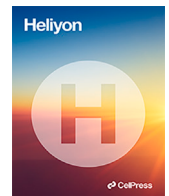




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TTS package: Computational tools for the application of the Time Temperature Superposition principle

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ABSTRACT

The TTS package has been developed in R software to predict the mechanical properties of viscoelastic materials, at short and long observation times/frequencies by applying the Time Temperature Superposition (TTS) principle. TTS is a physical principle used in material science to estimate mechanical properties beyond the experimental range of observed times/frequencies by shifting data curves obtained at other temperatures relative to a reference temperature in the dataset. It is a methodology related to accelerated life-tests and reliability, whereas the TTS library is one of the first open source computational tool to apply the TTS principle. This R package provides free computational tools to obtain master curves that characterize materials from a thermal-mechanical approach. The TTS package also proposes, implements and explains our own method to obtain the shift factors and the master curve in a TTS analysis, based on horizontal shifting of the first derivative function of viscoelastic properties. This procedure provides shift factors estimates and smooth master curve estimates using B-spline fitting, in a fully automatic way, without assuming any parametric expression. Williams-Landel-Ferry (WLF) and Arrhenius TTS parametric models are also implemented in the TTS package. They can be fitted from shifts obtained by the our first derivative based method.

1. Introduction

The main purpose of this work is to provide methodological and practical solutions for the application of the Time Temperature Superposition (TTS) principle. The TTS is a physical principle allowing to predict mechanical properties of amorphous viscoelastic materials (polymers, among others), out of the experimental observation range. Consequently, the application of the TTS principle is very useful to estimate mechanical properties, such as modulus, strain or compliance (depending on time/frequency), of viscoelastic materials at actual temperatures, where data collecting is often technically difficult and time consuming. Thus, it can be studied as a statistical based methodology in the framework of reliability and focused on providing predictions of mechanical properties,

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degradation level and lifetime. The increasing importance of the TTS principle and, by extension, of all those techniques that implement it, has to do with the large significance of polymer technology and its current prominence in chemical, pharmaceutical, medical and mechanical industries, among others. In fact, the use of the TTS principle has not stopped growing over the last 20 years, in connection with the needs of physicists, engineers and technicians in general to predict the mechanical behavior of materials at times and frequencies beyond those defined in the laboratory. Therefore, in the last 20 years, more than 3000 documents (which also received 70837 cites) that include the words “Time Temperature Superposition” in keywords, title or abstract have been published in journals indexed in Web of Science (core collection, SCI-EXPANDED). There has also been a sustained growth in scientific production, from an average of 100 articles published in the early 2000s to 200 per year at the end of the second decade of the century. In addition, these documents belong to diverse scientific domains, highlighting the polymer science, material science, mechanics, physics, and civil engineering. There has also been a sustained growth in scientific production, from an average of 100 articles published in the early 2000s to 200 per year at the end of the second decade of the century. Reference countries in the study and application of TTS are USA, China, Germany, Japan, India, France, UK, Canada and Spain, with institutions such as the CNRS, the Chinese Academy of Sciences, the US Department of Energy and the IIT System, among others, standing out. It is also worth noting that while the number of papers applying the TTS principle is numerous and growing, the number of papers proposing mathematical and computational methodologies to implement it is much smaller, hence one of the utilities of the present work.

In order to ensure material reliability, the use of adequate experimental methods, taking into account the type of material and applications, is needed. Once the material properties are experimentally obtained, the subsequent statistical data analysis and modeling tasks are crucial to extract representative and relevant information. These procedures are essential in material design and its characterization. In this study we focus on the problem of predicting, using statistical methods, the material performance out of experimental range obtained in laboratory. In this regard, the TTS R package is designed to analyze, estimate and predict the mechanical properties of viscoelastic materials, such as amorphous polymers [1]. It is available (free access) for all the users through Comprehensive R Archive Network (CRAN) [2]. CRAN is a network of ftp and web servers (mirrors) located in different places around the world that include the same versions of packages of functions developed in R. Once installed R, the users can also install the desired R package from a chosen a mirror or repository (better close to the user’s location). The package installation is performed once, whereas the package will have to be loaded whenever it is needed as part of a new session in the R program.

