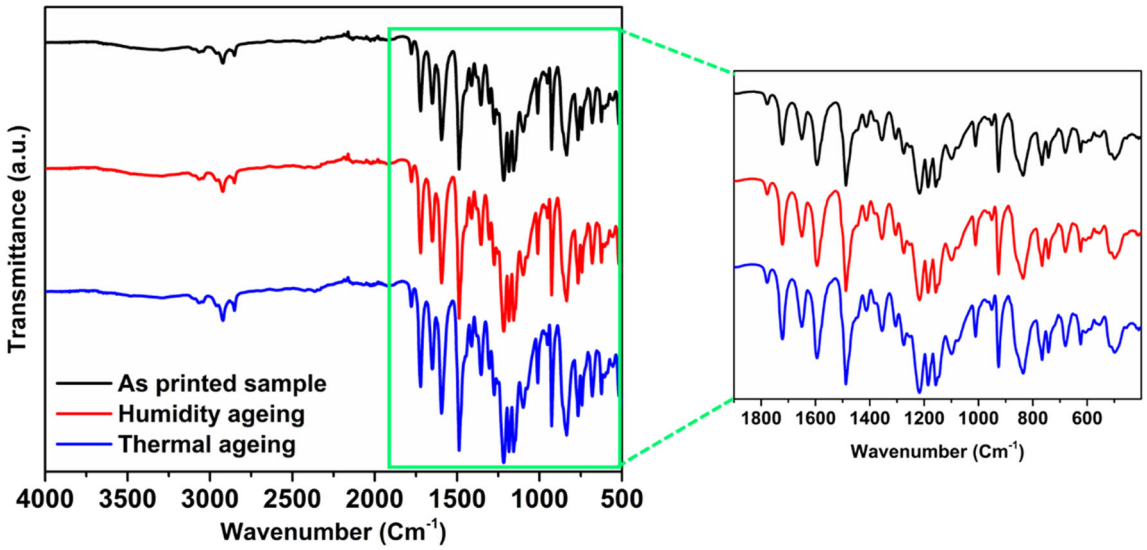

Figure 5 Infrared spectrums of as-printed and aged sample with zoom-in finger print region.

carbonyl symmetrical stretching vibration of the imide group, and a peak at 1355 and 742 cm^{-1} attributed to the C-N stretching and bending, respectively [24, 33]. The sharp peak situated at 1590 cm^{-1} corresponds to the C–C stretching of the aromatic rings, while those at 1230 and 1175 cm^{-1} are correlated to C–O–C stretching of the aromatic ether [34]. The C-H stretching vibrations of methyl groups appear at 2970 cm^{-1} [35].

Tensile and morphological properties

Using parameters previously identified [25], tensile bars were printed with the optimized printing parameters of 380 °C for nozzle temperature, 0.15 mm layer thickness and layer orientation of [0/15/-15°]. Printed samples were subjected to annealing treatment at a temperature of 250 °C for two hours to allow the relaxation of residual stresses and to enhance the degree of crystallinity. To evaluate the impact of physical aging on tensile properties, six PEEK/PEI specimens were prepared with identical printing conditions. The tensile testing results of aged samples were compared with those obtained for neat PEEK/PEI. From Fig. 6, it can be observed that a heat environment at 120 °C decrease the rigidity of sample by 10% while the strength of PEEK/PEI specimens is maintained. The impact of thermal aging on the tensile strength found in our study is similar to the work of Chen et al. [17]. They found that the tensile strength of the blend PEEK/PEI/PES (70/30/0)

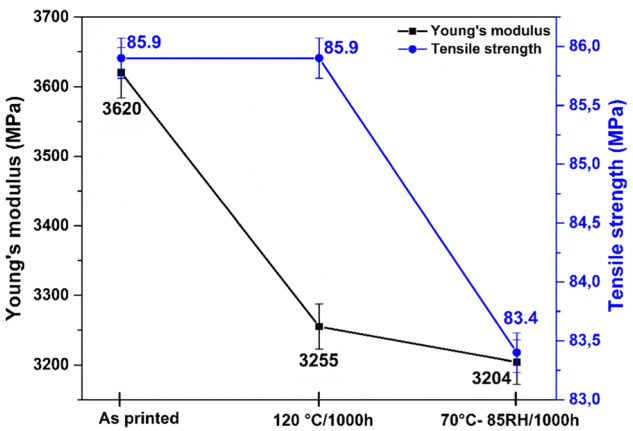

Figure 6 Tensile properties of as-printed and aged sample.

decreased by 9% after 168 h at a temperature of 158 °C. This confirms that the influence of thermal aging was small on tensile strength.

