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Water ageing effects on the elastic and viscoelastic behaviour of epoxy-based materials used in marine environment

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Abstract :

Both experimental tests and numerical simulations have been performed in this study to analyze the influence of long-term immersion (over 500 days) on the hygro-elastic and hygro-viscoelastic behaviour of epoxy resin samples. First, a diffusive and swelling campaign was carried out with water immersion at 25 °C and 60 °C. Various experimental tests have also been undertaken at different stages of ageing to highlight and quantify the influence of water diffusion on elastic and viscoelastic properties. A model is then proposed to simulate the hygro-viscoelastic behaviour of the studied material through finite element simulations. A good agreement between the experimental and numerical results is observed.

Highlights

► Viscoelastic properties evaluation is necessary to analyze the time-dependent mechanical behaviour under humid environmental conditions. ► Moisture uptake leads to changes in the visco-elastic behaviour. ► 4-parameters Burgers model provides a good fit for creep tests on epoxy samples for both dry and humid cases. ► An implementation of the viscoelastic model within a finite element software is possible through the use of Prony series.

Keywords : Thermosetting resin, creep, ageing, analytical modelling, finite element analysis

1. Introduction

Epoxy-based materials, especially glass-fiber reinforced polymers (GFRP) but also carbon-fiber reinforced polymers (CFRP) are widely used in a marine environment, for energy structures, boat and ships, due to their good resistance to corrosion and mechanical performance for a given weight.

As the global energy demand is increasing due to transport, construction and household consumption, several new energy domains are developing, and offshore renewable energy is one of these [1,2]. With stronger winds away from the coast, offshore wind turbines can not only produce more energy per day, but also run more often during the year as the wind is more consistent in offshore regions. On these energy producing structures, composite materials are mainly used for the turbine blades. Uniaxial, bi-axial and quasi-isotropic composite are used, together with foam cores, sandwich panels and adhesives [3,4]. Even though thermoplastic resins are starting to be studied, mainly for recycling and waste issues [5], thermoset resin are more frequently used at present due to their low-temperature manufacturing process and better physical properties. This is also true for the naval industry, as marine conditions are very similar. Thus, these epoxy-based materials and structures are subjected to a wet environment (humid air or immersion) and various severe mechanical loadings that may reduce their lifetime. It is therefore important to ensure their mechanical integrity through studies on their durability in a marine environment [6].

The present study specifically focuses on the long-term influence of water immersion on the mechanical behaviour of epoxy samples. The objective of this study is to make a connexion between elastic and viscoelastic properties for an epoxy matrix resin during wet ageing, as these properties are complementary in long-term ageing studies and have received less attention in the literature.

The first part of this paper is devoted to the hygro-elastic characterization, *i.e.* the study of water diffusion without any other external mechanical loadings. Water diffusion mechanisms must be identified in order to be able to predict their evolution for longer times. A second phenomenon, the hygroscopic swelling must also be linked with the diffusion in order to understand how internal stresses develop during water immersion. An associated mechanical model will be specified to study this hygro-mechanical behaviour.

The next part of this study is focused on mechanical (tensile and creep) tests to highlight the influence of water ageing on elastic and viscoelastic behaviour. To achieve this latter task, a dedicated experimental campaign involving different mechanical loadings and times of immersion is proposed.

The last part of this paper details the use of a viscoelastic model to represent the creep behaviour of the studied material. A Burgers model, able to represent nonlinear creep behaviours appears to be a good candidate for this work [7]. In this section, analytical calculations are performed to determine the evolution of viscoelastic properties due to water immersion. This viscoelastic model is then implemented in finite element software (Abaqus CAE©) to perform hygro-viscoelastic simulations to evaluate hygro-mechanical responses at different ageing times. The efficiency and capabilities of the proposed model and its numerical implementation are finally shown and discussed.

2. Materials & hygro-viscoelastic characterization

2.1 Materials

2.1.1 Manufacturing

This study focuses on one type of neat epoxy resin *LY556*, provided by Huntsman. The resin was mixed with an amine hardener XB3403, cast in a mould then cured for 2 hours at 120°C in a vacuum chamber and plates of 2.2 mm thick were obtained and cut with a water jet. Pycnometer analyses revealed a density of 1.19 ($\pm$ 5.10^{-4}) g/cm^3 for the cured resin.

These materials were conditioned at 50°C and RH<10% for at least 2 months in order to dry them before being placed in a wet condition in distilled water, 0.8% by weight of water was eliminated with this operation. Before immersion, DSC (Differential Scanning Calorimetry) tests were performed in order to quantify the glass transition temperature T_g at a dry state. A T_g of 121 (±0.2) °C (onset measurement) was obtained, before ageing. Two wet ageing conditions were selected: 25°C and 60°C in distilled water. Both these conditions are well below the glass transition temperature to avoid physical ageing that may affect the epoxy matrix [7,8]. Indeed, a structural relaxation of the polymer, that can appear when it is subjected to a temperature close to the T_g, is to be avoided as it may counter the influence of water by increasing some mechanical properties such as the ultimate tensile strength [10].

This paper presents four types of tests. Associated specimen geometries are specified in Table 1. Samples were manufactured by FMC, a French company in Brest, and controlled with a digital caliper.

Table 1: Description of the samples used for this study

Type of test	Geometry	Dimensions [mm]		
		length	width	thickness
Gravimetric	Square	50±0.06	50±0.05	2.23±0.03
Hygroscopic swelling	Rectangular	200±0.09	20±0.02	
Tensile	Dumbbell	150±0.07	10±0.04	
Creep	Dumbbell	150±0.07	10±0.05	

2.2 Hygro-elastic behaviour

2.2.1 Gravimetric tests and diffusion

To understand the overall hygro-mechanical behaviour of epoxy-based composites, uncoupled tests need to be performed. Gravimetric measurement is one of them and provides an indication of the kinetics of water molecules diffusion into samples.

Fig 1 shows the macroscopic water uptake *C(t)* versus the root time divided by the thickness of epoxy samples. It is obtained by weighing the gravimetric samples at different aging times *m(t)* and comparing them with the initial dry mass m_0 through the following expression:

$$C(t) = \frac{m(t) - m_0}{m_0} * 100 \quad (1)$$

Regular weighing was performed over more than 500 days, on square samples of (50x50x2.23) mm^3. Three samples were weighed for each condition.

