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### ► To cite this version:

Gwladys Lesimple, Bruno Fayolle, Stéphane Bizet, Thibaut Benethuilere, Eric Monteiro, et al.. Effect of water sorption in neat poly(ether ketone ketone) and its carbon fiber reinforced composite. 20th European Conference on Composite Materials - Composites Meet Sustainability, Jun 2022, Lausanne, Switzerland. pp.1087-1093, 10.5075/epfl-298799\_978-2-9701614-0-0 . hal-03976080

**HAL Id: hal-03976080**

**<https://hal.science/hal-03976080>**

Submitted on 6 Feb 2023

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## EFFECT OF WATER SORPTION IN NEAT POLY(ETHER KETONE KETONE) AND ITS CARBON FIBER REINFORCED COMPOSITE

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**Abstract:** *Poly(ether ketone ketone) (PEKK) is a high performance thermoplastic polymer with excellent mechanical properties, which aims to replace epoxy currently widely used as matrices in aircraft composites. Knowing the aircrafts service life, it is of great importance to evaluate the durability of its constitutive materials. In this paper, water sorption of both PEKK neat resin as well as in its continuous carbon fiber composite (C/PEKK) is fully characterized using both water immersion and dynamic vapor sorption (DVS) methods. Water transport in PEKK follows Henry's law whereas a clear deviation from this behavior is observed in C/PEKK at high relative humidities. Water diffusion in unidirectional consolidated C/PEKK has been modeled using finite element method based on water transport parameters determined in neat PEKK.*

**Keywords:** Thermoplastic; PEKK; water transport; CFRP; DVS

### 1. Introduction

Continuous carbon fiber reinforced thermoplastics are gaining in interest in the aeronautic field in the last decades. High performance thermoplastics such as poly(phenylene sulfide) (PPS), poly(ether imide) (PEI) and poly(aryl ether ketone) (PAEK) have the major advantage to be weldable, recyclable and have less constraining storage conditions than thermosets. Poly(ether ether ketone) (PEEK) is the most common polymer from the PAEK family whereas PEKK was developed later. During their use phase, the composite parts of an aircraft can come into contact with different aggressive environments such as temperature, humidity, radiations, aeronautic fluids, etc. Thus, it is necessary to assess the potential effects of these latter on the material.

Thermoplastics exhibit better chemical resistance than epoxy matrices which are currently widely used in aircraft structures. Several studies showed that epoxy resins can absorb up to 10 wt% water (1–4). This is mostly due to the high polarity of chemical groups contained in epoxy resins leading to hydrogen bonding to water molecules. This significant water uptake induces irreversible damage in both epoxy-based composites such as swelling leading to a reduction in delamination fracture (5). Moreover, micro cracks as well as intralaminar cracks are frequently observed (6,7). Water sorption in neat resin is usually described as fickian whereas it deviates from fickian behavior in carbon fiber reinforced epoxy composites due to irreversible damages (8–10).

Water sorption in neat PEEK and its carbon fiber reinforced composite has been studied by several authors since the 1980s. In water immersion, neat PEEK and C/PEEK follow Fick's law and absorb up to 0.55 wt% and 0.4 wt% water respectively (11–14). Very few literature provides data

on water transport in C/PEKK (15,16) and no paper was found in the case of neat PEKK. The present study aims to investigate water sorption mechanism in neat PEKK matrix as well as in C/PEKK composite using both water immersion and dynamic vapor sorption methods.

## 2. Experimental

### 2.1 Materials

Neat PEKK with a T/I ratio of 70/30 was provided by Arkema. Films of 50  $\mu\text{m}$  thickness are used for dynamic vapor sorption (DVS) measurements whereas 2 mm-thick plates are used for gravimetric measurements. Composite tapes (thickness 0.200 mm and controlled porosity) made of unidirectional continuous carbon fibers (AS7) and PEKK 70/30 are provided by Hexcel Reinforcements. The tapes have a porosity level of 3% and 9% and a carbon fiber volume content of 60v%. Tapes consolidated using a press applying 7 bars are considered non porous.

