

Towards a predictive model for the residual strength of polymer matrix composite core in High Temperature Low Sag conductors in function of the operating conditions**Baptiste GARY**
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SUMMARY

High Temperature Low Sag (HTLS) conductors with a carbon fiber composite core were first installed 20 years ago. Since then, their use has increased all over the world thanks to their excellent properties such as low coefficient of thermal expansion, corrosion resistance, high tensile strength, a greater aluminum section with an equivalent weight in comparison with ACSR (Aluminum Conductor Steel Reinforced), etc... Their interesting properties make them an ideal solution for reconductoring projects where there is a need for higher flexibility in the grid. Because of the shift towards more renewable energies in the generation mix, existing lines must handle more peaks: In the meantime, it is more and more difficult to build new lines and quite expensive to reinforce existing ones. Uprating lines by changing the standard conductors limited to 90°C by HTLS conductors using carbon fiber composite core is ideal. However, this technology being quite recent in the Overhead Line (OHL) industry, there is still a lack of consensus on the maximum operating temperature. Indeed, organic matrix in carbon fiber composite may suffer from different physical and chemical alterations at high temperature resulting in a loss of thermo-mechanical properties as glass transition temperature and tensile & flexural strengths. Depending on the ambient temperature, humidity and related exposure time, the kinetics may change significantly. Based on an extensive one year test plan in two laboratories, this paper aims to explain the different ageing processes as thermolysis, thermo-oxidation, water absorption, hydrolysis and their consequences on the microstructure and mechanical properties of the composite core. First results will be presented paving the way to the establishment of predictive equations. Combined physico-chemical and empirical models are proposed to predict the residual performances depending on the use of the conductor (ampacity and ambient conditions). Such models are useful for design engineers to anticipate the strength losses during the entire conductor lifecycle (as annealing of aluminum 1350-H19 in ACSR). They are also of great interest for asset management in the next few years when the first lines installed will be more than 30 years old.

KEYWORDS

HTLS conductor, Overhead transmission lines, Uprating, Composite core, Residual strength, Time-Temperature Superposition Principle (TTSP), Service lifetime prediction

1. Introduction

Polymeric matrix cores (type 4 [1]) used in High Temperature Low Sag conductors were first introduced 20 years ago. Their excellent properties as low coefficient of thermal expansion (10 times lower than steel), low density (4 times lower than steel) and excellent tensile strength (2 times higher than steel) allow the design of conductors with significantly higher properties. In this way, they offer low sag even at high temperature and lower electrical resistance due to a larger aluminum cross-section without weight penalty in comparison to conventional solutions as ACSR (Aluminum Conductor Steel Reinforced).

Because of global warming, most of the countries are installing more and more renewable capacities in remote area. This change in the generation mix is having important consequences on the transmission grids. Historically, the upgrading of existing lines required the removal and replacement of existing structures with heavier cables. However, a new approach has been developing to increase the transit power of existing lines without the need for new installations. HTLS conductors, especially type 4, perfectly meet this need, explaining the increasing success for more than 10 years [2].

Despite this success, there is still no IEC standard for type 4 conductors. This impossibility to find a consensus is linked to an important number of solutions on the market, but also different approaches in the definition of the maximum operating temperature. In fact, composites with polymeric matrix can face irreversible damages under high temperature or exposure to humid environment. At high temperature (near the glass transition temperature T_g), polymer matrix composites are susceptible to perish by oxidative degradation [3]. Although the fibers are stable at these temperatures (below 250°C), the matrix and especially the fiber-matrix interface can undergo degradation that significantly affects the physical and mechanical properties of the structure in the long term. In addition, moisture, in all its forms, is a degradation factor in organic matrix composites, often causing plasticization, swelling and alteration of physical and mechanical properties. Matrix and/or interface degradation resulting from moisture absorption is a concern in most composite applications subjected to atmospheric moisture [4]. Even if several authors studied these phenomenon [5–7], there is still no analytical or physico-chemical model taking predicting the effect of a cumulative ageing.