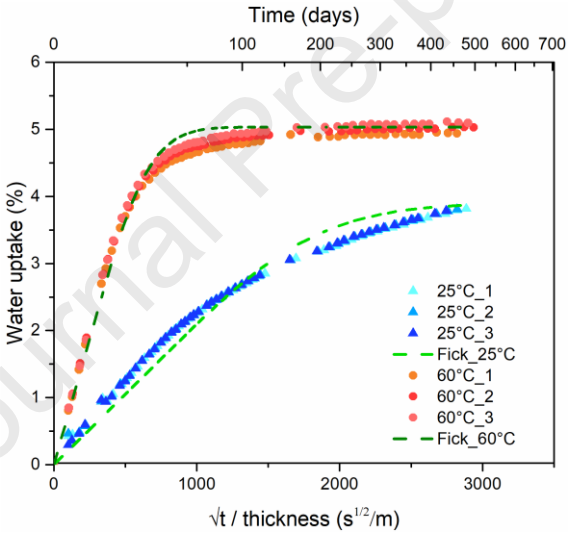


Fig 1: Gravimetric measurements performed on LY556 epoxy resin samples at 25°C and 60°C water immersion and identified Fickian model

It may be noted that the epoxy system does not show a saturation level at room temperature (25°C) yet, but at 60°C a plateau is reached.

In the case of thin plate diffusion, neglecting edge effects, unidirectional diffusion through the thickness (z-direction) is considered, i.e. $D_x = D_y = 0$. Thus, the 1-D Fick problem to be resolved can be written:

$$\frac{\partial c(x,t)}{\partial t} = D_z . \frac{\partial^2 c(z,t)}{\partial z^2} \quad (2)$$

Associated with the following initial and boundary conditions:

$$c(z,t) = 0 \quad \text{for} \quad 0 < z < e \text{ at } t = 0 \tag{3}$$

$$c(z,t) = C_{sat} \quad \text{for} \quad z = \{0, e\} \text{ at } t \geq 0 \tag{4}$$

where e corresponds to the thickness of the sample. The analytical solution to this problem, given by Crank in [11], is given below:

$$C(t) = C_{\text{sat}}\left(1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}exp\left[-(2n+1)^2\pi^2.\frac{D.t}{e^2}\right]\right) \tag{5}$$

Two parameters need to be identified, C_{sat} corresponding to the maximal water uptake, and D, the coefficient of diffusion through the z axis. This identification is made based on a least square minimization solution as the one described previously in [12] and presented in Table 2. These parameters will be used later in this paper in the finite element analyses to simulate the water diffusion.

Table 2: Diffusive parameters identified for the LY556 resin (* estimated value, saturation not reached)

Fick parameters	25°C	60°C
C_{sat} (%)	3.82*	5.03
D (m²/s)	5.68E-14	4.34E-13

Precautions need to be taken with these identified parameters as after more than 500 days, saturation was not reached for the lower temperature hygrothermal condition. It also may be noted that C_{sat} could depend on temperature. Long time exposure to high water temperatures may cause oxidation that leads to a greater affinity with water molecules as Wong postulates in his paper [13]. Additional hygroscopic swelling may also increase C_{sat} by providing more space for water to diffuse. Alongside diffusion measurements, mechanical states must also be studied, as water diffusion penetrates into the polymeric network.

2.2.2 Hygroscopic swelling

One of the first consequences of water diffusion within a material is its expansion, as shown on Fig 2.

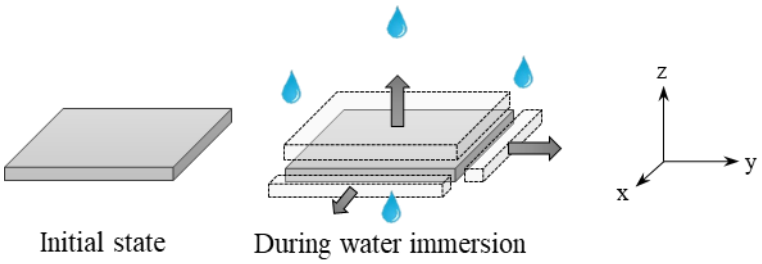


Fig 2: Hygroscopic swelling representation

In the case of water ageing studies, this is called hygroscopic swelling and links the local water content with the induced hygroscopic strain $\boldsymbol{\varepsilon}^h$:

$$\boldsymbol{\varepsilon}^h = \boldsymbol{\beta}(c) : \boldsymbol{I}c \tag{6}$$

where $\boldsymbol{I}$ is the second order identity tensor and $\boldsymbol{\beta}$ represents the hygroscopic strain tensor defined as:

$$\boldsymbol{\beta} = \begin{bmatrix} \beta_x^h & 0 & 0 \\ 0 & \beta_y^h & 0 \\ 0 & 0 & \beta_z^h \end{bmatrix} \tag{7}$$

Hygroscopic swelling is often neglected in long term ageing studies but it remains a key point in the hygro-elastic behaviour of the polymer as it may engender internal stresses [14], especially in transitory phases [15]. These may lead to failures in composite structures due to differential swelling between the hydrophilic matrix and the hydrophobic synthetic fibers [14,15].

The hygro-elastic strain tensor $\boldsymbol{\sigma}$ depends on the elastic stiffness tensor $\mathbf{L}$ and the total strain tensor $\boldsymbol{\varepsilon}$ such that

$$\boldsymbol{\sigma} = \boldsymbol{L} : (\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}^h) \tag{8}$$

Experimentally, regular measurements were performed with a laser on parallelepiped samples along their longitudinal axis.

These data are related with the water uptake of the samples to obtain the points as shown in Fig 3.