The short and long term prediction of the polymer properties and other viscoelastic materials can be done by the application of models based on the TTS principle [3]. The TTS principle is a physical concept applied to estimate the mechanical properties of linear viscoelastic materials, at a given temperature, beyond the experimental range of times/frequencies, that uses curves of mechanical properties obtained at different temperatures. For its correct application, it is assumed that (for all temperatures) there is the same shape and characteristic time variation [3]. As a result of its application, the so-called master curve is obtained. It is the trend of a given mechanical property (with respect to time or frequency), estimated a given temperature by vertical and horizontal shifting of those curves experimentally obtained at other temperatures [3–5]. The master curve, at a specific temperature, is able to provide estimates of material properties corresponding to times/frequencies beyond the time/frequency ranges of the experimental tests in the laboratory. The master curve is commonly estimated using parametric models that define the relation between the horizontal shift of each curve and the temperature. Williams Landel and Ferry proposed an empirical function to define this relation at temperatures above the glass transition temperature (T_g) [6], while the Arrhenius model can be used at temperatures below T_g [7]. There are also some new alternatives based on geometry, numerical analysis [4] and statistical flexible tools [5]. Specifically a method to obtain horizontal shifts based on arc length measurement is proposed in [4]. Moreover, Lorentz et al. [8] propose a method based on the causality principle to test the accuracy of the master curve estimate obtained by different methods. It is also important to stress the work of Álvarez-Vázquez et al. [9], that proposes a conversion law describing the relationship between relaxation curves obtained at different temperatures, assuming normal or Gumbel family. As a result, they provide a novel parametric way to estimate the shift factors for any temperature. In addition, as a sign of its importance, it is worth mentioning that the TTS principle has been extended to the concentration effect, proposing a concentration-temperature superposition for the ground boundary migration in alloys [10]. The stress roll was also included in TTS by Wang et al. [11]. It is also worthy to mention new recent approaches to develop TTS tasks such as the work of Miyano and Nakada [12], in which a parametric statistical procedure is proposed for the estimation of shift factors from which an accelerated life testing method for the estimation of the service life of carbon fiber reinforced plastics is developed, specifically when they are subjected to creep and fatigue. In addition, it is also worth mentioning other contributions, such as those of Chen et al. [13] who propose a new TTS method for the specific materials family of styrene-butadiene-styrene modified bitumen according to its special points of phase angle plateau regions in isochronal curves. Therefore, considering its usefulness, flexibility and new extensions, the application of the TTS principle is experiencing a great growth, being examples of recent applications those related to the estimation of the mechanical properties of natural materials such as bamboo, composites or even asphalt [14–16]. In fact, it is worth noting the growing importance of TTS studies in the field of civil engineering, for estimating the reliability and lifetime of structural materials such as bitumen or asphalt [17–19] against fatigue and creep phenomena, and even metals [20]. Indeed, two of the datasets included in the present work, an epoxy based and a styrene-butadiene-styrene based composite are related to these type of applications.

The TTS package [1] implements the recent methodologies we developed for the TTS principle application [5] to predict mechanical properties of viscoelastic materials (loss modulus, storage modulus, loss factor tangent, strain, compliance) at a specific temperature, and out of lab experimental frequencies or times. The method proposed by Naya et al. (MNAT, for the sake of simplicity) [5] is based on the shifting of the first derivative of the curves. The MNAT procedure implemented in the TTS package has been the starting point to document different applied works devoted to determine the PMMA activation energy [21], to obtain the loss modulus for trehalose and glycerol mixtures [22], and to estimate the viscoelastic properties of epoxy-graphene composites [23].

Taking into account the potential utility of the MNAT method [5], the TTS package has been developed to provide practitioners those computational tools that allow to apply the TTS principle, applying the MNAT procedure, in a straightforward and easy way. A more complete description of TTS principle is shown in Section 2.

In this work, the TTS analysis is applied to Dynamic Mechanical Thermal Analysis (DMTA) data to estimate the mechanical and viscoelastic properties of polymers out of the experimental data interval. The DMTA analytical technique is applied to study and characterize the mechanical behavior of viscoelastic materials such as polymers, by obtaining their response to stress and deformation depending on frequency, time and temperature. The dependence of viscoelastic variables such as the storage modulus (E'), loss modulus (E'') and tangent of loss factor $\tan\left(\frac{E'}{E''}\right)$ with respect to frequency and time, allow to use the DMTA data in material reliability analysis.

