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EFFECT OF AERONAUTIC FLUID SKYDROL ON NEAT POLY(ETHER KETONE KETONE) AND ITS CARBON FIBER REINFORCED COMPOSITE

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Abstract: *High performance thermoplastics such as poly(ether ketone ketone) are currently under development to replace thermoset matrices in composite parts of aircrafts. These composites are likely to be exposed to aggressive environments during their use phase. In this study, the effect of an aeronautical hydraulic fluid (Skydrol) is investigated by immersion of neat PEKK and carbon fiber reinforced PEKK (C/PEKK) in the fluid. Gravimetric measurements show no saturation plateau after 8000h immersion of neat PEKK. The effect of layup sequence of the composite is considered. Anomalous fluid sorption is observed in non-unidirectional composite. Tensile testing performed on neat PEKK shows very low degradation in mechanical properties after exposure to Skydrol.*

Keywords: PEKK; composite; hydraulic fluid; ageing

1. Introduction

High performances thermoplastics arouse interest to replace epoxy matrices in continuous carbon fiber composites for aeronautics. Contrary to thermoset resins, thermoplastic matrices have a long shelf life, allow welding of the composite parts and are recyclable. Poly(aryl ether ketone) (PAEK) is a family of high performance thermoplastics of which poly(ether ether ketone) (PEEK) has been extensively studied in the past 30 years (1–3). Another PAEK polymer, poly(ether ketone ketone) (PEKK) has gained in importance in recent years thanks to the possibility of modifying its melting temperature (T_m) while keeping a high glass transition temperature (T_g) (4,5).

During the use phase of the composite parts, the material can come into contact with different fluids necessary for the operation of the aircrafts such as water, fuel, de-icing, hydraulic fluid, etc. Hydraulic fluid is particularly aggressive for epoxy resins that are currently widely used as matrices in carbon fiber reinforced composites in the aeronautic field. Several studies showed the formation of chemical bonds between the epoxy resin and the hydraulic fluid which is usually composed of phosphate esters (6). Moreover, a study from Sugita et al. (7) on an epoxy adhesive and a C/epoxy composite shows that the adhesive absorbs around 180 wt% Skydrol after 555 days immersed in hydraulic fluid at 85°C. Immersion in hydraulic fluid at room temperature seems far less aggressive. The C/epoxy composite absorbs less than 1 w% and up to 3 wt% Skydrol at room temperature and 70°C respectively.

Stober et al. (8) showed very high resistance of neat PEEK to Skydrol with an uptake of ca. 1 wt% and complete reversibility of sorption. It is essential to understand the behavior of PEKK matrix

in hydraulic fluids before investigating the C/PEKK composite. The present study focuses on sorption behavior of neat PEKK as well as C/PEKK immersed in hydraulic fluid and the effect on mechanical properties.

2. Experimental

2.1 Materials

Neat PEKK plates were provided by Arkema with a T/I ratio of 70/30. The injected plates are used for gravimetric measurements and have a size of 10x10x2 mm³. Composite laminates are made of unidirectional continuous carbon fibers (AS7) impregnated with PEKK 70/30, provided by Hexcel Reinforcements. Composite laminates of layup sequences [0]₈ and [0/90]_{2s} (both consisted of 8 plies and referred as 'unidirectional' and 'cross-ply') are consolidated out of autoclave (*Figure 1*).

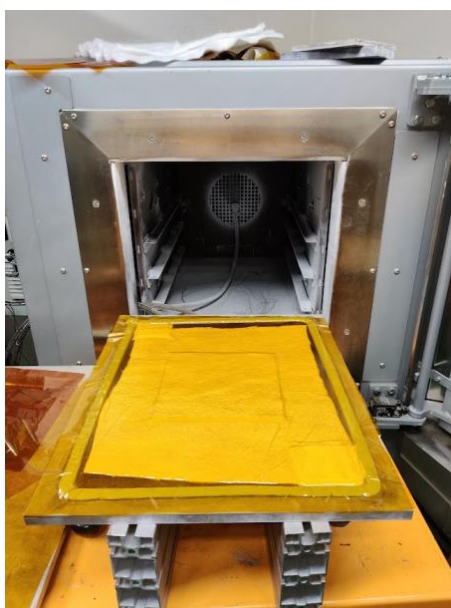


Figure 1. Oven used for out of autoclave consolidation of C/PEKK composite.