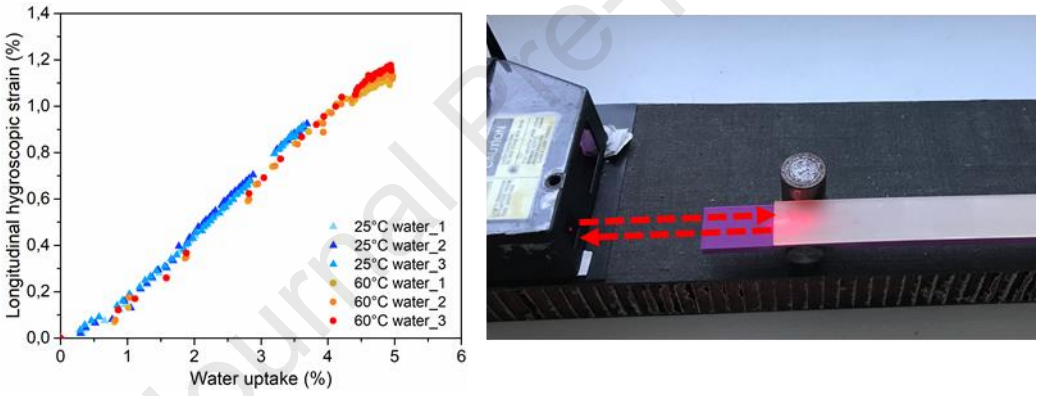


Fig 3: Experimental hygroscopic swelling with respect to water uptake for 25°C and 60°C conditions (left) and associated laser bench (right)

An interesting result is that the overall hygroscopic swelling behaviour with respect to water uptake is the same for both temperature conditions. Raising temperature will only accelerate the diffusion phenomenon and thus the hygroscopic swelling linked to it. Loh et al. [18] found similar results for an epoxy adhesive at different RH and immersion conditions, but at the same temperature. This result emphasizes the fact that swelling is only material dependent in the proposed study. Even though the local moisture fields may be different, since the diffusion kinetics are not the same for each temperature, the macroscopic hygroscopic swelling measured remains the same for an identical overall water content. Zhou et al. [19] suggest that the immediate swelling results from the breaking of Van der Waals bonding by water molecules and the formation of single hydrogen bond with the macromolecular network, while for longer aging times, multiple hydrogen bonds could be present and thus be harder to detach from the network.

It should be noted that the thermal swelling has been neglected here for two reasons. First, all the swelling measurements were performed at room temperature and after a sufficient delay for the samples aged at 60°C to cool down. Second, any thermal swelling is largely over-shadowed by the hygroscopic swelling. Indeed, many previous studies have confirmed this statement [11,18-20] by showing that the typical CTE (Coefficient of Thermal Expansion) for epoxy resin was around 0.005 % while hygroscopic swelling coefficient is close to 0.5 %.

These experiments have provided values of CME for each ageing condition, presented in Table 3 below.

Table 3: Determination of hygroscopic swelling coefficient β_h

Ageing temperature	25°C	60°C
β_h (%)	0.241 (±0.002)	0.232 (±0.004)

A linear regression analysis was used to obtain theses β_h coefficients. Some authors have identified this coefficient in a similar way [19-21], while others have proposed a different approach especially for the early stage where a diffusion may occur without an expansion due to a filling of the existing space in the polymer and thus a global [18] or local [12] moisture dependency can be identified.

2.3 Mechanical behaviour dependence on ageing

The aim of this section is to quantify the changes in mechanical properties at different stages of ageing. The first stage called T_0, is the dry state, reached after 2 months in a desiccator, and corresponding to a homogeneous low moisture field within the samples. Three other stages from T_1 to T_3 were chosen to be representative of the evolution of the water uptake and correspond to an overall water content from 2.2% to nearly 4% as specified in the Table 4 below. Finally, another stage was defined as T_{des} (desorption) to study the influence of absorption/desorption conditions on the mechanical properties. For this stage, after almost 500 days of water immersion the samples were subjected to 50 days of drying in a desiccator to remove the maximum amount of water in the epoxy samples in order to get a uniform water content within the epoxy sample. In the following, we will refer to unaged samples or states for the specimens which have not been aged by immersion (initial time T_0).

Table 4: Information on ageing states

Ageing state	Water content (%)	Ageing time (days)
T_0	0	0 (60 days of drying)
T_1	2.2	55
T_2	3.8	392
T_3	3.9	527

T_{des}	1.3	490 (water) + 50 days (drying)

The mechanical behaviour of the LY556 epoxy was evaluated through quasi-static and multi-step creep tests under tensile loads, as detailed in the following sections.

2.3.1 Influence of water immersion on tensile behaviour of resin

Tensile tests were performed in a temperature and humidity controlled laboratory (21°C, 50%RH) on a universal 10kN capacity Instron 5566 tensile machine. DIC measurements were used to evaluate the mechanical strain on dumbbell shaped resin samples, at a speed of 2 mm/min, at different stages of ageing as shown on Fig 4. For each ageing stage, 3 tensile tests were performed.

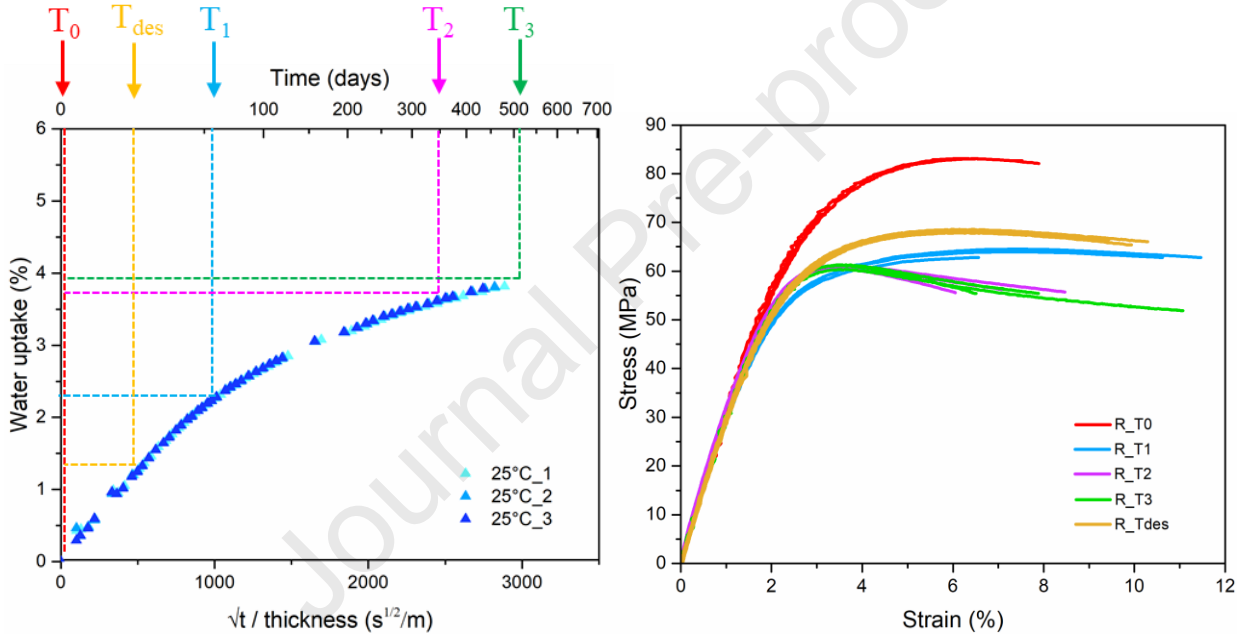


Fig 4: Illustration of ageing stages at 25°C and associated tensile tests

A clear evolution of the tensile behaviour is noted on Fig 4 (right) with a loss of tensile strength after only 2 months of water immersion. A stabilization of the mechanical performance in tension seems to appear for longer ageing times, while a partial drying after desorption (in yellow) allows a limited recovery.

