

# TIME-TEMPERATURE BEHAVIOUR OF A THERMO-SETTING POLYMER MATRIX

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## 1 General introduction

Over the past several decades, the aerospace industry has progressively replaced metallic materials with polymer matrix composites (PMCs). First used mainly in non-structural applications, PMCs are now widely used in more critical applications, such as wings, fuselage and more recently, aircraft engines.

Use of PMCs in such applications as aircraft engines requires materials able to withstand extreme service conditions, such as elevated temperatures, high mechanical loadings and a highly oxidative environment. With their exceptional thermo-oxidative properties, rated service temperatures exceeding 300°C and overall excellent mechanical properties, polyimides set themselves apart from other polymer matrices and are ideal candidates for such applications [1]. Furthermore, recent progresses in the development of new polyimide formulas allow for easier and cheaper out-of-autoclave manufacturing processes, such as Resin Transfer Molding, to be used.

In order for manufacturers to be able to predict the behavior of PMCs over the service life of a component, it is necessary to first understand the behavior of each individual phases of the material [2]. Therefore, when designing components for an application using PMCs, the first step should always be to analyze the behavior of the polymer matrix in the specific service conditions. In extreme environment such as an aircraft engine, the polymer matrix is likely to exhibit a viscoelastic behavior dependent on the mechanical loading and temperature. In addition, the combined effects of elevated temperature and the environment near the engines are likely to increase physical as well as

chemical aging [3] and could lead to a nonlinearly viscoelastic behavior.

The effect of temperature on the viscoelastic behavior of polymers has been widely studied by means of the time-temperature superposition principle [4,5,6]. Based on the free volume theory, the time-temperature superposition principle uses the effective time concept [7] to compare creep and compliance responses obtained at different temperatures. The concept implies that relaxation times, which increase with temperature, can be related to those at a reference temperature by a simple multiplicative horizontal shift factor. One main application of the concept consists in predicting long term creep responses of polymers using short time tests [4,5,6,8]. First developed for the case of polymer materials submitted to elevated temperatures [9], the principle of time superposition has since been extended to physical aging [10]. The combination of time-temperature and time-aging superposition principles allows for the prediction of long-term physical aging at service temperature by testing the material at higher temperature on a shorter time-scale.

When dealing with experimental data for physical aging, introduction of a complementary vertical shifting is often required [11,12]. However, while many authors use vertical shifting to determine the horizontal shift factor, it is generally found to be much smaller than the horizontal shift factor [11] and to exhibit a random behavior [13], and thus, is considered to be negligible and is not included into the final model. Nevertheless, some authors found that, in some case, a general trend could be observed in which the vertical shift factor decreases with increasing aging times [11,12]. This decrease of the vertical shift factor with increasing aging times is consistent with the general increase in stiffness

observed in physically aged polymers. Bradshaw and Brinson [12] even proposed that a linear relationship could be observed when representing the vertical shift factor as a function of the logarithm of aging time. However, in the general case where physical aging as well as temperature are considered, the vertical shift factor is assumed to be temperature-dependent only.

The time superposition principle is useful for evaluating the linearly viscoelastic properties of a material in reference conditions over a wide range of decades using limited experimental data. However, when dealing with the nonlinear behavior observed in extreme environment, more general models have to be used. A popular strategy is the development of thermodynamically based models in which the mathematical operator relating the strain and stress tensors meets the principles of thermodynamics, irrespectively of the loading histories [14]. Such a strategy was developed by Biot [15] in the case of linearly viscoelastic materials using the framework of the thermodynamics of irreversible processes. It was then extended to nonlinearly viscoelastic materials by Schapery [16]. In Schapery's theories, nonlinearizing functions were introduced to represent the nonlinear effect of applied strains on the measured stresses [17] and vice-versa [18] but can be easily extended to other parameters such as temperature [19,20]. Those phenomenological theories can be seen as extensions to the superposition principles to complex loading and temperature histories. The horizontal shift factor is replaced by the so-called material clock. Material clocks have been developed for a variety parameters including free volume [21], strains [17], stresses [18] or physical aging [22] or any combination of the formers [23]. More complex material clocks were also developed to take into account the general state of the material by using quantities such as the entropy [24] or the internal energy [25].