Samples of size 50x50 mm² are cut in the neat PEKK plates and composite laminates using a band saw and diamond saw respectively. The hydraulic fluid used in this study is Skydrol LD4, composed of different phosphate esters.

2.2 Gravimetric measurement

Neat PEKK and composites samples are dried in an oven at 120°C during 48 hours and crystallized at 200°C during 4 hours prior to Skydrol immersion. The samples are immersed in Skydrol at 70°C, in sealed glass jars placed in a temperature-controlled water bath. The samples are regularly surface-dried with paper towel and weighed using a Mettler Toledo analytical balance. The weight uptake is measured using the following equation:

$$w(t) = \frac{m(t) - m_0}{m_0} \quad (1)$$

With $m(t)$ the mass of the sample at time t and m_0 the initial mass of the dried sample. The mean weight uptake is averaged on four samples and two samples for neat PEKK and C/PEKK respectively.

2.3 Tensile testing

Tensile tests are performed on neat PEKK 7002 (ISO 527 1BA 2 mm-thick specimens) before (referred as 'dry') and after ageing in Skydrol. The specimens are immersed in Skydrol at 70°C in sealed glass jars as for gravimetric samples. Poly(tetrafluoroethylene) holders allow maintaining the samples vertically. Tensile tests are carried out using an Intron 5966 machine at 1 mm/min.

2.4 X-ray tomography

X-ray microtomography imaging is carried out on the Anatomix beamline at Synchrotron SOLEIL (9). The samples are cut in the thickness of the C/PEKK composites using a diamond wire saw to a size of 2x2x5 mm³. Two volumes corresponding to a cylinder of diameter 1.3 mm and height 1.3 mm have been investigated in each sample at different locations.

3. Results and discussion

3.1 Skydrol sorption in neat PEKK

Weight uptake of neat PEKK immersed in Skydrol at 70°C shows a constant increase during the first 300 days of exposure (*Figure 2*). A maximum is observed at this point corresponding to a weight uptake of 0.28 ± 0.01 wt% with no saturation plateau. As the exposure is still in progress, no conclusion will be made at this point on the existence of a plateau.

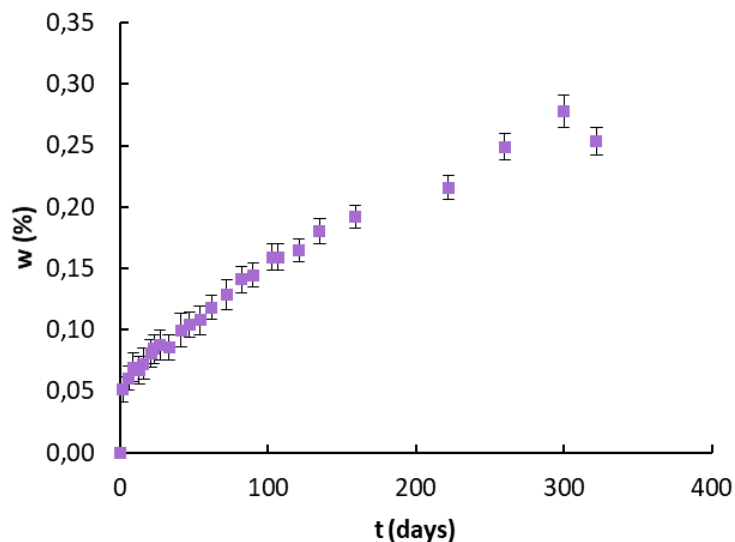


Figure 2. Weight uptake of neat PEKK as a function of immersion time in Skydrol at 70°C.