The innovations of the present work deal with providing computational tools to allow the practitioners to apply the TTS method developed by the authors. We can summarize then in the following points:

- Free software tools to perform Time Temperature Superposition analysis are provided.
- The first derivative shifting authors' own method (MNAT) to estimate shift factors is implemented in the present TTS package.
- In addition, Arrhenius and WLF typical parametric methods to estimate shift factors are also implemented.
- Nonparametric approach for TTS, specifically for the estimation of the master curve, is proposed, including splines fittings and the calculation of bootstrap confidence intervals.
- Smooth and accurate master curves are estimated by the methodology implemented by the authors in the TTS package.

The content of the paper is as follows. In Section 2, the state of the art on TTS studies is presented. In Section 3, the statistical methodologies implemented in the TTS package are described. In Section 4, a description of the TTS library is presented, whereas the Section 5 show how to use it by its application to two different case studies, namely the creep characterization of an epoxy based composite and a styrene-butadiene-styrene composite. Finally, Section 6 contains the main conclusions.

2. Time Temperature Superposition principle and master curve

One of the most important tasks in polymer science and polymer engineering is to characterize the behavior of polymers during their service and their lifetime. In fact, estimating their properties or long-term behavior from their short-term properties is also one of the most complex tasks. The long-term prediction of polymer properties can be approached taking into account viscoelasticity theory, which characterizes their mechanical behavior. Specifically, these estimates can be made from the application of the TTS principle. The TTS principle is one of the most useful extrapolation techniques, with a large number of applications, in polymer technology. In fact, it has been applied in a very wide range of linear, amorphous or semicrystalline polymers [24–28]. This principle, proposed by Leaderman [29], states that for thermo-rheologically simple viscoelastic materials (polymers), time and temperature are related according to a Time Temperature Superposition, which implies that the effects of time and temperature on mechanical properties (such as modulus) of polymers are generally equivalent [30]. The TTS principle is based on the fact that the curves representing the viscoelastic properties of a material, determined at different temperatures, are similar in shape when plotted against the logarithm of time or logarithm of frequency. They obey to the same underlying model. The TTS principle states that curves can be superimposed by moving them horizontally along the axis of the logarithm of time (or the logarithm of frequency) [31]. The result is a master curve of a specific mechanical property, defined at a specific temperature. Thus, the TTS principle can be defined as follows (1):

$$f(x, T) = b_T f(a_T x, T_0), \quad (1)$$

in the frequency domain, and by (2)

$$f(t, T) = b_T f(t/a_T, T_0), \quad (2)$$

as a function of time, where f accounts for the studied viscoelastic property as a function frequency, x , or time, t (both in logarithm scale), and temperature, T , given the temperature at which the viscoelastic property curve is obtained. T_0 is the reference temperature at which mechanical properties depending of frequency/time are required, whereas a_T y b_T are the horizontal and vertical shifts, respectively, that must be applied to the $f(x, T_0)$ or $f(t, T_0)$ curve in order to obtain the f curve at a temperature T . The a_T and b_T are temperature dependent. In other words, when $b_T = 1$, the TTS principle states that the temperature variation between T and T_0 is equivalent to multiply the frequency (or time) scale by a constant factor a_T , which is a function of temperature. The a_T is related to the relaxation time of each polymer at each temperature, and b_T is due to density changes as a consequence of temperature variation [32]. As above mentioned, the resulting curve, composed by the superposition of several viscoelastic curves, at a given T_0 , is defined as master curve. There are two main parametric models that define the dependence of a_T with the temperature: Arrhenius and WLF.

The WLF equation is based on the free volume theory. This is one of the theories intending to explain the phenomenon of the crystalline transition at molecular level. It considers that for a movement of a polymer segment to an adjacent sector, a minimum volume of voids is required. The Doolittle equation [3] is one of the first equations relating free volume to viscosity,

$$\eta = A \exp\left(\frac{Bv}{v_f}\right),$$

where η is the viscosity, whereas v and v_f are the occupied and free volumes, respectively, and A and B are model constants. This equation gives the theoretical background to the WLF model [6], which presents the following expression (3):