A consequent amount of work has already been published on the development of models for the horizontal shift factor as well as for the material clocks, taking into account a variety of parameters. However, development of models for the other nonlinearizing functions, which could be assimilated to vertical shift factors, have mainly been restricted to the inclusion of stress or strain [14,23]. In recent years, some authors have proposed nonlinearizing

functions dependent on the temperature [19,20]. However, to the knowledge of the authors, a model for the nonlinearizing functions dependent on physical aging has yet to be proposed.

In this paper, the mechanical behavior of a polyimide material submitted to elevated temperature is investigated using three-point bending tests. The dependence of the material's viscoelasticity on temperature and physical aging is examined and a model based on Schapery's constitutive theories [16] is developed. To that end, non-linearizing functions dependent on temperature as well as on physical aging are used.

## 2 Background

### 2.1 Physical aging

In engineering, physical aging is the most common kind of aging and is defined as the time-dependence of the material properties at a constant temperature and without any external stimuli, such as loading history or environmental interactions. Therefore, its driving force is generally assumed to be the non-equilibrium thermodynamic state of the material [26].

Physical aging not only has an effect on the volume of the material but also on its mechanical properties. As aging time increased, the material becomes more brittle and stiffer. Furthermore, since physical aging generally goes on during the whole service life of the material, it is imperative to take it into account when designing parts for structural applications.

If a material is assumed to be thermo-rheologically simple, then the impact of physical aging on the mechanical properties can be evaluated by extending the well-known time-temperature superposition principle to physical aging [10]. The mechanical behavior of a material aged for a time  $t_e$  at a isothermal temperature  $T$ , represented by the creep compliance  $S_{t_e, T}$ , can be related to its mechanical behavior when aged for a reference time  $t_{e, \text{ref}}$  at a reference temperature  $T_{\text{ref}}$ , represented by the creep compliance  $S_{t_{e, \text{ref}}, T_{\text{ref}}}$ , using the relationship:

$$S_{t_e, T}(t) = S_{t_{e, \text{ref}}, T_{\text{ref}}} \left( \frac{t}{a_{t_e, T}} \right) \quad (1)$$

where  $a_{t_e, T}$  is the horizontal shift factor. When combining time-temperature and time-aging superposition, the shift factor  $a_{t_e, T}$  can be decomposed into the product of two shift factors, namely the temperature shift factor  $a_T$  and the physical aging shift factor  $a_{t_e}$ .

In his work, Struik [10] proposed that, if a material is aged at an isothermal temperature  $T$  for a time  $t_e$ , then the shift factor  $a_{t_e}$  follows the linear relationship on the log-log scale:

$$a_{t_e}(t_e, T) = \left(\frac{t_{e, \text{ref}}}{t_e}\right)^{\mu(T)} \quad (2)$$

where  $\mu(T)$  is the shift rate and is dependent on the aging temperature.

When dealing with complex temperature histories, physical aging in a material is evaluated using the relative depart from volumetric equilibrium  $\delta$  defined as:

$$\delta(t, T) = \frac{v(t, T) - v_e(T)}{v_e(T)} \quad (3)$$

where  $v$  and  $v_e$  are the instantaneous and equilibrium volumes respectively. When a material is aged, it finds itself in non-equilibrium state characterized by its volume  $v$ . As physical aging is progressing, the volume slowly relaxes towards its equilibrium volume  $v_e$ . This volume relaxation can be modeled using the KAHR model in which the volume relaxation kinetics can be expressed as [26]:

$$\delta(t, T) = \sum_{m=1}^M \delta_m(t, T) \quad (4a)$$

$$\frac{d\delta_m}{dt}(t, T) = -\frac{\Lambda_m \delta_m(t, T)}{a_T a_\delta} \quad (4b)$$

where  $\delta_m$  is the component of the volumetric relaxation associated to the inverted relaxation time  $\Lambda_m$  in the reference state and  $a_\delta$  is the so-called structural shift factors. In the KAHR model, the shift factors are defined using the relationships:

$$a_T = \exp[-\theta_T(T - T_{\text{ref}})] \quad (5a)$$

$$a_\delta = \exp[-\theta_\delta \delta(t, T)] \quad (5b)$$

where  $\theta_T$  and  $\theta_\delta$  are adjustable parameters.