Different mechanical properties are analyzed in Fig. 5. The apparent elastic modulus seems to be little affected by water, going from 3.1 to 2.9 GPa (a reduction of 6%) after more than 500 days: since moisture

uptake introduces viscoelastic relaxation during the test, we prefer to denote by apparent elastic modulus the slope at the beginning of the stress-strain curve.

This suggests that the tensile behaviour is not affected for low strains (under 2%). However, the maximum stress decreases rapidly during the first months of ageing to stabilize between 60 and 65 MPa. Lastly, the failure strain seems to increase with ageing, allowing a larger extension for epoxy samples which contain water. These observations are consistent with the study of Sugiman [23].

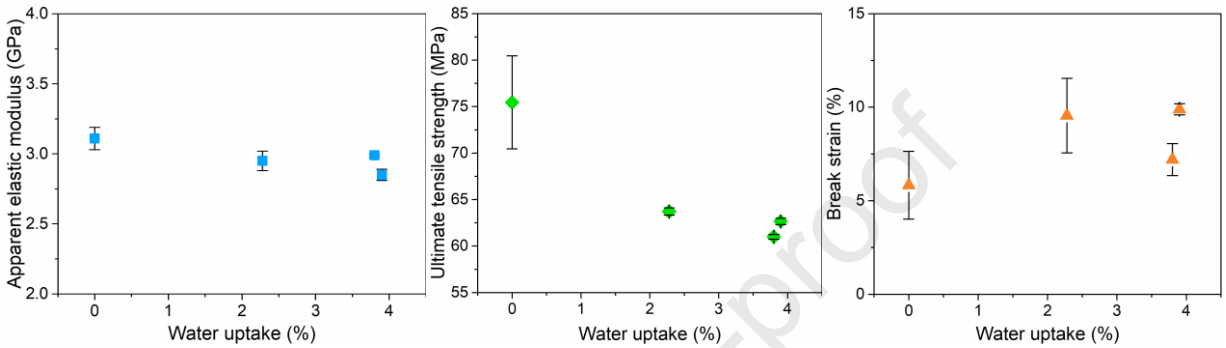


Fig 5: Changes in mechanical properties with respect to overall water content

The same epoxy resin was used in the work of Humeau [24], who highlighted a significant drop of each of the mentioned properties, even for the modulus of elasticity but with a previous version of the polyamine hardener XB4303. This result indicates that the hardener plays a significant role in the mechanical integrity of the polymer during wet ageing. Zafar et al. [25] found similar results to Humeau, in both distilled water and seawater. Thus, not only the type of resin needs to be investigated but also the type of hardener.

2.4 Ageing effects on viscoelastic behaviour

Since the resin used in this study belongs to a class of materials known as viscoelastic, it is necessary to quantify the viscoelastic behaviour, during water immersion. Between an elastic solid and a viscous liquid, thermoset materials present a response to external loads that depends on time and temperature, but water may also play a major role. Indeed, as viscoelasticity is closely linked with molecular mobility [9] and as water diffusion disturbs it by occupying the free volume of the polymer [25], it is important to clarify the influence of ageing on the viscoelastic behaviour of the epoxy resin.

Creep tests have been performed at different stages of ageing, here T_0, T_1, T_2 and T_3. For each of these stages, incremental creep tests have been conducted in the following way: four steps of creep are applied successively; each lasts one hour and is followed by three hours of recovery.

A loading sequence has been determined based on the elastic limit σ_e of the studied resin, determined from tensile tests, for the samples tested at T_0 (see Table 5). This statement is important since the elastic limit may decrease with water ageing; here the dry reference value was used throughout.

Table 5: Evolution of estimated elastic limit, equivalent stresses and imposed forces for each step of creep tests

Creep steps	1st	2nd	3rd	4th
% of initial σ_e	25	50	75	100
σ (MPa)	12.45	24.86	37.27	49.73
F (N)	274	547	820	1094

For this 16 hour experiment, performed in a room at 25°C with 55% < RH < 80%, the desorption of the epoxy samples during the creep test was neglected.

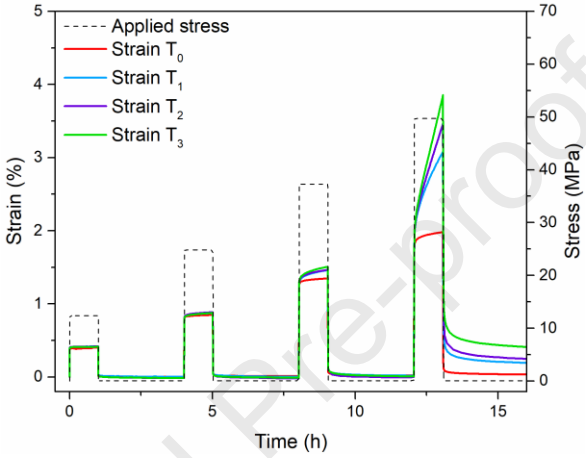


Fig 6: 4-step creep tests at a dry stage (T_0) and after 3 stages of ageing (T_1, T_2 and T_3)

For each ageing stage, after the instantaneous strain, a nonlinear evolution of the strain appears for every step of loading, Fig. 6. This nonlinear behaviour increases with the imposed stress. An almost full recovery is noted after each unloading phase except for the last step corresponding to 100% of the elastic limit where a residual strain is observed even for the dry state. However, this residual strain is higher for aged states than in the unaged state. As it is the viscoelasticity which is of interest, only steps under 75% were kept for the modelling in the following, to remain in a nonlinear elastic domain.