Specimens exposed to moist heat environment (70 °C and 85% RH) exhibited a noticeable decrease in the Young's modulus, going from 3620 to 3204 MPa (∼ 11.5%). Tensile strength also decreased after exposure to moist heat, going from 85.9 MPa to 83.4 MPa. This could be attributed to a plasticizing of the amorphous phase caused by the absorption of water molecules between the polymer chains [36]. As water molecules penetrate into the polymer structure, they break up the secondary Van der Waals bonds or the hydrogen bonds between polar groups of the polymer that contribute in large part to the material rigidity. The preferential bonding of these groups to water molecules will increase the mobility of the macromolecular chains or chain segments. This will in turn accelerates molecular reorientation with stress, resulting in a reduction in tensile properties of the polymer/blend. The 1000 h exposure gives plenty of time to water molecules to achieve an almost homogeneous distribution inside the material. Literature studies show that mechanical properties can also deteriorate because of microcrack formation due to uneven thermal contraction and expansion during hydrothermal conditions [37, 38].

By relating SEM observations to tensile results, it becomes possible to explain the variations of PEEK/PEI tensile properties after aging process. Figure 7 shows the surface morphology of PEEK/PEI specimens before and after aging. The as-printed samples (Fig. 7a) show homogeneous *and* stratified layers with strong interlaminar bonding, indicating proper binding between infill strands. Fracture surfaces of as-printed parts are relatively flat and characterized by the absence of voids and gaps between juxtaposed layers. Such characteristics promote higher Young's Modulus and tensile strength. Figure 7b shows the fracture surface of the aged specimen in a heat environment at 120 °C for 1000 h. SEM clearly shows voids between juxtaposed layers with weak interlayer bonding. This favors delamination, thus explaining the decrease in elastic modulus. The same phenomenon was observed in the case of specimens aged in moist heat (Fig. 7c). Large interlayer gaps between infill filaments are found. Such gaps favor the delamination of welded layers, thus explaining the decreased bending strength and inferior rigid behavior. Bad adhesion between layers makes it hard to transfer internally the stress imposed during tensile testing, whereas voids create punctual defects that weaken properties. The FDM printing process also creates defects inside the samples, which may expand in presence of moisture. This expansion will generate internal stress concentration that can favor micro-voids propagation. This will weaken the interfaces of the deposited polymer lines and between deposited layers [39].

Effects of chemical aging on thermal, structural and tensile properties

Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA)

DSC measurements were performed to evaluate the effect of chemical aging on the physical properties of the PEEK/PEI blend. Thermal events and crystallization ability of the as-printed and aged PEEK/PEI samples were established from the first heating and cooling DSC scans (Fig. 8a). The first heating cycle was used to characterize the thermal history experienced during the aging cycles. DMA thermograms of as-printed and aged samples are given in Fig. 8b. Storage modulus (E′) and loss modulus (E″) were measured as a function of temperature. E′ is related to the stored energy and describes the stiffness of the material while E″ relates to the energy dissipated as heat and irreversibly lost. As this 70/30 PEEK/PEI blend is a semi-crystalline material, amorphous and crystalline regions will yield different responses to dynamic mechanical analysis at a given temperature range [40]. Figure 8b shows that the unaged PEEK/PEI sample exhibits the highest storage and loss modulus. A progressive decrease in stiffness and energy dissipation is observed for PEEK/PEI samples aged by more than 168 h.

Values found for the glass transition (T_g), melting (T_m), crystallization (T_c), as well as the melting (ΔH_m) and crystallization (ΔH_c) enthalpies are summarized in Table 3. This table also includes the degree of crystallinity (X_c) which was calculated for each sample. The first heat flow exchange for all samples, located around 180–184 °C, is associated with the glass transition temperature (T_g). The measured T_g of aged PEEK/PEI parts is higher than the *as-printed* parts. It can also be observed that T_g is progressively increasing with aging time up to a point. This implies a progressive reduction in mobility for the