The KAHR model was adapted to the problem of physical aging by assuming that a linear relationship exists between the logarithm of the aging shift factor  $a_{t_e}$  and  $\delta$  [7,27]. In this new KAHR- $a_{t_e}$  model, the aging shift factor is expressed as:

$$\frac{1}{a_{t_e}(t, T)} = \left(\frac{c_0}{a_{\delta, T} a_\delta(t, T)}\right)^{c_1} \quad (6)$$

where  $c_0$  and  $c_1$  are adjustable parameters determined at the reference temperature.  $a_{\delta, T}$  is used to scale the shift factor  $a_\delta$  at a reference aging time from the current temperature to the reference temperature and is defined as:

$$a_{\delta, T} = \frac{a_\delta(t_{e, \text{ref}}, T_{\text{ref}})}{a_\delta(t_{e, \text{ref}}, T)} \quad (7)$$

Models such as the KAHR- $a_{t_e}$  models assumed that the viscoelastic behavior of a material in any service conditions can be obtained from the properties of the material in reference conditions using appropriate horizontal shift factors. However, in some cases, use of a vertical shift factor  $b_{t_e}$  can be necessary in order to obtain good master curves [11,12]. This lead to the following modification to Equation (1):

$$S_{t_e, T}(t) = b_{t_e, T} S_{t_e, \text{ref}, T_{\text{ref}}}\left(\frac{t}{a_{t_e, T}}\right) \quad (8)$$

## 2.2 Schapery's constitutive theories

When dealing with complex loading and temperature histories, more general models have to be used to represent the material behavior. One such model is the constitutive theory developed by Schapery [16] to predict nonlinearly viscoelastic behavior. This theory, based upon the thermodynamics of irreversible processes, has been developed in a number of papers over the last forty years and is best known in its unidirectional stress-based hereditary integral form [28]:

$$\varepsilon = g_0 S_0 \sigma + g_1 \int_0^\xi \Delta S (\xi - \xi') \frac{dg_2 \sigma}{d\xi'} d\xi' \quad (9)$$

where  $S_0$  and  $\Delta S$  are the instantaneous and transient compliance, respectively. In this case,  $\Delta S$  is expressed as a Prony series:

$$\Delta S = \sum_{n=1}^N S_n [1 - \exp(-\lambda_n t)] \quad (10)$$

where  $S_n$  is the component of the material's compliance associated to the inverted retardation time  $\lambda_n$ .

$\xi$  is the material clock and is a generalization of the horizontal shift factor to complex histories, leading to:

$$\xi = \int_0^t \frac{d\tau}{a_{t_e, T}(\tau)} \quad (11)$$

$g_0$ ,  $g_1$  and  $g_2$  are nonlinearizing functions introduced to represent the nonlinearly viscoelastic behavior of polymers in extreme conditions. Those functions could be considered as generalization of the vertical shift factor  $b_{t_e}$ . A lot of works in the literature have concentrated on the development of stress-dependent nonlinearizing functions [14,23]. For example, Schapery [22] considered the non-linearizing functions to be quadratic functions of stress. Lai and Bakker [23] proposed that  $g_0$  should be dependent of the first stress invariant while  $g_1$  and  $g_2$  would be dependent on the effective octahedral shear stress.

Sawant and Muliana [19] proposed temperature dependent nonlinearizing functions by assuming that function  $g_0$  was a linear function of the temperature while  $g_1$  and  $g_2$  were exponential functions of the temperature. Muliana and Sawant [20] assumed that all three functions were polynomial functions of temperature.

### 3 Experimental

#### 3.1 Material

The material studied is a polyimide matrix formulated for high temperature applications. All samples used for testing were cut from a 12.7cm

thick panel using a high precision low speed saw equipped with a diamond wafering blade. In compliance with ASTM D2990 standard, sample dimensions of 12.7mm in width, 3.18mm in thickness and 70mm in length were used.