For the first step, there is no major difference between the initial dry stage and an aged stage. An identical observation could be made between each aged stage, for each step, where all T_1, T_2 and T_3 curves are very close. However, as the load increases at each step, a strain gap appears between unaged and aged stages (+33% in the 4th step on average for the aged ones) but a clear difference increases throughout the loading sequence. This clearly shows that ageing affects the viscoelastic behaviour of the studied resin. However this variation of behaviour seems to appear at an early stage of ageing and tends to stabilize before the maximum water uptake is reached.

Fig 7 allows a better understanding of the influence on ageing on creep behaviour of epoxy samples. Not only creep compliance levels (here chosen at a given time of 1000s) are increasing with ageing and stresses, but also strong nonlinearities appear for high stress levels.

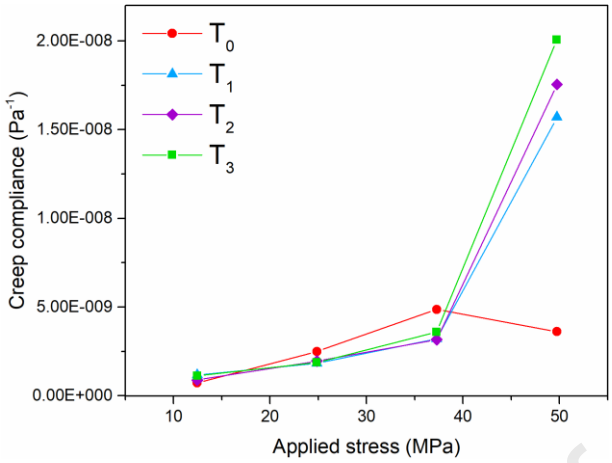


Fig 7: Creep compliance levels at 1000s for different ageing times and applied stresses

It should be noted that the hygroscopic strain is not taken into account in these creep tests on aged samples. Indeed, the duration of these tests is not long enough to start a desorption process, and the hygroscopic strain may remain unaffected. To be closer to the reality, we therefore propose to add the hygroscopic strain to the instantaneous and viscoelastic strain using the following 1D-expression:

$$\varepsilon_{total}(t) = \varepsilon_0 + \varepsilon_{ve}(t) + \varepsilon^h(c,t) \quad (9)$$

where ε_0 is to the instantaneous elastic strain, ε_{ve} the viscoelastic stain and ε^h, the strain related to the hygroscopic behaviour.

Fig. 8 then present the results of the creep tests associated with the hygroscopic strain ε^h

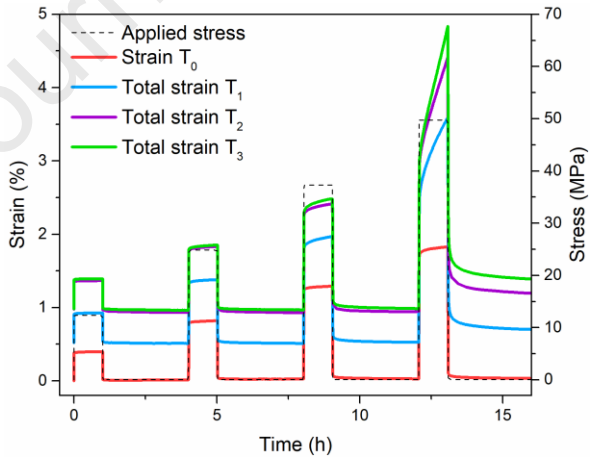


Fig 8: 4-step creep tests and associated hygroscopic strain for each stage of ageing

The creep strain is provided by the 4-step creep test (Fig 6) while the hygroscopic strain corresponds to a vertical shift directly determined from the hygroscopic swelling measurements detailed in the section 2.2.2. This representation provides a better visualization of the contribution to the measured strain, which are due to the water absorption or to an external loading. Indeed, for the first two steps, the hygroscopic strain is greater than the mechanical strain and thus must not be neglected. For the two following steps, the

creep strain and the hygroscopic one are of the same order of magnitude. This statement highlights the importance of knowing the water content of a material before performing a mechanical test.

3. Modelling and finite element hygro-viscoelastic analysis

The next section is divided in two parts. The first is devoted to an analytical model representing the viscoelastic behaviour of the epoxy-based samples. The second part is focused on integration of this model in finite element software to represent the hygro-viscoelastic physics of a specimen subjected to both mechanical loading and water diffusion.

3.1 Analytical analysis of viscoelastic ageing

The study of viscoelasticity makes it possible to determine constitutive laws for polymeric materials, describing their deformation following an imposed stress for a given time and temperature. Various combinations of linear or nonlinear viscoelastic models allow simulation of time dependent behaviour [26,27].

In this study, a Burgers model is proposed in order to represent the nonlinear creep behaviour of the epoxy resin, as well as its recovery. It can be seen as a combination of a Kelvin-Voigt model that fits well nonlinear creep phases and a Maxwell that shows good representation of recovery [28,29]. The Burgers model is composed of four elements: two springs and two dashpots, as shown on the Fig 9 below:

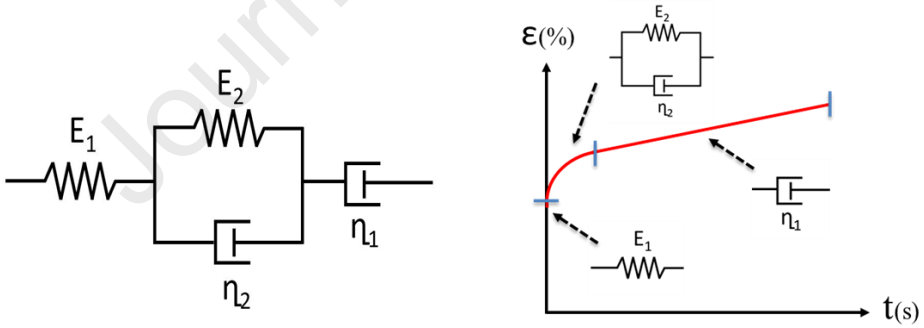


Fig 9: Representation of the 4 parameters Burgers model (left) and theoretical behaviour of the strain evolution (right)

The constitutive equation of the Burgers model in terms of stress proposed by Findley et al [29] is:

$$\sigma + \left(\frac{\eta_1}{E_1} + \frac{\eta_1}{E_2} + \frac{\eta_2}{E_2}\right)\dot{\sigma} + \frac{\eta_1\eta_2}{E_1E_2} = \eta_1\dot{\varepsilon} + \frac{\eta_1\eta_2}{E_2}\,\ddot{\varepsilon} \qquad (10)$$

The solution to this equation in terms of creep strain, using a Laplace transformation is:

$$\varepsilon\,(t) = \frac{\sigma_0}{E_1} + \frac{\sigma_0}{E_2}\,(1 - \exp(\frac{-E_2.t}{\eta_2})) + \frac{\sigma_0}{\eta_1}t \qquad (11)$$

where σ_0 is the applied stress

The first term in equation (Eq. 11) represents the instantaneous strain corresponding to the applied load. The second term is related to the transient stage where the strain increases with time in a nonlinear way. In the third term, the viscous flow represents the strain rate in the secondary creep stage. Thus, there are 4 main parameters needed to identify: E_1, E_2, η_1 and η_2.