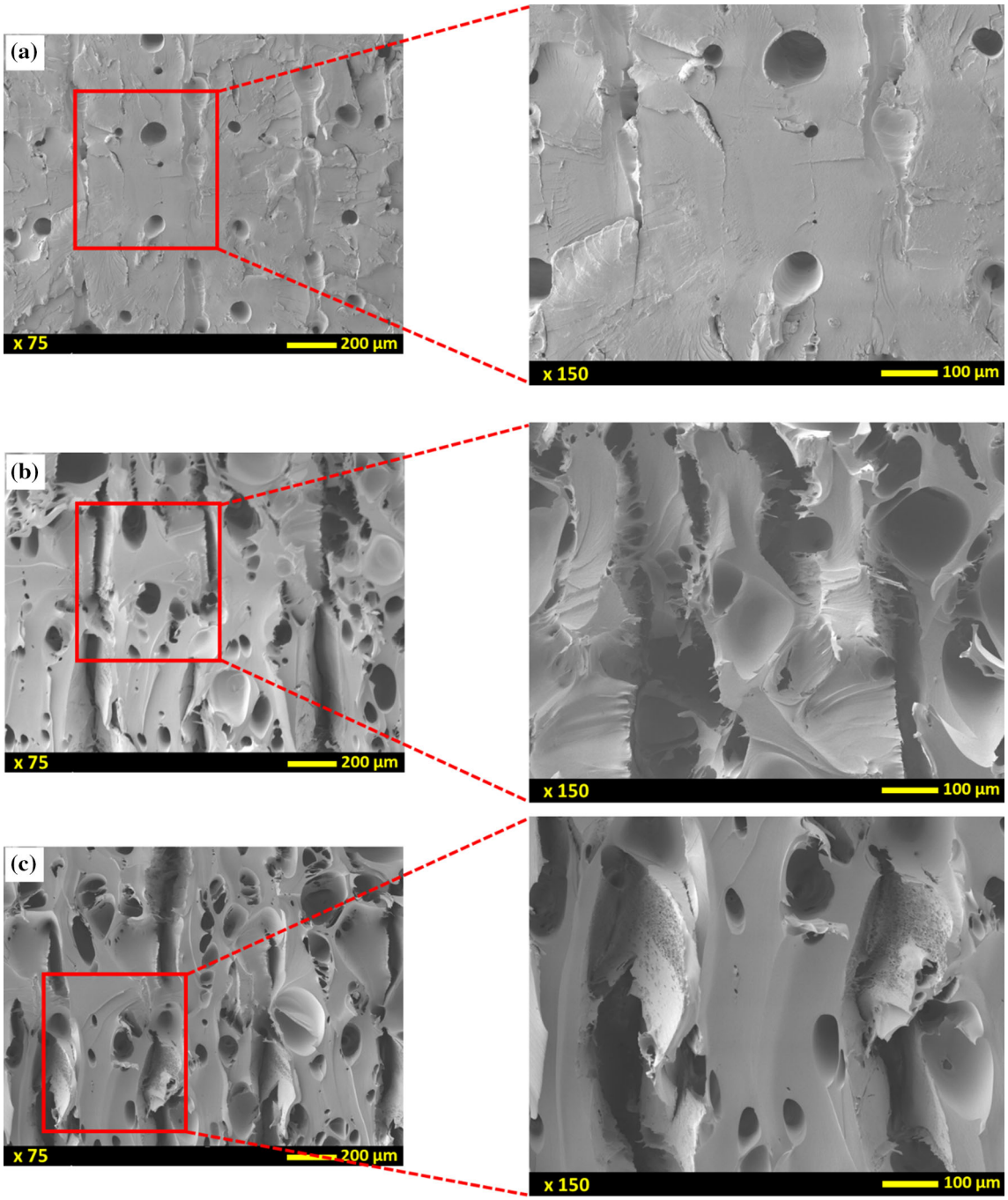

Figure 7 SEM micrographs of the fractured surfaces of **a** as-printed PEEK/PEI sample, and aged PEEK/PEI sample: **b** at dry heat treatment at 120 °C/1000 h and **c** at moist heat treatment at 70 °C-85% RH/1000 h.

amorphous segments of PEEK and PEI. To confirm this, DMA analysis of as-printed and aged specimens was performed (Fig. 8b). The measured $T_{g(DMA)}$ shows the same behavior as $T_{g(DSC)}$. T_g increased from 181.5 °C (as-printed) to 183.04 °C for the sample aged during 504 h (see Table 3). Results show that increased immersion time does not cause any negative impact on the T_g of aged samples, indicating the macromolecular chains stability of the amorphous phases of the PEEK/PEI blend. The second thermal transition, at around 336 °C, is associated to melting. The third transition at ~275 °C is related to the crystallization of PEEK, during which a rearrangement of molecular chains develop crystalline