The material's dry glass transition temperature,  $T_g$ , was investigated using a Dynamic Mechanical Analyzer (DMA) TA Q800, following the procedure proposed in FAA Regulation No DOT/FAA/AR-00/47 (Material Qualification and Equivalency for Polymer Matrix Composite Material Systems), which means using a testing frequency of 1Hz and a heating rate of  $5^\circ\text{C}.\text{min}^{-1}$ . For aerospace application, the glass transition temperature is defined as the onset of storage modulus which is determined by the intersection of the two slopes from the storage modulus on a logarithmic scale. This temperature was then used to determine the aging temperatures for the following aging tests.

#### 3.2 Three-point bending testing at elevated temperatures

The polymer's mechanical properties were investigated using three-point bending tests conducted on an MTS Insight 50kN electromechanical load frame equipped with a Lab-Temp LBO-series box environmental chamber from Thermcraft Inc.

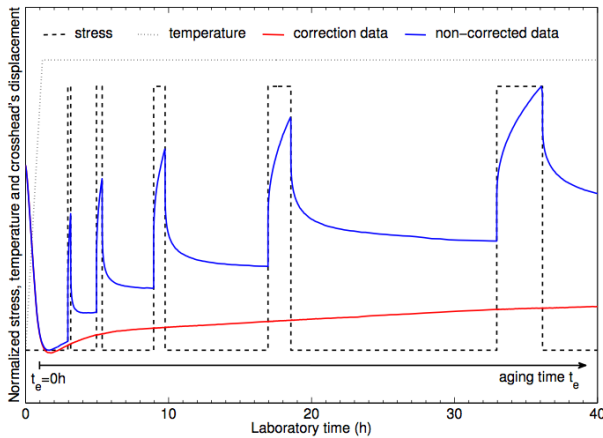
The mechanical tests were performed using a homemade three-point bending fixture, designed in compliance with ASTM D790 and ASTM D2990 standards for flexural properties of unreinforced plastics and flexural creep of plastics, respectively. The loading nose of the fixture was mounted on a 1kN crosshead which was controlled using MTS TestWorks 4 software. Using such a small crosshead allowed for an increased accuracy when measuring the applied load ( $\pm 0.1\text{N}$ ) and the displacement of the loading nose ( $\pm 0.01\text{mm}$ ). Temperature control was achieved by setting the temperature in the air surrounding the sample with the thermal controller while monitoring the specimen temperature with a thermocouple. The maximum deflection at the middle of the beam was directly obtained from the crosshead's displacement.

In order to measure the dependence of the polymer's mechanical properties to temperature and physical aging, series of creep tests were performed at various temperatures using the methodology proposed by Struik [10] for short-term isothermal aging tests. To that end, the material was first heated to the testing temperature and then a series of creep and recovery tests were performed at increasing intervals, with the duration of each creep tests equal to 10% of the total aging time as shown in Fig. 1.

The first creep test began two hours after the aging temperature is reached. Subsequent creep and recovery tests began after 4h, 8h, 16h and 32h respectively.

In order for physical aging effects to be measurable on the lab-time scale (approximately 48 hours), testing temperatures were chosen slightly below the glass transition temperature, namely,  $T_{ref} = T_g - 15^\circ\text{C}$ ,  $T_{ref} = T_g - 30^\circ\text{C}$ ,  $T_{ref} = T_g - 45^\circ\text{C}$ ,  $T_{ref} = T_g - 55^\circ\text{C}$  and  $T_{ref} = T_g - 80^\circ\text{C}$ . Also, when using three-point bending tests to evaluate the mechanical properties, it is important to keep inside the limits of linear viscoelasticity. Therefore, the tests were performed at a creep level of 10MPa.