$$\log_{10}(a_T) = -\frac{C_1(T - T_g)}{C_2 + (T - T_g)}, \quad (3)$$

where C_1 and C_2 are system parameters related to the changes of viscosity or relaxation time with respect to the glass transition temperature (T_g). Its calculation, not always necessary, greatly complicates obtaining a smooth master curve. Parameters C_1 and C_2 can be taken as constants $C_1 = 17.44$ and $C_2 = 51.6$ for a large number of amorphous polymers, whenever it is in the range ($T_g, T_g + 100K$). However, they should be considered as adjustable empirical parameters that can be determined by fitting to the a_T experimental data. On the other hand, the T_g can be replaced by the reference temperature of interest in each application, T_r or T_0 . Summarizing, the WLF equation, based on the hypothesis of existing a linear relationship between the measured mechanical property and the temperature, is valid only in the range ($T_g, T_g + 100K$), as pointed out in [33]. The WLF model can be applied in other intervals only in specific cases. This fact justifies the proposal of an alternative flexible model as the one proposed in [5] and implemented in the TTS package. Alternatively, when the reference temperature T_0 is below the T_g corresponding to the studied material, the most common TTS model is based on the Arrhenius equation (4):

$$\log(a_T) = \frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right), \quad (4)$$

in which E_a is the activation energy and R is the universal gas constant.

As already mentioned, TTS models are applicable (the data “verify TTS”) when an exact or near-exact match between the shapes of adjacent viscoelastic property curves (time or frequency dependent) is obtained. In addition, it is needed the dependence between the a_T shift (corresponding to temperature T) and the temperature meeting Arrhenius or WLF equations [34–36].

It is important to note that the MNAT methodology, proposed in [5], provides a new method to obtain a_T based on the shifting of the first derivative of the curves. It also proposes B-spline fitting jointly with bootstrap confidence bands to estimate the master curve. This flexible alternative implies that this TTS method has a much broader range of applicability (in terms of temperature) than the parametric alternatives. In addition, the estimates of the master curves are smoother, more accurate and precise [5].

In most of the studies, horizontal shift factors, a_T , are calculated using the commercial software included to manage rheometers and DMTA instruments [37–40]. In some works, these factors are obtained manually [30]. Alternatively, there are some references where the authors propose new methods based on iterative processes to obtain the a_T [31].

The procedures to estimate horizontal and vertical shift factors can be: (a) Manual methods (the displacements are done according to the experience of the analyst) as proposed by [30]. (b) Parametric methods from the WLF formula, with constants $C_1 = 17.44$ and $C_2 = 51.6$, which usually do not provide smooth master curves. (c) Numerical and statistical methods, including the proposal implemented in pkgTTS package [5,31]. In addition, there are several alternatives provided by commercial software that do not describe the procedure followed to obtain the shifts [37–40], although the use of optimization techniques and regression estimation methods are surely used.

The TTS models have been generally applied from the data provided by experimental techniques such as DMTA, Thermomechanical Analysis (TMA), and rheological analysis, among others. The estimation of the modulus of elasticity, storage modulus, loss modulus in a dynamic test depending on the frequency or the time, and the estimation of the deformation due to the physical phenomenon of creep, are two of the most important applications in this type of analysis.

The following sections describe the new library TTS, developed in R, providing the users and practitioners TTS computational tools that are usually only offered with commercial software.

3. TTS methodologies to estimate the master curve

This work aims at providing competitive and useful approaches to solve material characterization problems and to predict their physical properties during lifetime, using data modeling of thermal and mechanical analysis. Consequently, a new methodology to estimate the viscoelastic properties of polymeric materials depending on time and temperature is proposed and implemented in R software. In short, the proposed method provides estimates and predictions of viscoelastic properties of amorphous polymers at a given constant temperature and at times out of the experimental time range.

3.1. MNAT procedure

Naya et al. proposed a new procedure to obtain the shift factors from the first derivative curves [5]. Its aim is to obtain a smooth and reliable estimation of master curve, $\hat{\psi}(x, T)$ for viscoelastic properties, where x is time/frequency and T the temperature at which the master curve is required. For this purpose, the first step is the data collection. Consequently, the curves of viscoelastic properties, denoted by $Y_i(x, T_i)$ with $i = 1, 2, \dots, n$ (storage modulus E' , compliance J , etc.), are obtained by experimental testing such as DMTA in isothermal mode.

