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Phenomenological models for the isothermal physical aging of PEEK

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Abstract

Creep test is a useful tool to study thermal aging and deformation mechanisms of semi-crystalline polymers, such as polyether-ether-ketone (PEEK). Hou and Chen proposed a power law to fit creep data of PEEK aged at different temperatures and the master curve built from those data. This paper attempts to complement that analysis by introducing Kohlrausch function as an alternative to the fractional Maxwell's model associated to the power law. Although the fitting of experimental data and the mathematical conditions imposed to equations that describe curves that can be superimposed by translations, are obeyed by both models, this paper demonstrates that Kohlrausch function provides a better phenomenological description of the creep response of PEEK due to the physical interpretation of the fitting parameters and their dependence on the aging time and temperature.

Keywords: Mechanical engineering, Materials science

1. Introduction

Prediction of thermomechanical aging is extremely important to establish life management criteria [1, 2]. Since the viscoelastic behavior of materials is very sensitive to structural changes, mechanical tests have been widely used to predict aging effects on materials, particularly those made of semi-crystalline polymers [3].

Typically, aging is accelerated at the lab by changing environmental conditions or the initial state of the sample, in such a way that the measured property evolves in less time than on service. For example, if the mechanical behavior of a material is accelerated by the environmental temperature, then accelerated tests will consist of subjecting specimens to temperatures greater than that on service prior to and along the mechanical test; this is known as accelerated isothermal aging [3].

Building up a master curve by horizontal shifts of experimental creep data measured as a function of time at different temperatures, allows to extrapolate the creep behavior to larger (un-experienced) times [3, 4]. However, this master curve can be built if and only if the deformation mechanisms are the same along the whole temperature range of the measured creep data. In fact, it is worthwhile to point out that although accelerated tests are often employed, it is still under discussion whether the sum of the aging effects of each variable at a time —i.e. temperature, irradiation dose rate, aging time, etc.— is enough to reproduce an aging processes where several variables changes simultaneously [1, 5, 6, 7, 8, 9, 10].

Individual and master creep curves have been described in terms of mathematical models with easily manageable parameters. These mathematical models emulate the effect of a distribution of relaxation times without containing such a distribution explicitly; they are essentially empirical curve-fitting equations. One of first fitting models was proposed by Kohlrausch in 1863 to fit the exponential increase of the creep compliance of glass fibers [11]. Since then the model —sometimes referred as Williams-Watts equation, Kohlrausch-Williams-Watts equation (KWW) or stretched exponential— has been applied to plenty of materials [11, 12].

Particularly, Guo and Bradshaw [13] used this equation to get the characteristic relaxation time of creep of poly-ether-ether-ketone (PEEK) —an aromatic polymer widely used due to its excellent performance— at different temperatures in order to build a master curve using the time-temperature superposition principle [14]. However, Hou and Chen [4] applied another empirical model, called *power law*, to fit those data. Although the fitting parameters of the power law were calculated for the different aging times and temperatures, no physical interpretation was given to them [15, 16, 17].

Therefore, the first goal of this work is to fit the creep data of PEEK by the three parameters of the Kohlrausch equation in order to highlight the physical meaning of these parameters and their dependence on temperature and aging times. This

analysis will remark the changes of the deformation mechanisms along the glass transition of PEEK. The second goal is to determine the relationship among the parameters for both the power law and the Kohlrausch equation in order to verify whether they fulfill the mathematical conditions of curves that can be translated to build up a master curve.

2. Experimental

The adjustments and interpretation of the results presented here correspond to creep data of PEEK measured by Guo and Bradshaw [13].

2.1. Material

The material used in the study was 0.0762 mm (3 mils) thick PEEK film (Victrex® PEEK 15G) supplied by GE Advanced Materials. The reported glass transition temperatures of this material is 143 °C.

2.2. Test equipment

Creep tests were performed using a TA Instruments RSA3 Dynamic Mechanical Analyzer (DMA). The RSA3 DMA provides exceptional control of temperature, load and displacement during the creep tests.

2.3. Testing temperatures

All tests were performed at temperatures approximately 15−35 °C below T_g. These values are such that changes in physical aging can be measured within a lab time scale suitable for this study (each test lasting 24−48 hours). The test temperatures used here 110 °C, 120 °C and 130 °C ($T_g = 143.5$ °C).