### 2.2 Gravimetric measurement

For gravimetric measurements, samples of size 50x50 mm<sup>2</sup> are cut in the PEKK plates and composite tapes using a band saw and a diamond saw respectively. They are dried in an oven at 120°C during 48 hours prior to water immersion. The samples are immersed in distilled water at 30°C, 50°C and 70°C, in sealed glass jars placed in a temperature-controlled water bath, until saturation. The samples are regularly surface-dried with paper towel and weighed using a Mettler Toledo analytical balance. The water 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.

### 2.3 Dynamic Vapor Sorption

For DVS measurements, samples of size 25x15 mm<sup>2</sup> are cut in the PEKK film and tapes. The samples are placed in the DVS apparatus, hanged by a hook in the chamber which is controlled both in temperature and relative humidity (RH). The sample is weighed *in situ*. A RH cycle of following 0%-10%-0%-30%-0%-50%-0%-70%-0%-90%-0% is applied at constant temperature (70°C). Each RH step is applied until a plateau is observed in the sample mass.

## 3. Results and discussion

### 3.1 Water sorption in neat PEKK

Water transport parameters in neat PEKK have been determined through water immersion (*Figure 1*). Water sorption is found to follow Fick's law:

$$\frac{dw}{dt} = D \frac{\partial^2 w}{\partial x^2} \quad (2)$$

With  $D$  the diffusion coefficient of water in the polymer and  $x$  the position from the sample surface.

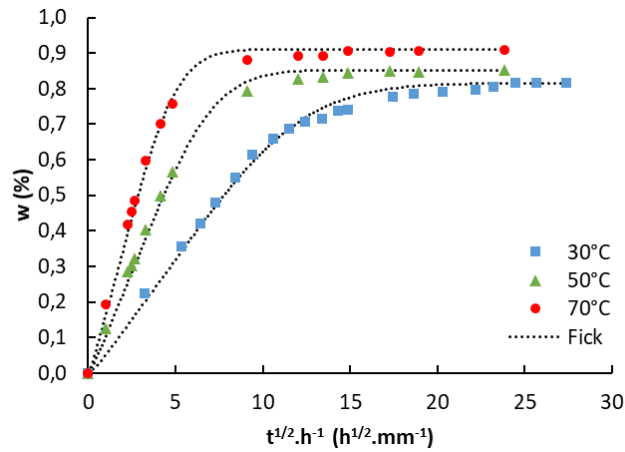


Figure 1. Water uptake in neat PEKK as a function of the square root of time divided by the sample thickness, measured by water immersion at 30°C, 50°C and 70°C.

Moreover, DVS measurement at different relative humidities ranging from 10% to 90% RH shows that water uptake in PEKK follows Henry's law such that (see also Figure 2):

$$C_{\infty} = Sp_{vap} = \frac{w_{\infty}\rho_p}{M_f} \quad (3)$$

With  $p_{vap}$  the water vapor pressure,  $S$  solubility of water into the polymer,  $\rho_p$  the polymer density and  $M_f$  the molar mass of water. This result is consistent with the low amount of water absorbed since PEKK is moderately polar.

### 3.2 Water sorption in composite

Water immersion as well as DVS were performed on a consolidated tape. The water uptake given is corrected from the mass fraction of PEKK in the composite in order to easily compare  $w_{\infty}$  with neat PEKK.

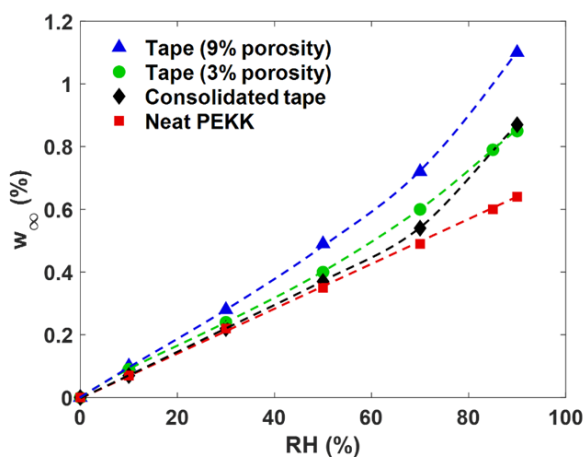
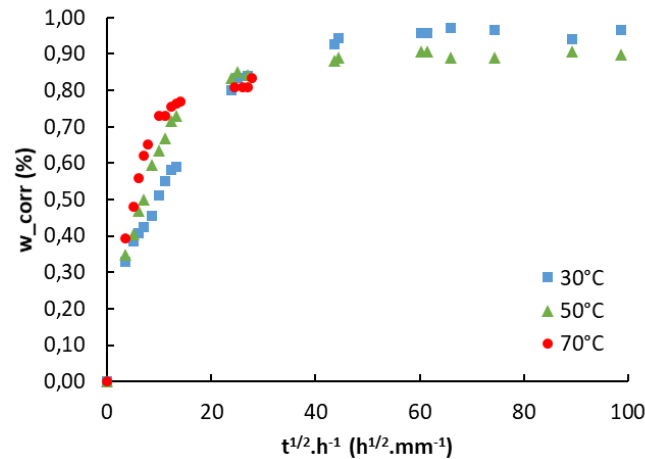