Elastic modulus E_1 can be easily identified since it is directly linked to the initial strain ε_0 and the applied stress σ_0 such that $E_1 = \sigma_0 / \varepsilon_0$. The identification of the other three parameters E_2, η_1 and η_2 is not straightforward: we thus formulate an optimization problem based on a least square approximation aiming at minimizing the gap between the experimental observations and the strain evolution obtained with the Burgers model. The identified mean values obtained from the three samples used for each creep test are presented below.

Fig 10 illustrates comparisons between the longitudinal strain curves for creep steps P_2 and P_3 obtained experimentally and with the Burgers model associated with its optimal parameters. We only focus on these two steps (at 50% and 75% of the elastic limit) since it may be questionable to use viscoelastic models for higher stress levels where strong nonlinear phenomena may occur. Moreover, the identification of the Burgers parameters is only based on the creep strain which is here almost entirely composed of the linear viscoelastic strain. Since the applied loads are way below the elastic limit, the evolving viscoelastic and viscoplastic strains may therefore be considered as negligible. For higher applied loads, this latter assumption is not correct and more evolved models should then be used. We can observe a very good agreement regardless of the time of ageing: The Burgers model indeed provides a good representation of the creep of epoxy materials, no matter what stage of ageing, as long as we stay in the primary and secondary creep area.

For creep stage P_2, we can observe an increase of the strain with ageing time. However, for creep stage P3, all strain curves for aged cases are quite identical, which seems to indicate that the changes in the visco-elastic behaviour appear at an early stage of the diffusion process.

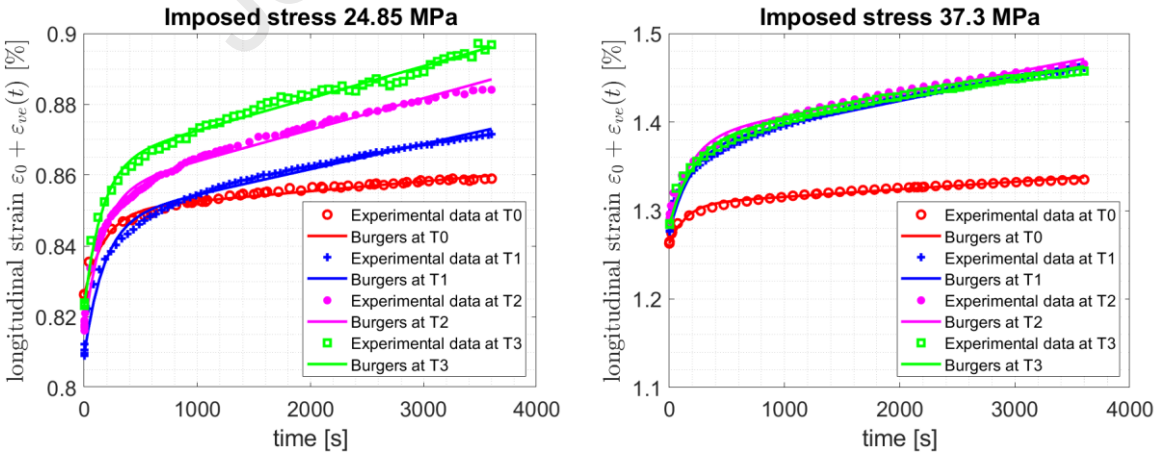


Fig 10: Comparisons between experimental creep data and corresponding identified Burgers strain curves for each time of ageing: results for creep stage P_2 (left) and creep stage P_3 (right)

Fig 11 proposes an analysis of the evolution of the 4 Burgers parameters with respect to the time of ageing. Fig 11-left shows the results for parameters E_1 and E_2: as expected, elastic modulus remains the same regardless times of ageing or the applied loads. One can notice that the identified values of E_1 for each creep test is in the range of the ones obtained from the stress-strain curves shown on Fig 4. The behaviour of parameter E_2 greatly differs from E_1: firstly, we can notice that a significant drop appears at the beginning of ageing for both creep stages. Secondly, parameter E2 tends to stabilize. However, one can observe that the E_2 values are lower for highest values of the applied stress which imply that the visco-elastic behaviour partly depends on the external loadings.

Fig 11-right presents the same type of analysis for Burgers parameters η_1 and η_2: the same conclusions can be drawn since we can clearly observe that η_1 and η_2 depends on the times of ageing and the applied stresses. Concerning η_1, this parameter which reflects the inverse of the strain rate for secondary creep stage, decreases with the applied stress which can be clearly seen on Fig 6 and 8.

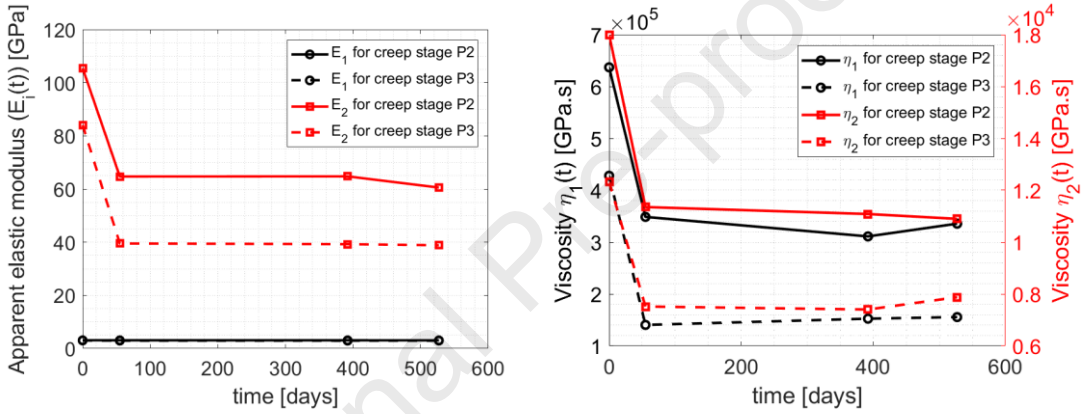


Fig 11: Evolution of identified Burgers parameters with respect to time of ageing: elastic moduli E_1 and E_2 (left) and viscosity η_1 and η_2 (right)

Therefore, moisture, as temperature increases the strain rate of epoxy-based material. Other authors indicate similar conclusions in their studies [30][31].