2.4. Stress level

Description of the mechanical behavior has been based upon linear viscoelasticity. In this case, the stress/strain response of the material under a general load history can be obtained by superposing the response of the material to a series of individual load steps via the Boltzmann superposition principle (Tschoegl 1989).

Before exploring the effects of physical aging on the creep/stress relaxation properties, determination of the maximum stress level for creep tests in the linear viscoelastic range was established. Each specimen was repeatedly rejuvenated, quenched to the desired temperature and tested at an aging time of 5/16 hours at increasingly higher stress/strain levels. The transition from linear to nonlinear

behavior is evident when the stress/strain level is such that significant changes in compliance is observed.

Using the approach above, the linear viscoelastic range was determined at 110 °C, 120 °C and 130 °C for PEEK. All creep tests were performed at stress/strain levels known to be in the linear viscoelastic range [13].

2.5. Isothermal aging test method [13]

The isothermal aging tests were carried out in uniaxial extension following the procedure established by Struik (1978). All isothermal physical aging were short-term, with the ratio of loading time to aging time $t/t_e \leq 0,1$.

Displacement was controlled/monitored by the suitable test module using the motor and transducer of RSA3 DMA. The convection oven is designed for rigorous temperature control; temperature stability was found to be within ± 0.1 °C.

The specimen is rejuvenated to erase past aging effects as described previously. The specimen is then quenched to the desired aging temperature.

The aging clock begins ($t_e = 0$) when the specimen first reaches the desired aging temperature. In general, it took 15−35 s after beginning the quench for the PEEK to reach temperature, respectively. In the first 3 minutes after $t_e = 0$, the temperature changed 0.5−1 °C and remained within ± 0.1 °C thereafter.

In the sequenced tests, the aging time (t_e) at each load point was 5/16, 5/8, 5/4, 5/2, 5, 10 and 20 h.

3. Results

Previous to the tests PEEK samples were aged isothermally at different temperatures (110, 120 and 130 °C) and aging times (t_e = 5/16, 5/8, 5/4, 5/2, 5, 10 and 20 h). They measured both creep and stress relaxation at each aging condition and built up master curves for both quasi-static mechanical tests in order to verify the interconversion of the viscoelastic material functions, according to the theory of linear viscoelasticity [18].

Guo and Bradshaw used Kohlrausch function to calculate the characteristic retardation times of the segments of curves measured at each aging time; then they determined the horizontal shifts according to the differences in the corresponding retardation times.

Kohlrausch's equation can be written as

$$J(t) = J_0 \cdot e^{\left(\frac{t}{\tau}\right)^{\gamma}} \tag{1}$$

being,

J_0: initial compliance [Pa^{-1}].

γ: Kohlrausch's coefficient [17].

τ: characteristic retardation time [s].

However, Guo and Bradshaw did not determine J_0 and γ for each aging time but directly for the master curve. So, the first step to correlate the fitting parameters to the aging time and temperature was to calculate the whole set of parameters that fit the creep data measured by Guo and Bradshaw; they are summarized in Table 1. Fig. 1 show the excellent fit of Eq. (1) to the individual creep curves measured at 110, 120 and 130 °C, using the tabulated parameters.

4. Discussion

4.1. Deformation mechanisms

Hou and Chen achieved a good fit of the individual creep curves measured at different aging times and temperatures using a four-parameter equation. This equation corresponds to two fractional Maxwell's models [4]. Although a physical interpretation has been proposed in the literature for the fractional model [15, 16], Hou

Table 1. Parameters of Kohlrausch function for the indicating aging time (t_e) and aging temperature (T).