Figure 2. Water uptake at saturation as a function of the relative humidity measured by DVS at 70°C for neat PEKK, consolidated tape and porous tapes. Water uptake measured in composite is corrected with the PEKK matrix content.

The consolidated unidirectional composite does not follow fickian behavior (*Figure 3*). The diffusion mechanism seems to include two steps: first water sorption is driven by diffusion in the PEKK matrix, then the sorption rate decreases corresponding possibly to the filling of residual micro-voids (17).



*Figure 3. Water uptake in a C/PEKK consolidated tape as a function of the square root of time divided by the thickness, measured by water immersion at 30°C, 50°C and 70°C. Water uptake measured in composite is corrected with the PEKK matrix content.*

DVS measurement on the consolidated tape shows a deviation from Henry’s law at high relative humidities i.e. from 70% RH (*Figure 2*). This phenomenon which is not observed in neat PEKK, is typical of water clustering in micro-voids and is in accordance with the non fickian diffusion in C/PEKK.

*Table 1: Diffusion coefficient and water uptake at saturation in neat PEKK and C/PEKK measured by water immersion.*

T (°C)	PEKK		C/PEKK	
	Dx10 <sup>12</sup> (m <sup>2</sup> .s <sup>-1</sup> )	w <sub>∞</sub> (%)	‘Apparent’ Dx10 <sup>12</sup> (m <sup>2</sup> .s <sup>-1</sup> )	w <sub>∞</sub> (%) / w <sub>∞,corr</sub> (%)
30°C	0.4 ± 0.1	0.82 ± 0.02	0.4 ± 0.1	0.33 ± 0.02 / 0.97 ± 0.06
50°C	1.1 ± 0.1	0.85 ± 0.01	0.7 ± 0.1	0.31 ± 0.02 / 0.91 ± 0.06
70°C	2.2 ± 0.2	0.91 ± 0.01	1.0 ± 0.2	0.28 ± 0.01 / 0.82 ± 0.03

Concerning water uptake, the composite absorbs the same amount of water as neat PEKK up to 70% RH where w<sub>∞</sub> starts greatly increasing due to the filling of cavities.

The same measurements are carried out on unconsolidated tapes with 3% et 9% porosity in order to highlight de effect of porosity on water sorption mechanism. As expected, water uptake as a function of relative humidity in both porous tapes deviate from Henry’s law. Moreover, the higher the porosity, the lower the relative humidity at which the deviation starts. Water immersion confirms the void filling in unconsolidated tapes (*Figure 4*).

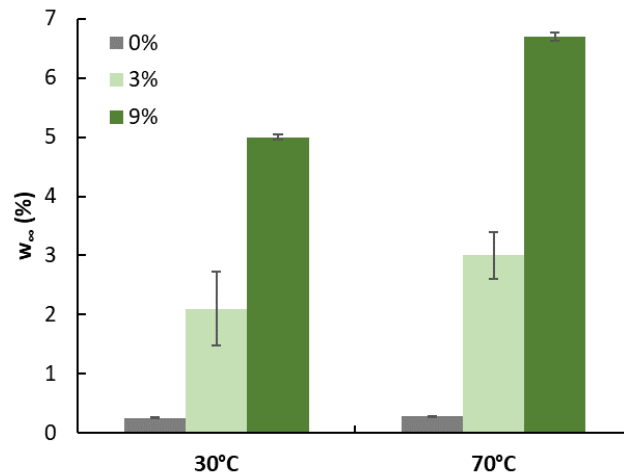


Figure 4. Water uptake in C/PEKK tapes, consolidated (0%) and unconsolidated (3% and 9% porosity) measured by water immersion at 30°C and 70°C.