In this context, in February 2020 has been launch an experimental 1 year campaign with the target to build a kinetic model at the destination of utilities. This model would take as input data the conductor operating conditions, and would give as output data the residual performances such as tensile strength, flexural strength and glass transition temperature.

In this paper, first of all, we will review the tested composites, their degradation modes and the experimental campaign. Then, we will present the experimental results and the resulting equations paving the way to predictive models.

2. Theory

2.1 Composite materials

The composite materials considered in this study are organic matrix reinforced with carbon and/or glass fibers with an average fiber volume fraction of about 70%. The thermosetting matrix is a mix of epoxy monomer and anhydride curing agent. The polymerization between epoxy and anhydride monomers creates the final polymeric network which is responsible for the thermal, chemical and mechanical properties of the composite. Composite rods considered in this paper are produced through the pultrusion process. This technique includes two main steps: First of all, the impregnation of the fiber roving in epoxy resin baths and the curing of the impregnated fibers in a heated die, providing the final shape once the matrix is fully cured.

2.2 Hydro/hygrothermal ageing

When polymers are exposed to humid environment, the diffusion of water molecules into the polymer network can be explained by a molecular approach based on the interactions between water molecules and polar groups of the polymer. In epoxy resins, water absorption is related to the presence of polar groups playing the role of hydrophilic sites. These polar groups can be classified according to their hydrophilicity (i.e. the corresponding water content at saturation) [8]. The most hydrophilic polymers

undergo plasticization (Figure 1). In fact, the water absorption leads to a gradual destruction of the intermolecular interactions and their replacement by stronger ones, of the hydrogen bond type, between water molecules and polar groups of the polymer chains. The partial degradation of the mechanical cohesion of the network is at the origin of the increase in molecular mobility [9]. Therefore, it results in a decrease in the glass transition temperature. This plasticization effect is generally reversible, however, this reversibility can be altered if water absorption is accompanied by a hydrolysis, i.e. the reaction of water molecules with specific polymer groups. The hydrolysis reaction is thermally activated and can be catalyzed by the formation of carboxylic acids [10].

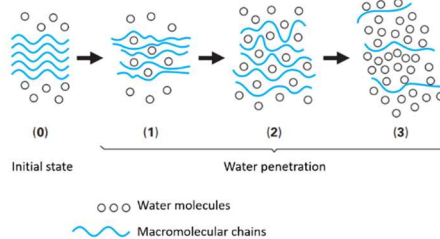


Figure 1 : Schematization of the plasticization effect in a polymer [11]

2.3 Thermal ageing

The thermal ageing of composites is of particular concern due to their expanding use for structural applications where high temperatures are common environmental conditions [12]. Thermal ageing is a chemical ageing, which modifies the chemical structure of the macromolecular skeleton through a series of elementary reactions which are each one thermally activated. It includes thermolysis and thermo-oxidation, depending on the oxygen partial pressure. These reaction mechanisms may alter the mechanical properties of the composite and thus lowering their service life [13]. Thermal ageing occurs both on the surface and in the volume. Surface aging is induced by thermo-oxidation which generates micro-cracking and impacts the ultimate mechanical properties of the composite. On the other hand, volume aging is induced by thermolysis and modifies the mechanical behaviour of the material as a whole by lowering the glass transition temperature as an example [14].

3 Materials and methods

3.1 Materials

In this study, two kinds of composite rods are considered:

- Hybrid Glass/Carbon fiber rods (Figure 2.a) with a micro core in glass fibers in order to reduce the shear stress and enhance the alignment of carbon fibers, a center in carbon fibers to ensure high mechanical properties and a low coefficient of thermal expansion, and an outer layer made of glass fibers to prevent galvanic corrosion between aluminum and carbon fibers. These rods are employed for High Voltage Composite Reinforced Conductors (HVCRC®)
- Only carbon fiber rods, here called 100% carbon (Figure 2.b). There is no glass fibers because rods are clad with aluminum layer to prevent moisture penetration between composite rod and aluminum wires.

The rods are manufactured by the process described in §2.1. In addition to composites, neat epoxy resin samples were produced by casting the resin into a mold in order to perform physico-chemical and hydrothermal ageing tests.