| T (°C)	t_e (h)	$\log J_0$ (Pa^{-1})	$\log\tau$ (s)	γ
110	0,3125	−9,26	3,32	0,41
	0,625	−9,27	3,67	0,42
	1,25	−9,27	3,93	0,43
	2,5	−9,26	4,15	0,47
	5	−9,26	4,6	0,41
	10	−9,26	4,74	0,49
	20	−9,26	5,04	0,47
Mean		−9,26 ± 0,01		0,44 ± 0,03
120	0,3125	−9,31	3,18	0,41
	0,625	−9,3	3,4	0,47
	1,25	−9,3	3,7	0,45
	2,5	−9,29	3,83	0,51
	5	−9,3	4,27	0,49
	10	−9,3	4,56	0,5
	20	−9,3	4,96	0,47
Mean		−9,3 ± 0,01		0,47 ± 0,03
130	0,3125	−9,3	2,56	0,47
	0,625	−9,31	2,78	0,46
	1,25	−9,31	3,02	0,49
	2,5	−9,3	3,26	0,52
	5	−9,29	3,47	0,55
	10	−9,29	3,68	0,53
	20	−9,3	3,89	0,53
Mean		−9,3 ± 0,01		0,51 ± 0,03
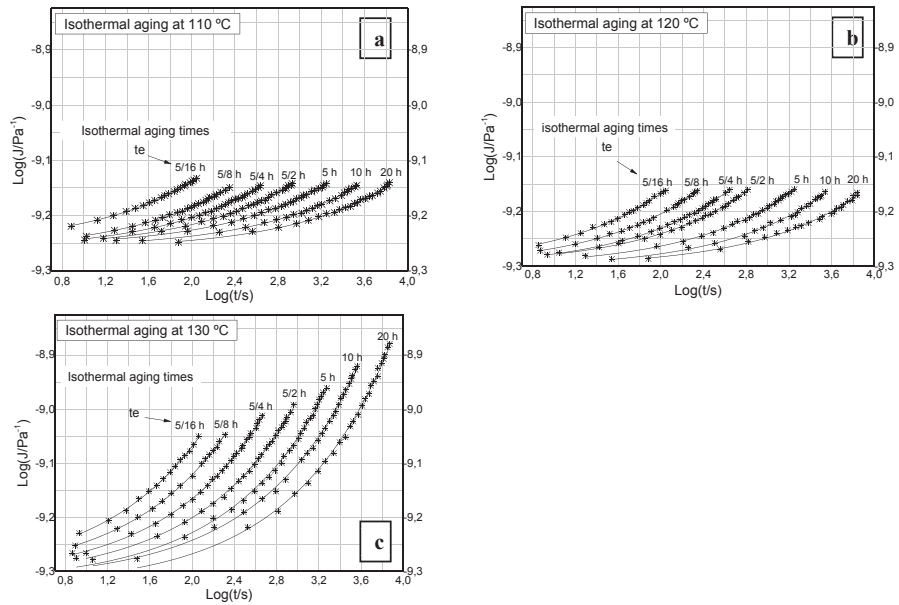
Fig. 1. Creep data for PEEK [4] fitted by Eq. (1) for isothermal aging at: 110 °C (a), 120 °C (b) and 130 °C (c); the proper fit is remarkable.

and Chen did not discuss what two different morphological aspects or what two different deformation mechanisms activates along the creep response of PEEK.

On the other hand, as shown in Fig. 1, three parameters are enough to achieve a very good fit of the individual creep curves for each isothermal aging and temperature. The three parameters are: the initial adaptability (J_0), the average retardation time (t) and Kohlrausch coefficient (γ), whose physical interpretations are detailed below.

J_0 is associated with the elastic system response since it is inversely proportional to the module not relaxed tensile, which describes the stiffness of the material. From Table 1 it comes straightforward that J_0 does not depend on the aging time at least within the experimental error used to measure J. So, a J_0 average is deemed for each temperature, as shown in Table 1.

τ is the characteristic retardation time associated to the deformation mechanism acting during the creep test. Fig. 2 shows, in a double log plot, how this time increases as the isothermal aging time increases. A linear regression fits quite well the experimental data, that is, this allows to set the decay time τ for PEEK sample aged for a time t_e, as,

$$\tau(t_e) = \tau_0 \left(\frac{t_e}{t_r}\right)^{\xi} \tag{2}$$

where τ_0 is the reference retardation time for an aging time t_r and ξ is the slope. Table 2 summarizes the values of τ_0 and ξ for each aging temperature. Struik
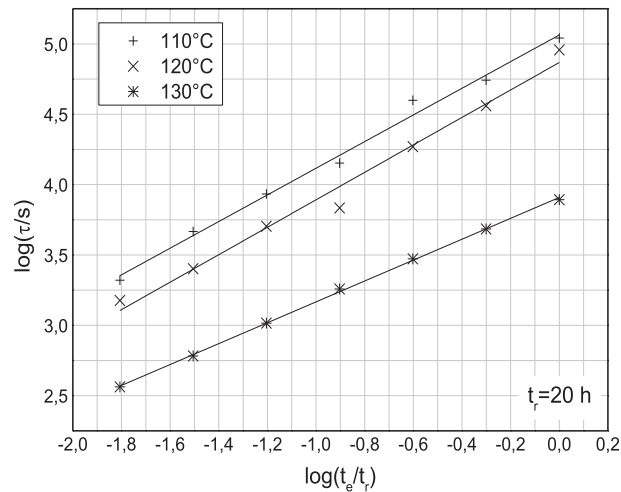
Fig. 2. Dependence of the average retardation time with the aging time, at each temperature of isothermal aging.