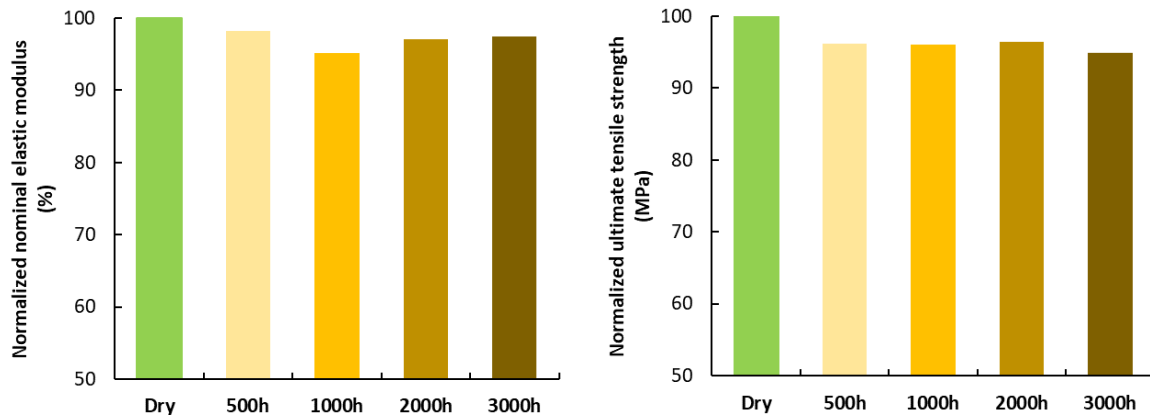


Figure 3. Elastic modulus and ultimate tensile strength of neat PEKK before and after exposure to Skydrol at 70°C.

Tensile tests performed on neat PEKK exposed to Skydrol at 70°C show very low decrease in elastic modulus (-3%) and ultimate tensile strength (-5%) after 3000 hours of exposure (Figure 3). These results are consistent with the low absorption of Skydrol (0.17 wt%). Thus, Skydrol do not seem to degrade neat PEKK after 3000 hours of immersion.

3.2 Skydrol sorption in C/PEKK

Exposure of C/PEKK unidirectional and cross-ply ([0/90]_{2s}) composite to Skydrol at 70°C show very different behaviors in terms of weight uptake (Figure 4). Unidirectional composite absorbs almost no Skydrol, corresponding to the quantity of fluid absorbed by neat PEKK. Nevertheless, cross-ply composite part absorbs around ten times more Skydrol than unidirectional layup.

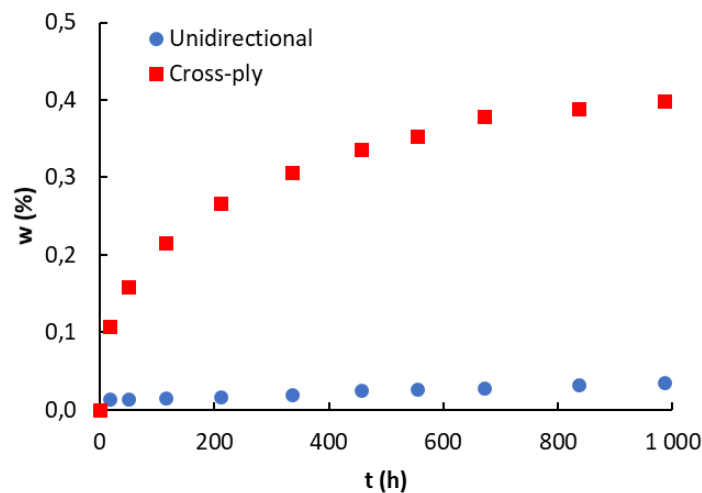


Figure 4. Weight uptake of unidirectional and cross-ply composite C/PEKK as a function of immersion time in Skydrol at 70°C.