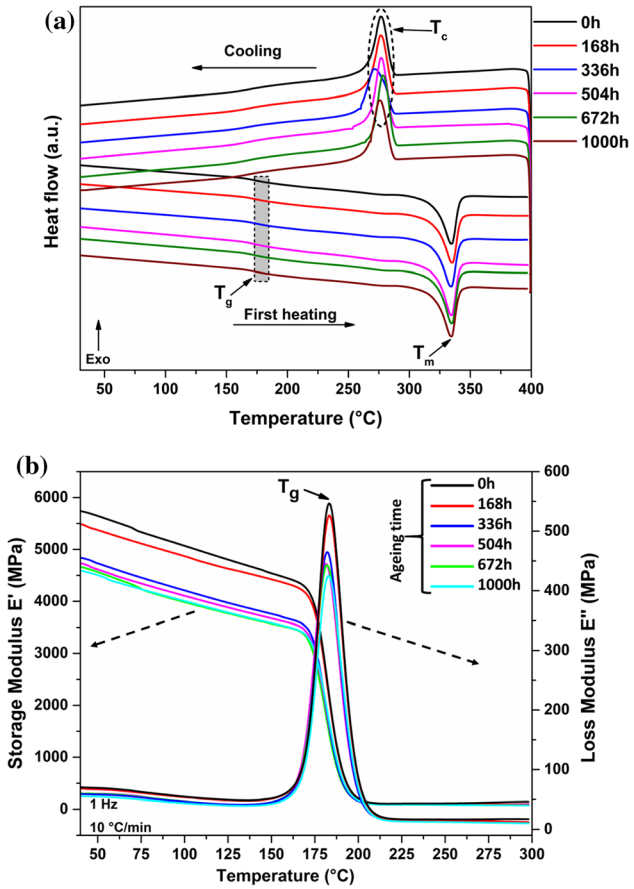

Figure 8 **a** Differential scanning calorimetry scans of as-printed and aged PEEK/PEI samples. **b** DMA traces of as-printed and aged PEEK/PEI samples.

lamellae inside the continuous amorphous structure [8]. This thermal transition shows small variations with increasing aging time in Skydrol. From Table 3, we can notice that PEEK/PEI blend maintains its semi-crystalline character after aging process. It can be observed that the X_c of aged samples are higher than for *as-printed* PEEK/PEI, with a maximum of $X_c = 37.14\%$ when the sample is aged for a period of 504 h. This could be explained by the fact that aging at 70 °C gives more time to molecular chains to reorder and generate more crystalline phases [23]. Moreover, the increase in X_c from 34.49 to 37.14% correlates strongly with the T_g of PEEK/PEI samples, where the loss of mobility for the polymer chains could be attributed to their partial anchoring inside the crystalline region [41]. The stability of thermal and structural properties of PEEK/PEI sample after 1000 h of aging in the most advanced aviation hydraulic fluid (SKYDROL® LD-4 at 70 °C) confirms that this blend can be used as a good replacement for metal in the aerospace industry.

Tensile and morphological properties

Figure 9 shows the tensile properties of FDM-3D printed PEEK/PEI before and after different chemical aging times. Effects of this for PEEK/PEI samples are illustrated in Fig. 9a–c for Young's modulus, tensile strength and strain at break. A large drop in Young's modulus can be observed after 168 h, decreasing from 3620 to 3300 MPa. Skydrol absorbed in inter-layer porosity is the probable cause for this 8.8% decrease. Other results show, however, that the rigid behavior of samples remains quasi-stable for aging time up to 168 h. When considering the standard deviations observed in all measurements, it is

Table 3 Transitions temperatures, enthalpies, and degree of crystallinity for as-printed and aged PEEK/PEI samples