has studied this empirical relationship —using μ instead of ξ in [8], in his well-known paper about mechanical and physical aging of semicrystalline polymers. In his analysis of creep data of several polymers he verified that $\xi = 1$ at $T < T_g$ while decreases to 0 as the amorphous region becomes more mobile with the increase in temperature.

From Table 2, it is shown that between 110 and 120 °C the thermal dependence characterized by the same deformation mechanism ($\xi \approx 1$). In contrast, at 130 °C ξ reduces to 0,74 which makes it plausible that the creep is due to another deformation process. Indeed, the behavior of the observed PEEK at 110 and 120 °C responds to the region 1 ($T < T_g$) pointed out by Struik while changes to region 2 ($T \sim T_g$) for 130 °C; that is, the change of deformation mechanisms imply that amorphous areas in vitreous state acquire mobility [6]. Furthermore, the difference in the deformation mechanism of PEEK, when aging temperature approximates the T_g, was observed for Ogale Mc Cullough, who determined that the PEEK shows a reduction of the parameter ξ practically from 1 to around 0,7 when T_g-T <25 °C [19].

Finally, γ is associated with the dispersion of retardation times; $0 < \gamma < 1$ and $\gamma = 1$ for a single characteristic time [20]. This parameter remains practically independent

Table 2. Values of the parameters in Eq. (2), for $t_e = 20$ h.

T (°C)	log (τ_0)	ξ
110	5,0	0,95
120	4,9	0,98
130	3,9	0,74

not only of the aging time but also of the aging temperature, with one relative error of less than 7% ($\gamma = 0{,}47 \pm 0{,}04$).

4.2. Translation of creep curves for different ageing times

As Guo and Bradshaw showed in their work it is possible to build up a master curve at a given temperature, using horizontal translations of the creep curves at different aging times.

Povolo and Fontelos [21] stated the mathematical conditions of the functions y(x) parameterized in a variable z (or a function h (z)), which guarantee the construction of a master curve. According to them, x, y and h (z) must be related through the implicit function:

$$F(y - \mu.x, x - \beta.\mathrm{h}(z)) = 0 \tag{3}$$

where μ and β are the slopes of translation paths of the curves in the planes: y-x and x-h(z), respectively.

That is, since the creep curves of PEEK aged at different times allow to build up a master curve, the expression used to adjust them should be able to be rewritten as the implicit function —eq. (3).

The expression proposed by Hou and Chen, that is,

$$J(t) = \frac{(t/\tau)^{\alpha}}{E.\Gamma(1+\alpha)} + \frac{(t/\tau)^{\beta}}{E.\Gamma(1+\beta)} \tag{4}$$

can be rewritten as

$$\log(\mathrm{J}(t)) - \log\left[\frac{10^{\alpha.(\log t - \log\tau(te))}}{E.\Gamma(1+\alpha)} + \frac{10^{\beta.(\log t - \log\tau(te))}}{E.\Gamma(1+\beta)}\right] = 0 \tag{5}$$

On considering the change of variables

$y = \log(J(t))$
$x = \log(t)$
$z = te$
$\mathrm{h}(z) = \log\tau(te)$

Eq. (5) has the form of the Eq. (3) with $\mu = 0$ and $\beta = 1$ if and only if E, α and β does not depend on the aging time. This condition is fulfilled, according to what is recorded in Table 1 of the work of Hou and Chen. In spite of this, they perform the translation taking as variable y = log (J * E), which does not modify the previous analysis, taking into account that E does not depend on the time of aging.

Similarly, for Eq. (1), the same change of variables leads to the implicit function:

$$\log(J(t)) - \log(J_0) - 10^{\gamma(\log t - \log \tau(te))}\log(e) = 0 \tag{6}$$

that takes the form of the Eq. (3) with $\mu = 0$ and $\beta = 1$ if and only if J_0 and γ do not depend on the aging time. Table 1 shows that this condition is also fulfilled.