The total water uptake is in accordance with the void content nevertheless, cavities do not seem to be fully filled with liquid water when saturation plateau is reached.

### 3.4 Water transport model in unidirectional C/PEKK

Since the tapes do not follow a fickian behavior, we propose to model by finite element method (FEM) water transport in unidirectional consolidated composite. The composite is simulated by incorporating continuous cylinders representing impermeable carbon fibers. Their localization is based on micrographs of the samples used within the framework of this study. The water transport is assumed to be completely driven by water diffusion in the PEKK matrix (with diffusion coefficient  $D$ ) with neither capillary nor cavity filling mechanisms. As expected, the 2D model shows a slower diffusion of water in the composite compared to the neat PEKK (Figure 5).

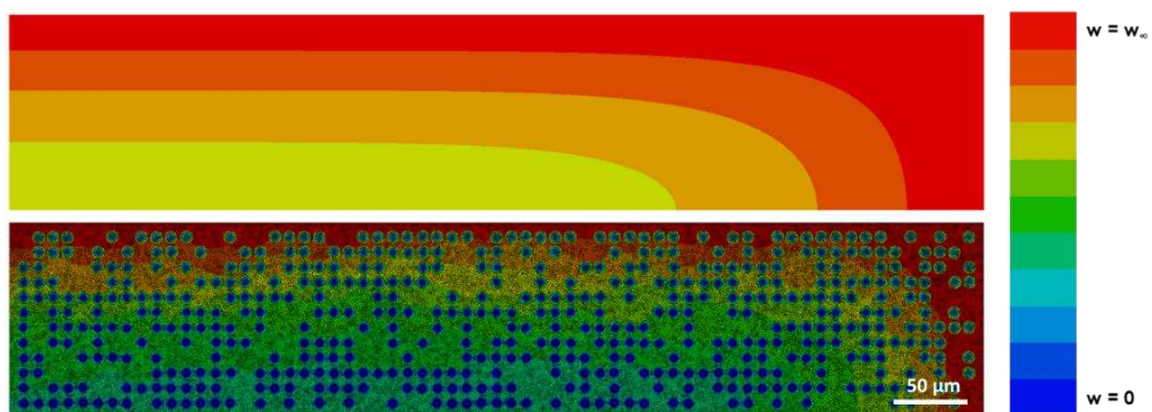


Figure 5. Water diffusion in neat PEKK (top) and C/PEKK (bottom) at the same exposure time. The top right corner of a sample is represented.

Carbon fibers, indeed, slow down the diffusion by extending the diffusion path for water into the composite. The ‘apparent’ diffusion coefficient, measured on the first linear part of the sorption curve, is lower in the composite than in PEKK (Table 1).

#### 4. Conclusions

Water sorption mechanism in carbon fiber reinforced PEKK tapes in unconsolidated and consolidated states was investigated. Preliminary study showed that neat PEKK absorbs less than 1 wt% water and that water diffusion follows fickian behavior and Henry's law from 0 to 90% relative humidity. Exposure of C/PEKK consolidated tape to humidity shows a deviation from Henry's law at high relative humidities, typical of the presence of water clustering in micro voids. Increase of the phenomenon using tapes with controlled porosity confirms the filling of cavities at high relative humidities. Water sorption in C/PEKK does not follow classical fickian behavior due to the presence of carbon fibers and voids, leading to more complex sorption mechanisms. We have successfully proposed a FEM modelling to simulate water transport in C/PEKK by taking into account water transport in neat PEKK and fiber geometry.

#### Acknowledgements

This work was conducted under the framework of HAICoPAS, a PSPC project (projet de recherche et développement structurant pour la compétitivité). BPI France is acknowledged for funding the PhD work of G. Lesimple (project number: PSPC.AAP-7.0\_HAICoPAS). The authors thank Arkema, Hexcel for fruitful discussions and the Industrial Chair Arkema (Arkema/CNTS-ENSAM-Cnam) for partial support.

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