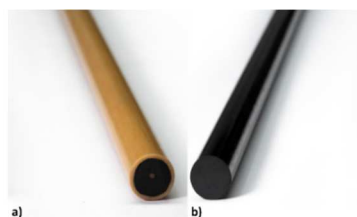


Figure 2 : Capture of the radial section of a) An hybrid rod with a diameter of 8.76 mm and b) 100% carbon fibre rod with a diameter of 7.06 mm

3.2 Methods

3.2.1 Initial properties

Several techniques were employed to identify the material's properties prior to aging tests. The Differential Scanning Calorimetry (DSC Q1000, TA Instruments) and Dynamic Mechanical Analysis (DMA Q800, TA Instruments) techniques were used to measure the glass transition temperature (T_g) of both neat matrix and composite materials, which is a characteristic property of polymers marking the change from glassy to rubbery states. Both results were found to be above 220°C.

Mechanical properties of composite rods were evaluated by 4-point flexure tests on an MTS machine. All test were performed with a 5 mm/min load speed. Mechanical properties of initial rods are given in Table 1.

Table 1: Initial 4-point flexure properties of hybrid and 100% carbon rods (the standard deviation was calculated from 7 samples)

Flexure properties	Hybrid rod	100 % carbon fiber rod
Ultimate flexure strength (MPa)	2016 ± 66.3	2412.3 ± 283.8
Ultimate flexure deformation (mm)	39.3 ± 2.26	20.3 ± 2.8
Flexure modulus	101.5 ± 1.04	140.9 ± 1.67

Furthermore, qualitative and quantitative analyses of the porosity ratio were carried out using ImageJ image analysis software on radial cross-sections of composite rods previously polished. The samples were cut and embedded in a low shrinkage epoxy resin, then polishing was carried out using a MECAPOL P320 machine.

3.2.2 Ageing conditions

- Hydrothermal ageing

Gravimetric analysis was used to monitor the evolution of neat resin and carbon fiber reinforced composites (CFRP) specimens' weight during immersion in hermetically sealed recipients filled with demineralized water. The ageing temperatures selected for this study were: 30, 50, 70 and 90°C. At least five samples were removed and wiped at regular times to remove surface moisture and finally weighed using a 0.01 mg precision balance. For each sample, the percentage mass gain (also called water content) is calculated using Equation 1.

$$M_i(\%) = \frac{m - m_0}{m_0} \times 100 \quad \text{Equation 1}$$

where m and m_0 are the sample weight during and before ageing, respectively.

- Thermal ageing

Thermal ageing was applied to hybrid rods at 4 different temperatures: 180, 200, 210 and 220 °C. 100% carbon rods were aged only at 220 °C. These rods were placed in hot air circulation ovens for the ageing period which depended on the ageing temperature. A set of 8 samples was taken for each duration: 7 samples for the 4-point flexure tests and 1 sample for the microscopic observations.

4 Results and discussion

4.1 Hydrothermal ageing

Water uptake induces reversible (plasticization) and irreversible (hydrolysis) changes in physical and chemical properties of polymers, respectively. In particular, epoxy-anhydride networks can undergo hydrolysis reaction due to the presence of unreacted epoxy groups and ester groups in the network. This reaction leads to the formation of new hydroxyl groups (acids and alcohols) which increases the number of polar groups in the network and thus, its hydrophilicity. It can be written as follows [15]:



where E is an ester group, W a water molecule, and Ac and Al are respectively acid and alcohol groups resulting from hydrolysis. These changes affect water transport properties and consequently, polymer structure which is responsible for the material damage [10,16]. The hydrolysis rate over time related to chain scissions can be written as follows:

$$\frac{d[E]}{dt} = -k_h[E][W] \quad \text{Equation 2}$$

where [E] and [W] account respectively for ester and water concentration in the polymer and k_h is the hydrolysis reaction rate constant. The glass transition temperature decreases during hydrolysis. Several authors proposed correlations between the chemical structure and the glass transition temperature for both linear and crosslinked polymers [17–19]. In ideal epoxy network (without dangling chains), the glass transition temperature is an increasing function of the concentration of crosslink nodes n . DiMarzio proposed a relationship between T_g and n for polymer networks [20]:

$$T_g = \frac{T_{gl}}{1 - K_{DM} \times F \times n} \quad \text{Equation 3}$$

where T_{gl} represents the glass transition temperature of an hypothetical linear polymer composed of the same chemistry as the polymer network, K_{DM} is an universal constant ($K_{DM} \approx 2.91$ for epoxy networks with trifunctional crosslinks [21]), F is the flex parameter characterizing the stiffness of the elastically active chains. After ageing, the concentrations of nodes is related to the concentration of chain scissions (S) by:

$$n = n_0 - 2S \quad \text{Equation 4}$$

where n and n_0 are the concentration of nodes during and before ageing. Considering Equation 3 and Equation 4, the relationship between the glass transition temperature of dry unaged (T_{g0}) and aged (T_g) samples may be written as follows:

$$\frac{1}{T_g} - \frac{1}{T_{g0}} = -\frac{K_{DM}F}{T_{gl}}(n - n_0) \quad \text{Equation 5}$$

Unlike hydrolysis, the plasticization leads to a reversible decrease in T_g . Taking into account the free volume approach of plasticization [22] and Simha-Boyer's rule [23], a simplified relationship between the glass transition temperature of the wet (T_g) and dry (T_{g0}) polymer can be written as follows [24]:

$$\frac{1}{T_g} = \frac{1}{T_{g0}} + A_p v \quad \text{Equation 6}$$

where $A_p = \frac{1}{T_{gw}} - \frac{1}{T_{g0}}$. T_{gw} is the glass transition temperature of water (~ 120 °K) and v is the water volume fraction which can be assimilated to its mass fraction.

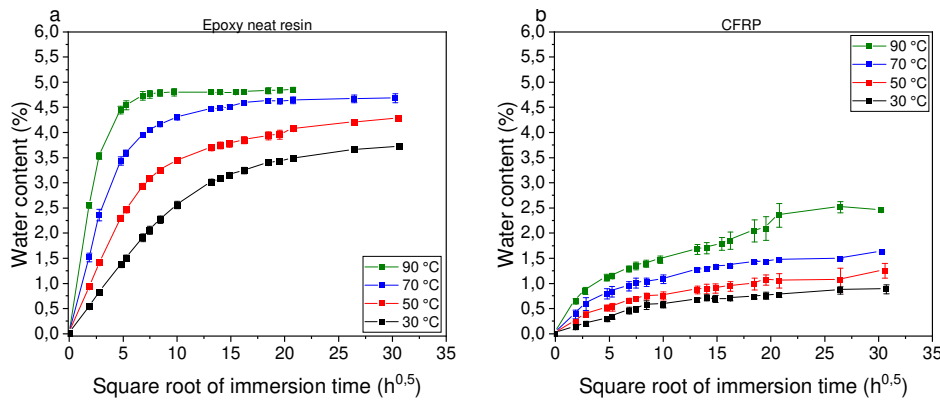


Figure 3 : Water content as a function of square root of time for a) neat epoxy resin and b) CFRP composite

The water absorption curves of both neat epoxy and CFRP samples are given in Figure 3. For epoxy resin, the water uptake obeys the common Fick's law. The water uptake increases gradually until reaching an equilibrium plateau for samples immersed at 70 and 90 °C. Samples aged at 30 and 50 °C did not reach effective saturation after 900h of immersion. On the other hand, CFRP samples exhibit a two stages behaviour with a short pseudo-equilibrium state. In addition, CFRP samples immersed at 90 °C present an acceleration of water sorption after 400h of ageing related to hydrolysis reaction. In order to compare diffusion coefficients, the Fick's second law and a Double-Stage Fick models were applied to neat resin and CFRP, respectively. Obtained results are plotted in Arrhenius diagrams in Figure 4. The calculated activation energy is about 37.5 kJ/mol for both materials.