Aging time (Hour)	$T_{g(DSC)}$(C°)	$T_{g(DMA)}$(C°)	T_m(C°)	T_c(C°)	ΔH_m(j.g^{-1})	ΔH_c(j.g^{-1})	X_c(%)	Cycle de Chauffage
0	180.87	181.55	336.83	276.59	31.39	29.97	34.49	1^{ére} cycle
	172.30		334.90	276.59	28.76	29.97	31.60	2ème cycle
168	181.83	181.86	337.05	275.41	31.61	38.62	34.73	1^{ére} cycle
	172.58		335.00	275.41	29.11	38.62	31.98	2ème cycle
336	183.91	182.06	336.87	270.83	31.38	31.19	34.48	1^{ére} cycle
	172.84		334.67	270.83	28.32	31.62	31.12	2ème cycle
504	183.85	183.04	336.97	276.72	33.80	36.03	37.14	1^{ére} cycle
	172.12		334.84	276.71	30.31	36.03	33.30	2ème cycle
672	182.92	182.62	336.68	278.06	33.34	35.29	36.63	1^{ére} cycle
	172.20		335.19	278.06	29.44	35.29	32.55	2ème cycle
1000	180.53	182.31	336.71	275.32	32.50	33.36	35.71	1^{ére} cycle
	172.76		334.73	275.32	28.78	33.36	31.62	2ème cycle

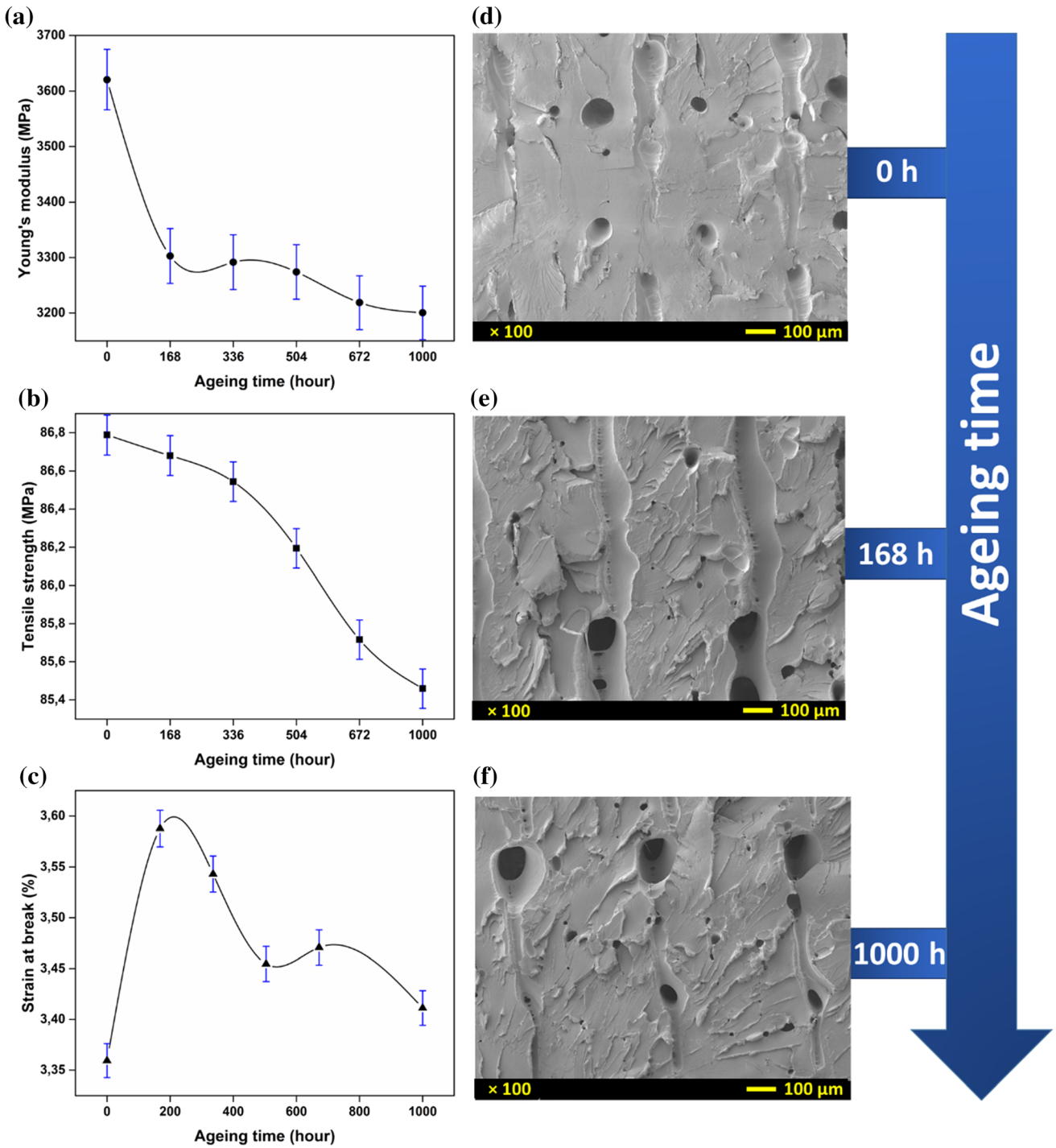

Figure 9 SEM micrographs of the fractured surfaces of **a** as-printed, **b** aged sample for 168 h, **c** aged sample for 1000 h.