That is, both the mathematical model used by Hou and Chen and that given by Eq. (1) allow to adjust the experimental data by using analytic expression representing the horizontal translation established graphically. In this way, a master curve of creep up to a time of 10^5 s = 27,7 h is achieved.

One of the most relevant characteristics of a family of translation curves is the ability to predict the response in the x-y plane when the parameter z is varied. As an example, from the creep data at 110 °C of a sample aged only 5/16 h, we can predict the creep response for an aging $t_e = 20$ h.

Since $\Delta\log(t_e) = \log(20)-\log(5/16)$, then from Eq. (2) and considering that $\log\tau(5/16$ h$) = 3,32$ then we get, $\log\tau(20$ h$) = 5,04$. Finally, the predicted creep curve is given by:

$$\log J(20h) = -9,26 + 0,4343.10^{0,47.(\log t - 5,04)} \tag{7}$$

This function, represented by the line of Fig. 3, provides an excellent fitting to the measured data.

Struik has dedicated several contributions [6, 7, 8, 9] to point out that the extrapolation of results using horizontal translations is only valid while the same deformation mechanism is active. The most significant corollary is that the extrapolated test time should not exceed the isothermal aging time [8]. In the example considered the aging time was 20 h while the duration of the creep test reached 3 hours.
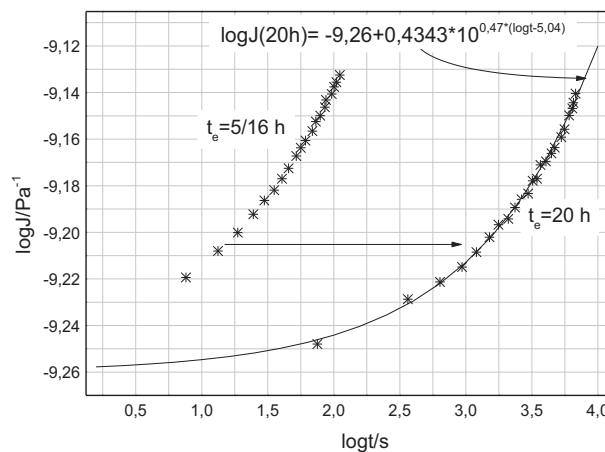

Fig. 3. Prediction of the creep curve at $t_e = 20$ h from creep data after an isothermal aging $t_e = 5/16$ h.

It should be noted that the abscissa, log (t/τ), of the representation log (J*E) *vs.* log (t/τ) used by Hou *et al.* [4] makes it difficult to determine the range time of the master curve and does not allow to predict the creep values for other aging times, since the functional dependence neither of E nor τ with aging time is expressed.

4.3. Translation of the curves for different temperatures creep

Hou and Chen adopted log (J*E) as a variable for the y-axis; in this way, they removed any mismatch due to the dependence of E with temperature. Similarly, this work considers the representation log (J/J$_0$) for the y-axis.

The analysis of the conditions to be fulfilled to make a master curve from individual curves can be also applied to the creep curves measured at different temperatures. It is enough to consider z = T and y = log (J*E) or log (J/J$_0$) as appropriate.

Curves can be shifted horizontally only if α and β (fractional model) or γ (Kohlrausch function) do not depend on the temperature. As Table 1 of [4] and Table 1 of this work show that α, β and γ, respectively, are independent of temperature, then the measured curves at different temperatures can be horizontally shifted to generate a master curve, according to the time-temperature superposition principle [22]. That is, the master curves built by superposition of measured data at different ageing times at a certain temperature, can be superposed by horizontal shifts onto one master curve built at a reference temperature, T$_r$.