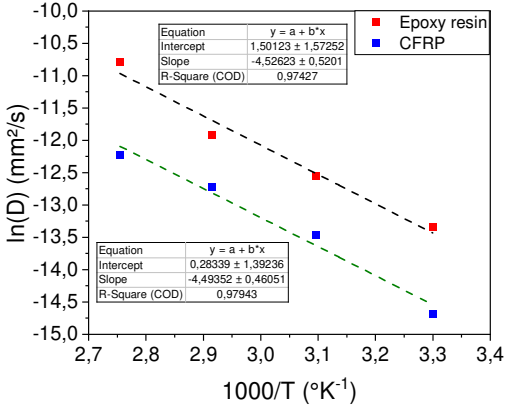


Figure 4 : Arrhenius diagrams of the coefficient of water diffusion in neat epoxy resin and CFRP composite

In order to evaluate the impact of water content on the physico-chemical properties of neat resin and composite samples, DMA tests were carried out after different ageing durations. Figure 5.a shows that the T_g for neat epoxy resin decreases linearly with water content until around 4.5%, after that, a deviation from the linear approximation is observed. In addition, the plasticization theory given by Equation 6 seems to fit experimental data. After drying, an irreversible decrease of about 24 °C of T_g is found due to hydrolytic degradation of the resin. On the other hand, Figure 5.b presents the evolution of T_g for CFRP samples. It is clear that the recovery of T_g after drying is significantly higher compared to neat resin samples. In addition, after a first rapid drop of about 10 °C, the T_g of hydrolysed samples seems to be constant over time and water content. It is noteworthy that immersion in water, specifically at high temperatures, represent harsh conditions that accelerate ageing phenomena. During in-service life, the maximum water content will not exceed 0.7 % as checked by the exposition of CFRP samples in Dynamic Vapour Sorption machine at 70 °C and 85% RH for 7 days. Furthermore, data after one year exposure at room temperature show that water content does not exceed 0.3% for a maximum ΔT_g lower than 30 °C. This drop in T_g is largely recovered once the sample is dried ($\Delta T_g \leq 10$ °C).

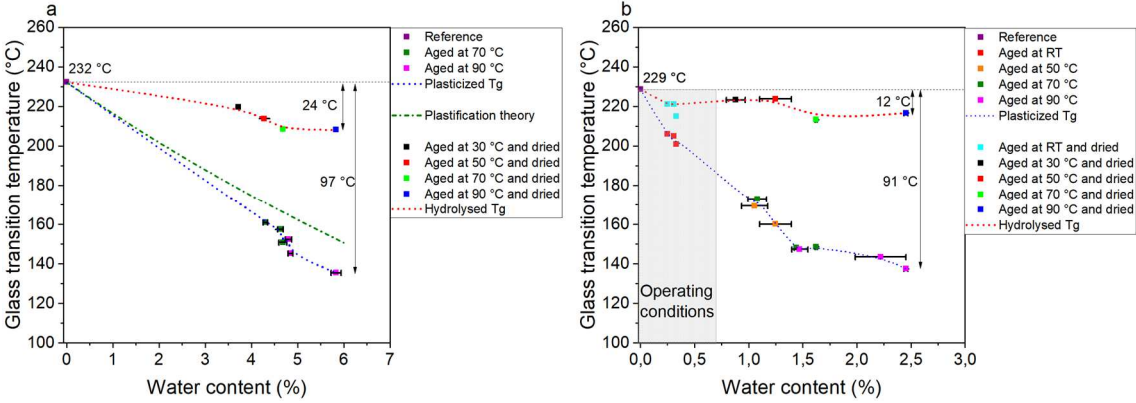


Figure 5: T_g versus water content for a) neat epoxy resin and b) CFRP. Zone from 0% to 0.7% represents real life conditions before installation of composite rods on power lines