In the next section, the proposed model is implemented in a finite element software: comparisons with experimental data will be made and we will show simulated local fields difficult to reach with experimental studies only.

3.2 Hygro-viscoelastic finite element analyses

A 2D rectangular plate of 2.2 mm x 10 mm was considered in this work to represent the LY556 epoxy sample. A Young's modulus of 3.1 GPa was provided by tensile tests while hygro-elastic parameters determined in the first part of this paper were chosen for a study at 25°C. Thus a diffusion coefficient D of 5.82×10^{-14} m²/s, a maximum water uptake C_{sat} equal to 3.82% and a hygroscopic swelling coefficient β_h of

315 0.241% were used. Fig 12 presents the boundary value problem which represents the experimental tests depicted on Fig 6 and 8.

The finite elements simulations were made using Abaqus CAE© software where a viscous step was used for the calculation of the visco-elastic behaviour while a coupled temperature-displacement step was chosen for the aged states, since the Fourier thermal law is analogous to Fickian diffusion model. 5000 CPE4T
320 meshed elements under plane stress assumption were used in all simulations.

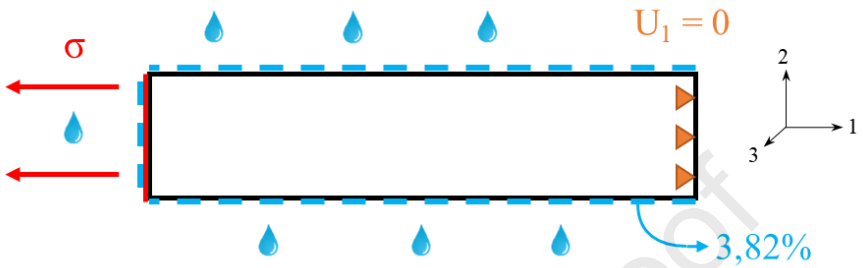


Fig 12: Scheme of the resin subjected to both water diffusion and applied stress

Viscoelastic parameters were added to model the time dependent behaviour. In Abaqus, a viscoelastic material may be modelled with a Prony series expansion of the dimensionless relaxation modulus *G(t)* such
325 that:

$$G(t) = G_1\left[g_1.e^{-t/\tau_1} + g_2.e^{-t/\tau_2}\right] \quad (12)$$

where coefficients g_i associated with relaxation times τ_i are material constants.

A calculation of these parameters was performed based on the work of Vu et al [32] that detailed how to translate Burgers parameters (E_1, E_2, η_1 and η_2) into Prony series coefficients. The identified parameters for each time of ageing used in the Abaqus simulations are detailed in Table 6.

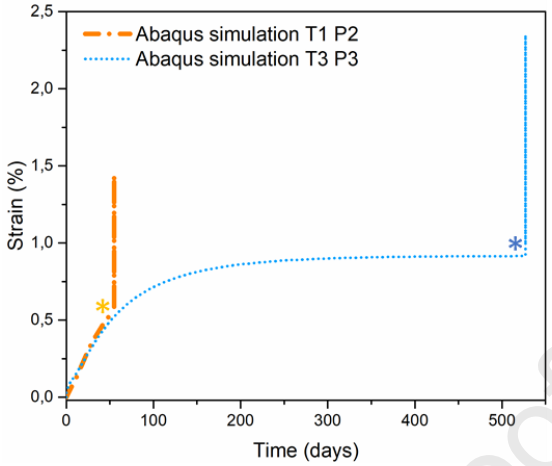
330

Table 6: Prony series parameters used in Abaqus simulations

Ageing stage	T_0		T_1		T_3	
Creep step	P_2	P_3	P_2	P_3	P_2	P_3
E_1 (x10^9 Pa)	3.089	2.981	3.016	2.834	3.057	2.937
g_1	0.9715	0.9656	0.9544	0.9303	0.9518	0.9292
g_2	0.0284	0.0343	0.0455	0.0696	0.0481	0.0707
τ_1 (s)	212 287	148 650	118 890	51 614	115 343	56 964
τ_2 (s)	165	141	265	290	171	188

Hygro-viscoelastic simulations were performed to analyze the evolution of local hygro-mechanical fields due to both water diffusion and creep loads. Two cases are presented here. The first corresponds to a 55
335 day immersion (T_1 stage) followed by a creep test with an applied load of 24.9 MPa (see Table 5), named P_2 on Fig 13. The other case is related to another aged stage (T_3) reached after 527 days of water immersion

and followed by a creep load of 37.3 MPa. These two cases have been chosen to highlight the influence of transitory and steady diffusion phases on local mechanical fields.



340 **Fig 13:** Evolution of the total longitudinal strain: hygro-viscoelastic simulations for time T_1 associated to load P_2 and time T_3 associated to load P_3

This figure shows a clear representation of the evolution of the longitudinal strain during both water ageing and a creep test. Here and on Fig 14, the strain on the y-axis is related to the total strain, as explained in Eq. 9. After 55 days of water immersion, a hygroscopic strain of 0.56% is reached (orange star) while nearly
345 1% of further strain is obtained for the studied resin, after more than 527 days (blue star). As the diffusion tends to stabilize, so does local hygroscopic swelling. The vertical bars represent a 1 hour test that are shown in more detail on the following Fig. 14.