The temperature dependence of the retardation time, τ, is depicted in Fig. 4. The linear regression clearly demonstrates that the data cannot be adjusted by a straight line, *i.e.* the Arrhenius law is not obeyed. This feature has been noticed by Achereiner *et al.* [3] for several semicrystalline polymers below the melting temperature
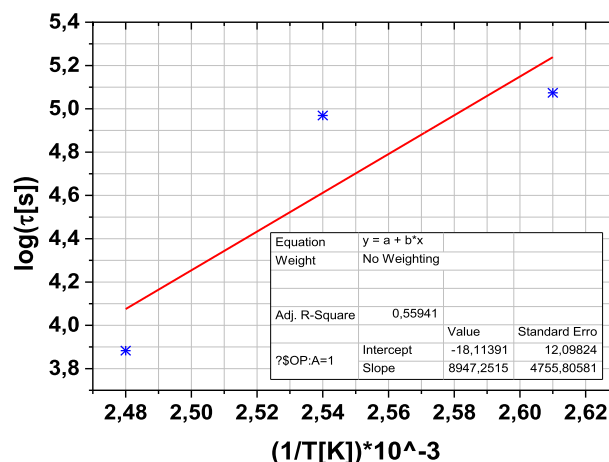

Equation	y = a + b*x	
Weight	No Weighting	
Adj. R-Square	0,55941	
	Value	Standard Erro
	Intercept	-18,11391	12,09824
?$OP:A=1	Slope	8947,2515	4755,80581

Fig. 4. Dependence of the average retardation time with the aging temperature. Arrhenius law is not valid.
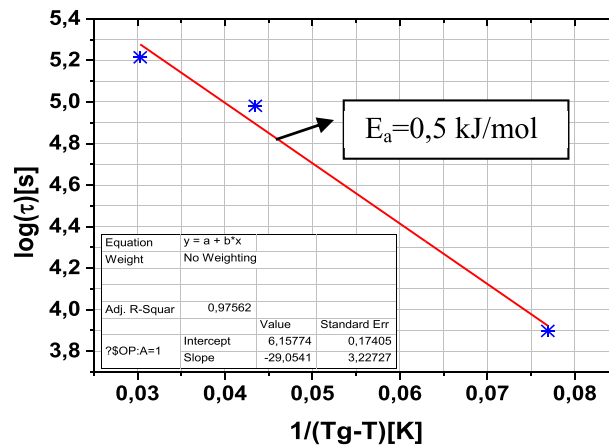
Fig. 5. Activation energy from the linear fitting using VFTH equation.

and by Alves *et al.* for another aromatic polymer: polyethylene terephthalate (PET) [23]. This behavior is attributed to the typical profile of relaxation times in the glass transition region, where the temperature dependence cannot be described by a single activation process.

Although the Vogel-Fulcher-Tamman-Hesse equation (VFTH)

$$\tau = \tau_o e^{\frac{E_a}{k(T-T_o)}} \tag{8}$$

has been employed to describe the temperature dependence of relaxation times for temperatures greater than the glass transition temperature, since at 130 °C $\xi < 1$, it is worthwhile to check whether VFTH equation is valid. As illustrated in Fig. 5, the lineal fitting of the three data points agree with this equation, however, the value of the activation energy, E_a, is not according to those for semicrystalline polymers [3, 24]. Therefore, there is no a single temperature dependence of τ; this agrees with the change in ξ values along the temperature range (see Table 2), where PEEK chains in the amorphous region are increasing their mobility.

5. Conclusions

This work presented a comparison between two phenomenological expressions used to describe creep data of PEEK measured at different aging times and temperatures: the power law associated to the fractional model and Kohlrausch function.

Both equations properly fit the data, however, in clear contrast with the parameters of the fractional model, the parameters of Kohlrausch expression: J_0, τ and γ are directly related to physical parameters of the deformation mechanisms. In fact, J_0 quantifies the elastic response, τ is the characteristic retardation time of the deformation mechanism acting during the creep test and γ is associated with the width of the distribution function of retardation times. Statistical dispersion in the values of J_0 and

γ is within the experimental error, thus, both parameters are not dependent on the aging time.

Therefore, both equations can be rewritten as an implicit function that represents a family of curves in the log (J) *vs.* log(t) plane, parametrized by the temperature; that is, both expressions satisfy the mathematical requirements of functions that can be superposed by horizontal shifts.

Furthermore, since γ is virtually constant at the three temperatures, the creep response at different temperatures could be predicted from a single creep curve measured at a reference temperature, according to properties of the implicit function that characterize a set of curves that can superpose by horizontal shifts.

Finally, the dependence of the relaxation time on both aging time and temperature remarks the presence of more than a single deformation mechanism along the glass transition region.

Declarations

Author contribution statement

Claudio Daniel Arenas, Élida B Hermida: Conceived and designed the analysis; Analyzed and interpreted the data; Contributed analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

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