4.2 Thermal ageing

4.2.1 Weight loss

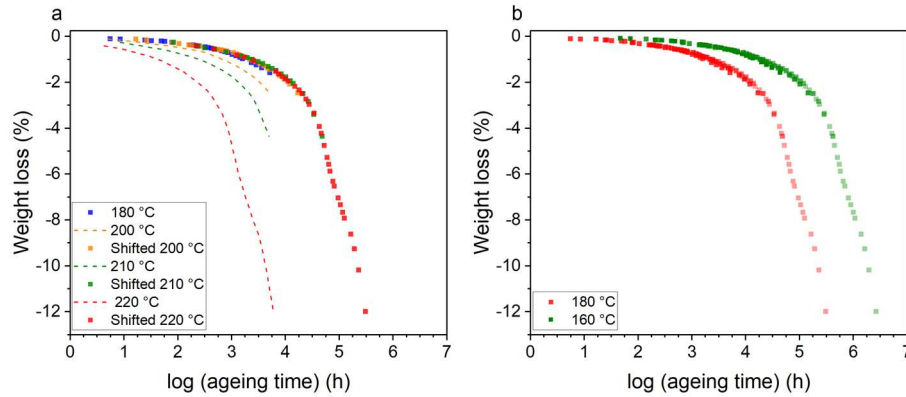


Figure 6 : a) Time-Temperature equivalence master curve of weight loss at 180 °C as reference temperature and b) extrapolation of weight loss data at 160 °C

During the operating period, rods are exposed to high temperatures due to the heating of cables by Joule effect. In the absence of reactive molecules in the exposure environment (oxygen or water), polymers can decompose under their own instability. In general, these radical reactions are initiated by the breaking of the weakest chemical bonds. Thus the formation of radicals is always accompanied by the emission of various volatile organic compounds (VOCs), which leads to a weight loss. At moderate exposure temperatures, i.e. at $T < T_g$, thermolysis has trivial effects on thermoset networks. However, it can induce post-crosslinking reactions leading to densification of the network and thus an increase in T_g . Both reactions (breaking of weak bonds, post-crosslinking) lead to polymer shrinkage resulting in internal tensile stresses in the matrix that can cause core cracking. In the presence of oxygen, this latter reacts with polymer groups by the grafting of oxygen molecules onto the network resulting in both its densification and release of volatile products. In both cases (thermolysis and thermo-oxidation), the released volatile products generate micro-cavities which constitute crack initiation sites. In order to understand hybrid composite rods behaviour during thermal ageing, gravimetric method was used to monitor weight loss as an indicator of degradation. In order to propose their extrapolation to real in-service conditions, Time-Temperature Superposition Principle (TTSP) was applied to experimental data at different ageing temperatures and results are presented in Figure 6. The TTSP is based on the theory that increasing the temperature is equivalent to shortening the time of the response of the material, herein accelerating the weight loss during ageing. In this study, 180 °C was considered as reference temperature and weight losses at 200, 210 and 210 °C were shifted horizontally to build the master curve at 180 °C (Figure 6.a). The empirical relationship between temperature and time effect on weight loss is then formulated in an Arrhenius law as follows:

$$\log(a_T) = \frac{\Delta H}{2.303R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad \text{Equation 7}$$

where a_T is the horizontal shift factor, ΔH is the activation energy (kJ/mol), R is the universal gas constant, T is the exposure temperature and T_0 is the reference temperature. The shift factor corresponding to each temperature and the calculated activation energy are given in Table 2. These parameters were then used to extrapolate the master curve to 160 °C (the predicted in-service temperature of power lines) and the new master curve is represented in Figure 6.b. For an expected in-service life of 30 years at 160 °C, the predicted weight loss is of the order of 3.3 %.

4.2.2 Mechanical properties

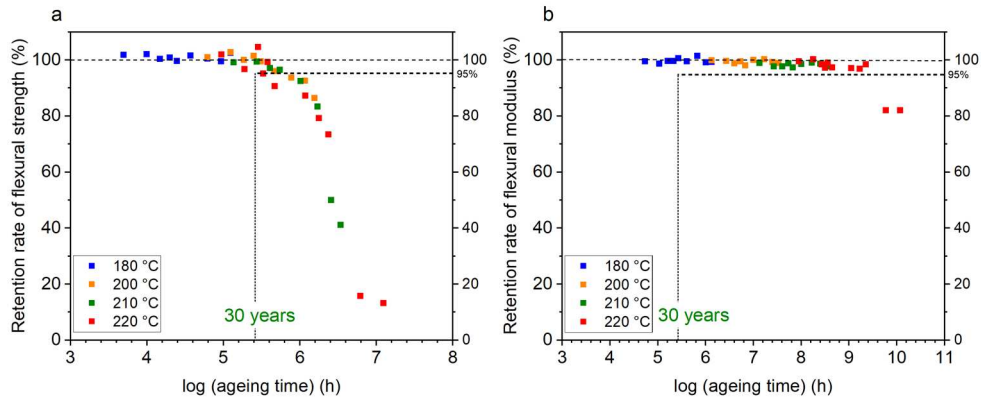


Figure 7 : TTPS master curves extrapolated to 160 °C of: a) Flexural strength and b) flexural modulus