Since testing was performed at elevated temperature inside an environmental chamber, it was necessary

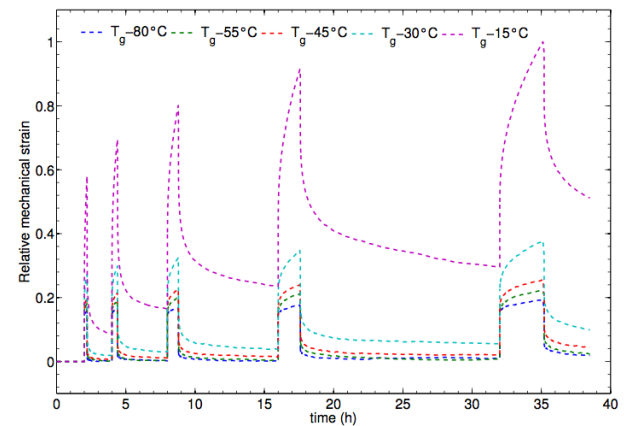


**Fig. 1:** Temperature and loading histories applied to the sample during a test. The data in blue represent the crosshead's displacement for a combined stress and temperature history. The data in red represents the crosshead's displacement for temperature history only. Subtracting the red data from the blue data allows for the evaluation of the crosshead's displacement due to the mechanical strain.

to evaluate the effect of temperature on the whole setup during testing in order to be able to separate the beam's deflection due to thermal effects and the deflection due to mechanical behavior. To that end, correction tests were performed at each testing temperature by submitting a sample to a small contact load of 1N. Data from one such correction test can be found in Fig. 1. It shows that the initial increase in temperature is accompanied by an overall thermal expansion of the setup. Then, shortly after the test temperature is achieved, the beam's deflection reached a maximum before decreasing. This decrease in the deflection can be explained by a contraction of the polymer sample due to physical aging. Finally, the beam's deflection due to the mechanical behavior is obtained by subtracting the correction data from the creep and recovery data, leading to displacement data such as presented in Fig. 2. From this data, it can be seen that increasing the test temperature leads to a much more compliant material. Furthermore, the creep and recovery times are increased as demonstrated by the fact that, at higher temperatures, the material does not fully recover between two creep tests.

#### 4 Model development

The aim of this work is to propose a model capable of predicting the viscoelastic behavior of the material under various temperature and physical aging histories.



**Fig. 2:** Corrected creep and recovery data for the five test temperatures. Increasing the test temperature leads to a much more compliant material. Furthermore, at higher temperatures, the material does not fully recover between two creep tests.

Since a lot of previous work has been done on the development of horizontal shift factors and material clock, the main subject of this work is the development of the nonlinearizing functions  $g_0$ ,  $g_1$  and  $g_2$  taking into account temperature and physical aging.

The temperature dependence of the nonlinearizing functions is introduced using the *arctangent* function instead of the exponential or polymeric functions often used. The main advantage of this function is that it is bounded for arguments converging towards  $\pm\infty$  while also exhibiting a monotonic behavior. Therefore, the temperature-dependent nonlinearizing functions can be written:

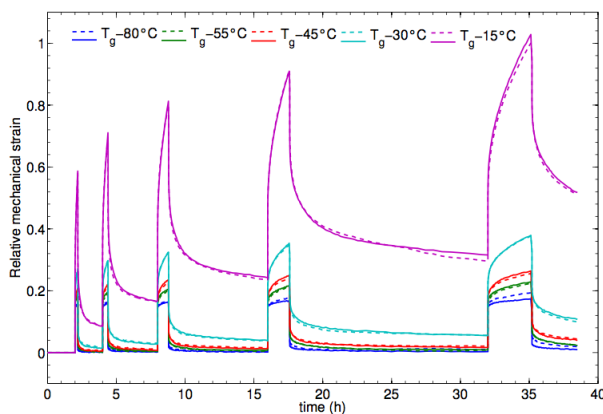
$$g_{iT} = 1 + \alpha_i \text{atan}[\beta_i(T - T_{\text{ref}})] \quad (12)$$

where  $\alpha_i$  and  $\beta_i$  are adjustable parameters and  $0 \leq \alpha_i \leq 1$ .

In their work, Bradshaw and Brinson [12] proposed a linear relationship between the vertical shift factor  $b_{t_e}$  and the logarithm of aging time when considering isothermal aging:

$$b_{t_e} = 1 + \gamma \log\left(\frac{t_e}{t_{e,\text{ref}}}\right) \quad (13)$$

where  $\gamma$  is an adjustable parameter. Using Equations (2), (5b) and (6), it can be shown that Equation (12) is similar to assuming a linear relationship between



**Fig. 3:** Experimental data (dashed lines) and model's predictions (continuous lines) for the five test temperatures. The model leads to a very good fit of the experimental data.