difficult to consider as significant the changes in Young's modulus between 168 and 1000 h of immersion. As shown in Fig. 9b, the tensile strength of samples aged 1000 h shows an insignificant variation (~1.6%) compared to unaged samples (85.45 against 86.78 MPa). In a work carried out on the chemical aging of PEEK [33], it was found that PEEK material retains 85 to 100% of its tensile strength for the majority of the solvents tested (Skydrol, Kerosene, Xylene, 20% H2SO4, etc.…). It was shown resist to immersion in these solvents for 4 weeks without any change in properties [33]. Obtained results confirm

that the presence of 70 wt% of PEEK plays a protective effect in the PEEK/PEI blend against the aggressive behavior of the aeronautical fluid Skydrol. Moreover, study on strain at break shows no effects of a 1000 h immersion in Skydrol fluid at 70 °C. For all tested samples, the strain at break varies between 3.35 and 3.41% (Fig. 9c). These results confirm the lack of obvious effects from chemical aging on the strain at break of PEEK/PEI blend.

The microstructure of the rupture face for the as-printed and aged samples at immersion time of 168 and 1000 h are shown in Fig. 9. It can be observed that all layers are well juxtaposed upon each other, without exhibiting any agglomerations or layers variations. Strong interlaminar bonding between layers makes it generally possible to transfer internally the stress imposed during tensile testing, whereas bad adhesion creates punctual defects that weaken the sample's properties [8].

By relating mechanical properties to microscopic observations, it becomes easier to explain the deviation of Young's modulus values for samples after 168 h of immersion in Skydrol liquid. The presence of voids between juxtaposed layers in aged samples (Fig. 9e, f) could explain the observed decrease in Young's modulus following the initial Skydrol absorption. But the lack of decrease in tensile strength properties for aged samples shows that these voids between juxtaposed layers are not punctual defects stress concentrators that weaken the part's strength.

Conclusion

This article reports the effects of environmental and chemical aging on the structural, morphological, thermal and tensile properties of 3D printed PEEK/PEI parts. The main conclusions from this work are as follows.

- Differential scanning calorimetry (DSC) of all samples revealed no significant changes in glass transition temperature (T_g) and degree of crystallinity X_c after physical aging process. This thermal stability during aging in dry and moist heat environment for the PEEK/PEI blend was confirmed through Thermogravimetric analysis (TGA).
- Compared to as-printed sample, physically aged samples show a 10 to 11.5% decrease in their rigidity depending if samples were exposed to dry heat or to moist heat respectively. Moreover, tensile strength results show no variation after dry aging process, while a 2.9% decrease is observed for moist aged samples. SEM images show clearly the presence of voids and defects between juxtaposed layers, resulting in delamination that explain the decrease of elastic modulus. Stress concentration, generated when moisture enters these defects, cause an expansion of defects from the inside that affect negatively the tensile behavior of PEEK/PEI parts.
- DSC and DMA measurements were performed on as-printed samples and samples aged 1000 h in Skydrol hydraulic fluid. Results show that the increase in immersion time does not cause any negative impact on the operating and service temperatures (T_g). This indicates the stability of the macromolecular chains of the amorphous phases in the PEEK/PEI blend.
- Tensile results show an initial drop in rigidity after the first 168 h of chemical aging. The observed 8.8% drop in Young's modulus compared to as-printed PEEK/PEI could be attributed to Skydrol absorbed in the observed interlayer porosity. The negligible variations observed in tensile strength and strain at break for aged samples show that parts made with PEEK/PEI can withstand Skydrol exposure for 1000 h without any significant change in strength and strain properties.
- Obtained results of a durability study of PEEK/PEI 3D printed parts show that the prepared blend remains stable after aging under rigorous aging conditions and environmental extremes. This is similar to the operating conditions in aeronautical industry to which parts produced by additive manufacturing could be subjected.

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Declarations

Conflict of interest The authors certify that they have NO affiliations with or involvement in any organization or entity with any financial interest, or non-financial interest in the subject matter or materials discussed in this manuscript.

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