Flexural tests were conducted up to 5000 h of exposition of composite rods at different temperatures in order to evaluate the impact of accelerated thermal aging on their mechanical properties. Extrapolated master curves of flexural strength and modulus to 160 °C are given in Figure 7 and related shift factors and calculated activation energies are summarised in Table 2. It's clear from Figure 7.a that after 30 years of exposure at 160 °C, the residual flexural strength is higher than 95 % of the original value. As regards to the modulus, the decrease is almost imperceptible even after prolonged exposure duration and at higher temperatures. This is noticeable also from the higher activation energy related to flexural modulus compared to the activation energies of flexural strength. Although flexural tests are easier to perform on composites in order to assess damage in the matrix, there are currently no end-of-life criteria for flexural tests, as conductors are almost never subjected to pure bending stresses during their lifetime. Instead, most standards require a minimum residual tensile strength of 95% of the original value.

Table 2: Time-Temperature Superposition Principle shift factor $\log(a_T)$ and activation energy E_a results for different physical properties (reference temperature = 180 °C)

	Weight loss		Flexural strength		Flexural modulus	
	$\log(a_T)$	E_a (kJ/mol)	$\log(a_T)$	E_a (kJ/mol)	$\log(a_T)$	E_a (kJ/mol)
180 °C	0	175	0	279.6	0	474.3
200 °C	-0,519		-1,398		-1,699	
210 °C	-0,991		-2,041		-3,000	
220 °C	-1,716		-2,602		-4,544	

4.2.3 Effect of void fraction

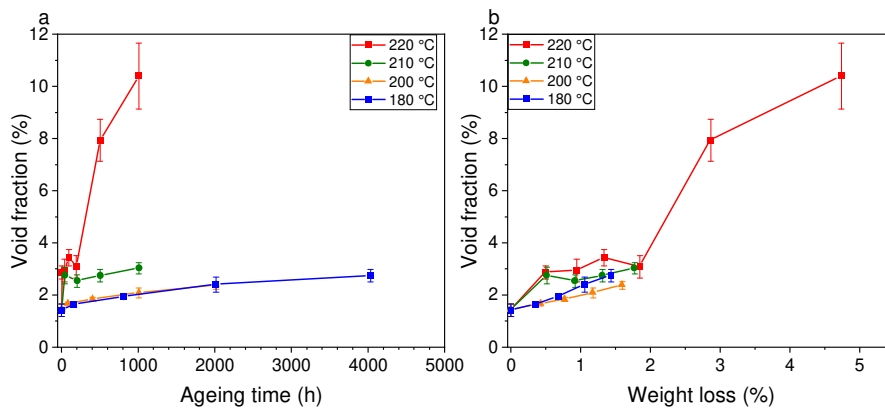


Figure 8 : Changes in void fraction in carbon fibre cross-sections as a function of a) ageing time and b) weight loss of hybrid rods

In order to propose an end-of life criterion for hybrid rods on the basis of flexural tests, Figure 8 represents the evolution of void fraction in carbon fiber cross-sections as a function of exposure time and the corresponding weight loss. It can be seen that, as the exposure temperature approaches the glass transition temperature, the increase of void content is almost instantly in particular at 220 °C. In contrast, at relatively moderate ageing temperature (180 and 200 °C), the evolution of void fraction follows an asymptotic trend which does not exceed 3% after 4000h at 180 °C. This trend is confirmed by the void fraction vs weight loss curves presented by Figure 8.b which indicates that void fraction evolution is acceptable until around 2 % of weight loss. Beyond this value, a significant increase in the void fraction is observed, reaching 10 % when rods are exposed during 1000h at 220 °C. A plausible explanation of this evolution is based on the hypothesis of the formation of volatile compounds by chain scission is thermally accelerated. Some of the released volatile products remain trapped in the bulk composite that causes an increase in gas concentration. As most of volatile compounds have low solubility threshold in epoxy/anhydride matrices [7], they accumulate locally and lead to the formation of cavities which are usually crack initiation zones. Thereafter, the retention rate of flexural strength and modulus were plotted as a function of void content in Figure 9.