Fluid sorption in composite is a complex mechanism, taking into account different phases of the material such as the matrix, the fibers, the interface between matrix and fibers, possible voids, etc. Our previous results show low fluid sorption in neat PEKK. We can assume that carbon fibers do not absorb fluid. As the unidirectional C/PEKK absorbs low amounts of Skydrol as observed in neat PEKK, the interface between matrix and fibers does not seem to be a preferential site for

fluid sorption. Finally, a hypothesis would be that cross-ply C/PEKK has a non-negligible, although low, void content that Skydrol can penetrate and fill in.

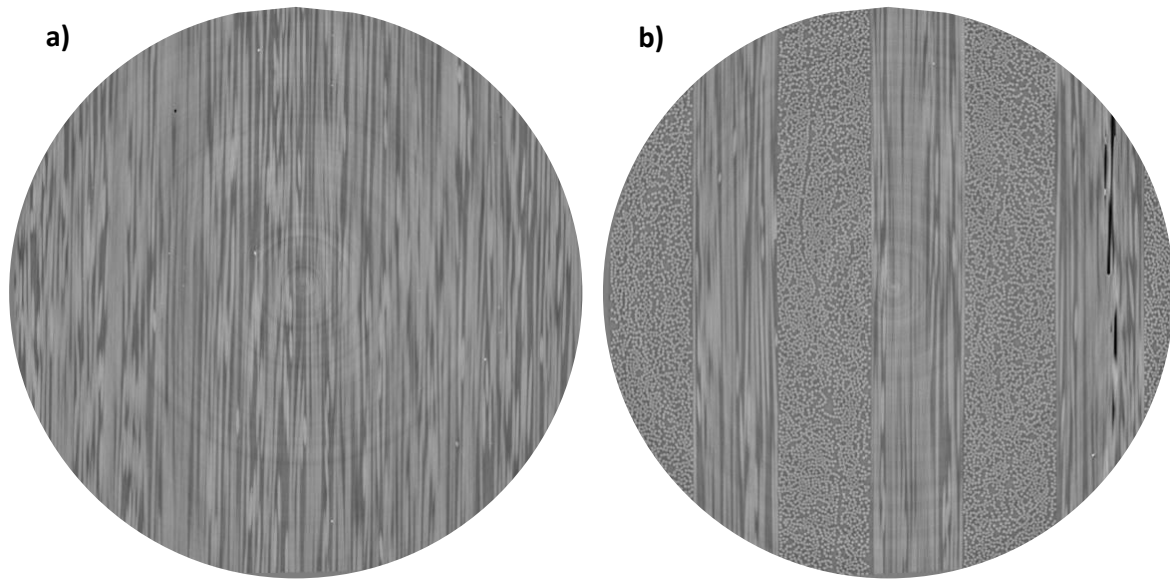


Figure 5. X-ray tomography imaging of C/PEKK (a) unidirectional and (b) cross-ply laminates.

X-ray tomography confirms the negligible porosity content in unidirectional C/PEKK (Figure 5a.). Furthermore, cross-ply composite layup seems to hinder the filling of micro cavities with the molten resin during the consolidation process, resulting in some porous areas in the composite. X-ray tomography brings to light the high anisotropy of porosities which are located in the direction of fibers (Figure 5b.). Moreover, the distribution of cavities is particularly heterogeneous. As the Skydrol has a low surface tension ($28.2 \text{ mN}\cdot\text{m}^{-1}$ at 25°C), the fluid can easily fill in the micro cavities leading to an increase in weight uptake when the composite is fully immersed.

4. Conclusions

The present study focusses on the sorption of Skydrol by neat PEKK and C/PEKK composite by immersion in the fluid at 70°C . It has been shown that the diffusion of Skydrol in neat PEKK is very slow and that the weight uptake is lower than 0.30 wt% after 300 days. Mechanical properties of PEKK are preserved after 3000 hours. Immersion of unidirectional composite shows Skydrol uptake in the order of magnitude of the matrix capacity of sorption whereas cross-ply composite exhibit abnormally high weight uptake. X-ray tomography showed the presence of relatively porous areas in the cross-ply composite which constitute the main cause for such fluid uptake. Further investigation on C/PEKK mechanical properties are planned.

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