$b_{t_e}$  and  $\delta$ . Therefore, assuming that all nonlinearizing functions follow the same relationship with aging leads to:

$$g_{i_{t_e}}(t, T) = 1 + \gamma_i(T)\delta(t, T) \quad (14)$$

where  $\gamma_i(T)$  are an adjustable parameters dependent on temperature.

Finally, the temperature- and physical aging-dependent nonlinearizing functions are obtained by multiplying the functions proposed in Equations (12) and (13):

$$g_i(t, T) = g_{iT}(t, T)g_{i_{t_e}}(t, T) \quad (15)$$

## 5 Results analysis

The experimental data obtained from the series of creep and recovery tests performed at various temperatures is used to obtain the set of material's parameters necessary for the model proposed in Section 4.

### 5.1 Optimization of the material's parameters

The optimization of the material's parameters has been performed using the multi-objective minimization algorithm *fminimax* from the software Matlab's optimization toolbox. The optimization problem solved by this function can be written as:

$$\min_x \max_i \left( \frac{\sum_{j=1}^{N_i} [F_{i,j} - f_{i,j}(x)]^2}{\sum_{j=1}^{N_i} F_{i,j}^2} \right) \quad (16)$$

where  $F_{i,j}$  and  $f_{i,j}$  are the numerical and predicted values for the  $j^{\text{th}}$  datapoint from the  $i^{\text{th}}$  data-set, respectively.  $N_i$  is the number of datapoint for the  $i^{\text{th}}$  data-set and  $x$  is the set of material's parameters to optimized. The function *fminimax* optimizes the material's parameters by minimizing the worst-case scenario  $i$ .

The optimization of the material's parameters is performed using all the experimental data presented in Fig. 2, simultaneously.

### 5.2 The set of material's parameters

The set of material's parameters to optimize includes the viscoelastic properties  $S_0$ ,  $S_n$  and  $\lambda_n$  in reference

conditions. The reference conditions in this case are  $T_{\text{ref}} = T_g - 15^\circ\text{C}$  for the temperature and  $\delta_{\text{ref}}(t = \infty, T_{\text{ref}}) = 0$  for the physical aging. The number of inverted retardation times  $\lambda_n$  is fixed to one by decade from  $\lambda_n = 10^{-4}\text{s}^{-1}$  up to  $\lambda_n = 10^7\text{s}^{-1}$ .

The horizontal shift factor is modeled using the KAHR- $a_{\text{te}}$  model as recalled in Equation (3) to (7). In this work, the kinetic Equation (4) is solved using a 4<sup>th</sup> order Runge-Kutta scheme. The initial value is chosen to be:

$$\delta(0, T) = \sum_{m=1}^M \delta_m(0, T) = \alpha_g(T - T_0) \quad (17)$$

where  $\alpha_g$  is the glassy coefficient of thermal expansion and  $T_0$  is the initial or storage temperature. The inverted relaxation times  $\Lambda_m$  are chosen similarly to the inverted retardation times  $\lambda_n$ . Thus, the parameters necessary for the horizontal shift factor are  $\theta_T$ ,  $\theta_\delta$ ,  $c_0$ ,  $c_1$ ,  $\alpha_g$  and  $\delta_m$ .

The vertical shift factors used are the ones proposed in Equations (12), (14) and (15). In order to use them,  $\alpha_i$ ,  $\beta_i$  and  $\gamma_i$  for  $i \in \{0, 1, 2\}$  must be computed.

### 5.3 Model's prediction

Experimental data and model predictions are presented in Fig. 3.