In addition, data from tensile tests performed on hybrid rods aged at 220 °C during about 500h are given by black points for comparison. A common criterion can be given for 90% of retention rate of flexural strength, which corresponds to ~3% of void fraction (Figure 9.a). Above this value, a drastic drop in flexural strength is observed. Regarding flexural modulus, before that void fraction reaches 3.5 %, the retention rate is satisfactory and is consistent to tensile test results as showed in Figure 9.b. Regarding ASTM B987-20 standard requirements, glass/carbon composite core must withstand 95% of the minimum tensile strength (2137 MPa in this case, which corresponds to 2030 MPa) after thermal ageing. With an average tensile strength value of about 2850 MPa, the composite core strength remains at 2285 MPa after 500h of exposure (void fraction ~8%), which is higher than the end-of-life criterion specified by the test standardisation.

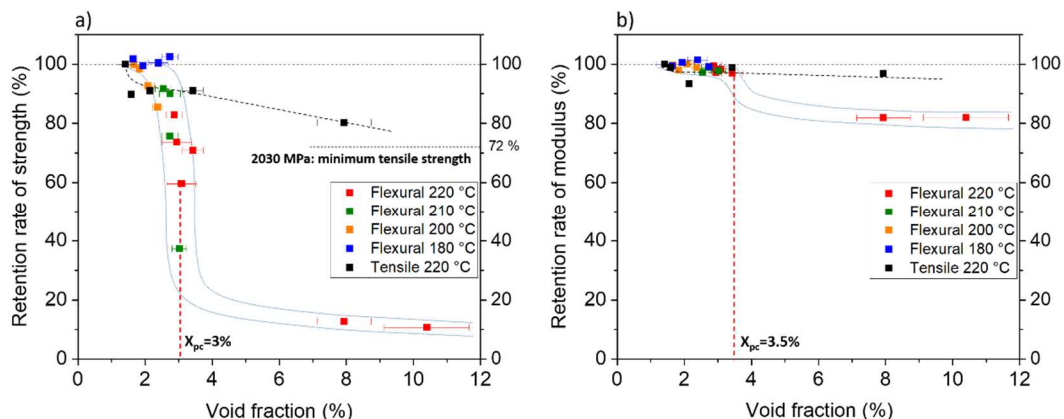


Figure 9 : Retention rate of a) flexural strength and b) modulus against void fraction

5 Conclusions

Accelerated humid ageing tests revealed the double response of the studied composite depending on water content in the material. A significant drop of T_g is found to be partially reversible. In addition, hydrolysis decreases the T_g by only around 12 °C even after high water uptakes are observed. Data from long term storage of hybrid rods showed that the maximum water content of 0.3 % does not affect the material properties. Given that composite rods will operate at high temperatures, this should lead to fully drying the material and thus, preserving its physico-chemical in-use properties.

Thermal ageing tests revealed that thermolysis is the main degradation phenomena which is thermo-activated. Time-Temperature Superposition principle was successfully applied to different material properties (weight loss, flexural properties) and extrapolated data to an effective in-service temperature of 160 °C revealed the good thermal stability of composite rods. A proposal of end of life criterion based on the void fraction evolution induced by thermolysis seems to be different for flexural and tensile results. However, these latter need to be completed at different temperatures in order to better understand the material behaviour and to propose a robust predictive model. This model should take into account different operating conditions (temperature, relative humidity, ampacity, etc...) and material initial

properties (sizes, T_g , mechanical properties, etc...) and propose a predictive evolution of the material's physico-chemical and mechanical properties over its service life to predict the expected life in years.

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