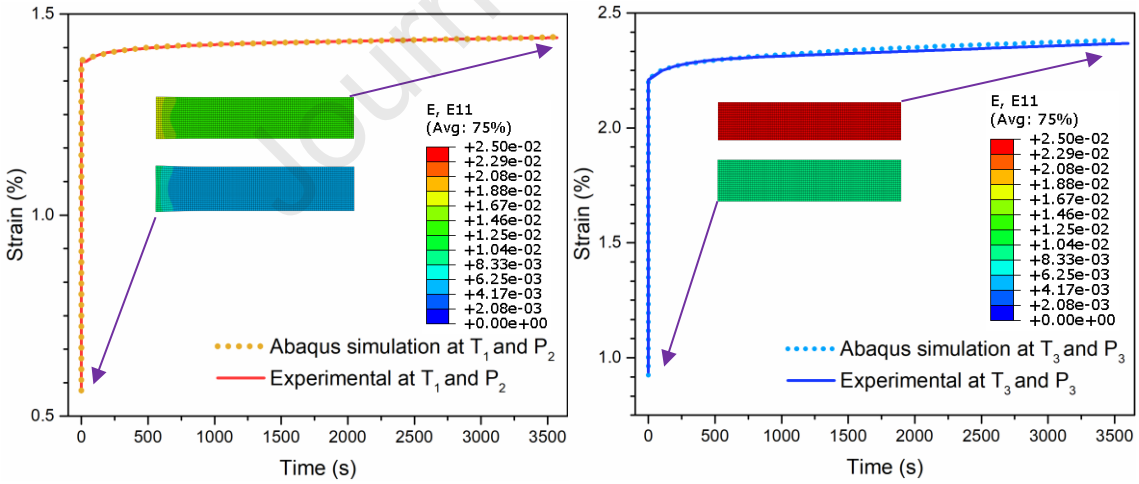


Fig 14: Hygro-viscoelastic simulations and experimental comparisons of longitudinal strain for two creep stages
350 P2 and P3

The first case presented on Fig 14 on the left is obtained for a transient stage of diffusion. This causes a heterogeneous ε_{11} strain field of the sample, due to the heterogeneous hygroscopic swelling on the left edge of the resin. The creep load adds a uniform strain on the sample and thus, the ε_{11} strain field is still heterogeneous after one hour of creep for the T_1 stage. For a longer ageing time, when T_3 is reached, a

355 homogeneous water field content is reached and therefore an identical strain field is presented on the Fig 15 on the right. Associated water and stress profiles are then shown in Fig 15.

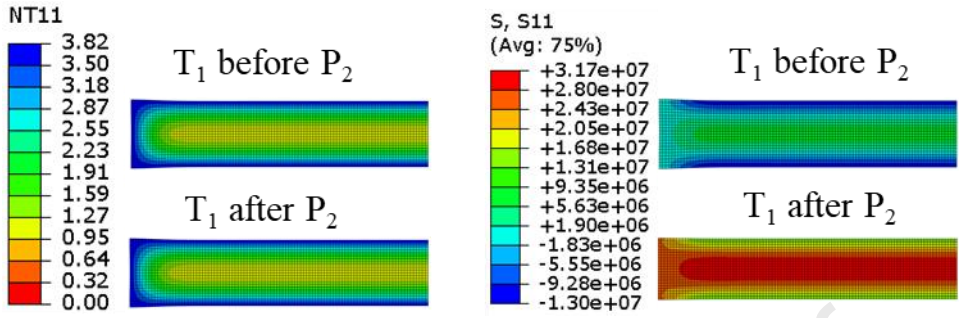


Fig 15: Water content denoted NT11 and stress field denoted S11 corresponding to the 1 - axis

360

Fig 15 gives additional details on the hygro-mechanical fields reached at T_1. At this stage, a global water content of 2.2% is obtained but locally, it goes from 1% in the center to 3.82% at the edge. Thus, internal stresses appear even before the start of any creep loading. While both the top and bottom of the sample are subjected to compression stresses (around 13 MPa), the center of the polymer undergoes to tensile stresses 365 (7 MPa at maximum). After one hour of creep (24.86 MPa), no real changes appear for the water field content since the diffusion process is very slow. Regarding the stress fields, since the local stress field coming from the visco-elastic part is homogeneous, we can observe a homogeneous increase of 24.86 MPa on the stress field presented on the top right corner of Fig 15.

4. Conclusions

370 The work here proposed a different approach to study the durability of epoxy-based material by covering both experimental and numerical hygro-elastic and hygro-viscoelastic aspects. Some results may be summarized as follows:

First, hygroscopic swelling due to water immersion is only material dependent. Neither the temperature nor the humid condition modify the expansion behaviour for this type of isotropic polymer. Moreover, this 375 parameter has to be taken into account in long term ageing studies as the hygroscopic strain may be close to that due to external loadings.

For mechanical tests, tensile behaviour seems to be modified with ageing only for large strains. In that case, tensile strength quickly decreases but may partially recover after drying. As the elastic limit lowers with water absorption, for a given load close to σ_e, large strain differences may appear after ageing.

380 Within a context of time dependency and thus a viscoelastic approach, creep rate is the parameter most affected by water ageing and quickly raises with increasing loads. A Burgers model appears suitable to represent the creep behaviour of epoxy samples within the elastic domain and allowed physical evolutions

of the polymer due to water ageing to be explained. The proposed model also allowed an analysis of its parameters regarding both ageing and applied stress levels.

Lastly, finite element analyses allowed different local hygro-mechanical fields at different water ageing times to be quantified. For the transient stages of diffusion, a heterogeneous water content caused gradients of both strain and stress that remained during subsequent creep loading. In order to fully validate the hygro-viscoelastic model and its numerical implementation, comparisons will be made between model-based simulations and experimental data for other applied stresses and ageing times. Those results will be presented in a subsequent paper dealing with composite materials.

These results form the first part of a study of durability of marine composites. Similar investigations have been performed on composites with this methodology, in order to first understand the importance of the presence of fibers on the viscoelastic behaviour. Then, fully coupled tests (*in-situ* creep tests) have been performed on composites to evaluate the viscoelastic property changes during long term (>1000h) experiments as water diffuses during the test. These results will be presented shortly.

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Highlights

- Viscoelastic properties evaluation is necessary to analyze the time-dependent mechanical behaviour under humid environmental conditions
- Moisture uptake leads to changes in the visco-elastic behaviour
- 4-parameters Burgers model provides a good fit for creep tests on epoxy samples for both dry and humid cases.
- An implementation of the viscoelastic model within a finite element software is possible through the use of Prony series.

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Author Statement

Water ageing effects on the elastic and viscoelastic behavior of epoxy-based materials used in marine environment

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Peter DAVIES, covered the supervision of experimental data as well as the corrections in the manuscript.

Mael ARHANT, offered his help through the production of data and reviewing the figures of this work

Benjamin FLAGEUL, produced a large quantity of experiments leading to this paper.

Frédéric JACQUEMIN, was in charge of this project in terms of coordination and supervision.

Therefore, all of these members are concerned with this study.

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