The model is able to represent the viscoelastic

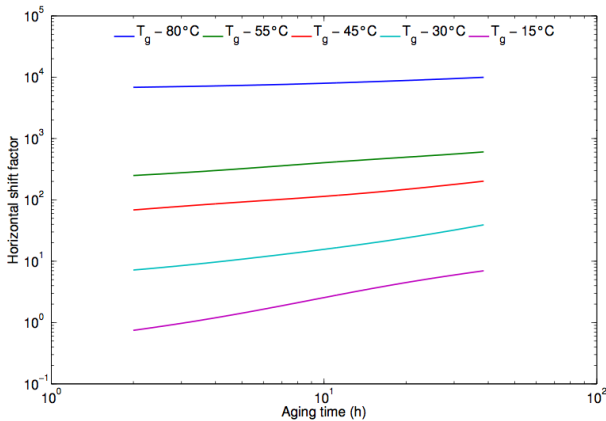


Fig. 4: Evolution of the horizontal shift factor with respect to aging temperature and physical aging time. Increasing temperature leads to a decrease of the absolute value of the shift factor while, increasing aging time leads to an increasing shift factor.

behavior of the material with great accuracy for all temperatures considered.

The evolution of the horizontal shift factor with respect to temperature and physical aging is represented in Fig. 4. It can be seen that an increase in the aging temperature leads to a decrease of the overall value of the shift factor, i.e. the material becomes more compliant, and an increase in its slope, which means that as temperature increase, physical aging has more and more importance. Furthermore, the slope is positive, thus increasing aging time leads to a stiffer material.

The dependence of the nonlinearizing functions to physical aging at the reference temperature is represented in Fig. 5. It can be seen that the absolute values of the nonlinearizing functions decrease with increasing aging time, which, once again, means that increasing aging times leads to a stiffer material. During the 40 hour-test, the absolute values for the nonlinearizing functions decrease by about 3% for  $g_0$  and by about 0.5% for  $g_1$  and  $g_2$ . Compared to the absolute values for a fully aged material, the nonlinearizing functions at the beginning of the test are about 6% higher for  $g_0$  and about 1% higher for  $g_1$  and  $g_2$ . A decrease of 6% of  $g_0$  between an unaged and a fully aged material means that the instantaneous compliance modulus decreases by 6% during the service life of the material, which is non-negligible and must be taken into account when designing parts. On the other hand, the dependence

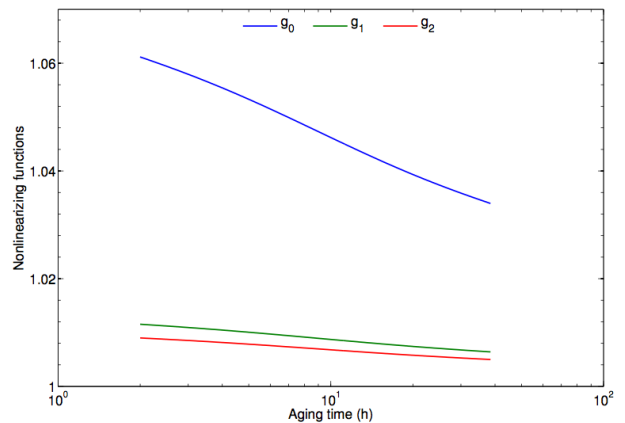


Fig. 5: Evolution of the nonlinearizing functions at the reference temperature with respect to aging time. The slopes are negative which means that the material becomes stiffer as aging time increases. The function  $g_0$  seems to have more importance than the other two.



of  $g_1$  and  $g_2$  to physical aging seems much less important. 1% is not much of an impact. However, when using creep and recovery tests, it can be difficult to separate the nonlinearizing functions  $g_1$  and  $g_2$  and the material clock. Since the material clock is much more dependent to physical aging than the nonlinearizing functions, the dependence of those functions to physical aging is difficult to evaluate.

## 6 Conclusion

In this work, nonlinearizing functions for the well-known Schapery hereditary integral, dependent on temperature as well as on physical aging have been proposed.

The set of model's parameters have been obtained using Matlab's *fminimax* optimization function and experimental data obtained from series of creep and recovery data at various temperatures.

The model's capacity to represent the experimental data has been evaluated and was shown to be very good.

At the reference temperature, just below the glass transition temperature, the nonlinearizing function  $g_0$  was shown to have a non-negligible dependence to physical aging. However, for the other two nonlinearizing functions,  $g_1$  and  $g_2$ , this dependence is not as clear-cut.

The results presented in this paper shows that when designing parts using polyimide matrix for high temperature structural applications, nonlinearizing functions dependent on physical aging as well as an horizontal shift factor are needed to take into account the effects of physical aging on the viscoelastic properties of the material over its service life.

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