The experimental curves are usually composed of a few number of discrete observations that we can denote by (x_j, y_j) with $j = 1, 2, \dots, m$. The x_1, \dots, x_m are the abscissas, assuming $x_1 < x_2 < \dots < x_m$, whereas the ordinates are y_1, \dots, y_m or some observed real number corresponding to x_j . The discrete nature of data could prevent the estimation of a smooth master curve. Thus, for overcoming the problem of discrete data, the curves are fitted using interpolation cubic splines as shown in [41] to obtain smooth functions (5),

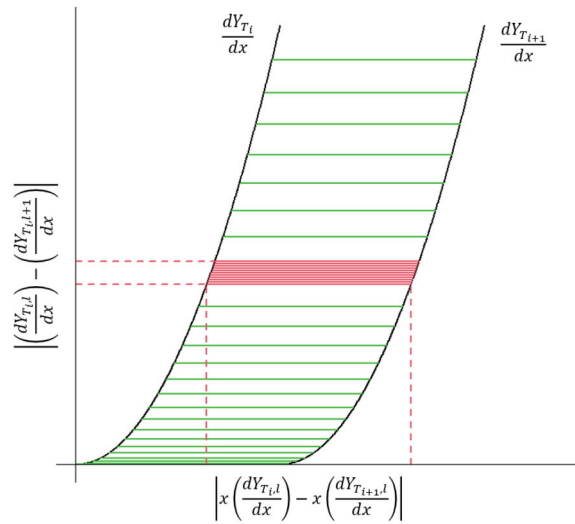


Fig. 1. Scheme of the process to obtain the horizontal shifts based on the L_1 distance calculation.

$$s(x) = y_j + b_j(x - x_j)^2 + c_j(x - x_j)^3, \tag{5}$$

for $x_j \leq x \leq x_{j+1}$, with $j = 1, 2, \dots, m - 1$, where the expressions of b_j , c_j , and d_j are shown in expressions (6)-(8):

$$b_j = \frac{y_{j+1} - y_j}{h_j} - h_j(\sigma_{j+1} + 2\sigma_j), \tag{6}$$

$$c_j = 3\sigma_j, \tag{7}$$

and

$$d_j = \frac{\sigma_{j+1} - \sigma_j}{h_j}, \tag{8}$$

with $h_j = x_{j+1} - x_j$ and $\sigma_j = \frac{s''(x_j)}{6}$.

Once continuous curves are obtained, the next step is to calculate the first derivative of each experimental curve using, for example, cubic smoothing splines [42]. When the derivative of each curve is estimated, the reference temperature, T_0 , is defined and the master curve is obtained by shifting horizontally and vertically the remaining curves on the T_0 curve. The goal of working with the first derivative curve is that only horizontal shifts should be applied. Therefore, we aim at estimating the a_T (and b_T if necessary) shifts, assuming that they coincide with the horizontal shifts of the first derivative curves. The a_T shift between two adjacent curves is obtained by dividing their L_1 distance by the mechanical property common range. The L_1 distance is defined by the expression $d_{L_1}(f, g) = \int_b^a |f(x) - g(x)| dx$, that accounts for the area between two functions, $f(x)$ and $g(x)$, depending on x , whereas $d_{L_1}(f, g)/(b - a)$ is the mean discrepancy between two curves, with $(b - a)$ the range of the mechanical property values common for the two curves. Thus, considering that there are $l = 1, 2, \dots, L$ points of overlap between curves i and $i + 1$ in the coordinate of the shifted frequency (alternatively, shifted time) domain, the a_T shift between two adjacent curves (i and $i + 1$) is estimated from (9)

$$\log_{10} a_T = \frac{\sum_{l=1}^L \left| x \left(\frac{dY_{T_i,l}}{dx} \right) - x \left(\frac{dY_{T_{i+1},l}}{dx} \right) \right|}{\left| \frac{dY_{T_i,l}}{dx} - \frac{dY_{T_{i+1},l}}{dx} \right|}, \tag{9}$$

whereby $x \left(\frac{dY_{T_i,l}}{dx} \right)$ is the value of frequency (or time) corresponding to $\frac{dY_{T_i,l}}{dx}$, that is the value of the first derivative of $Y_i(x, T_i)$, evaluated in the l horizontal asymptote or time-frequency, for which there is also an available value for $\frac{dY_{T_{i+1},l}}{dx}$.

Overall, there are L points in the common experimental range between $\frac{dY_{x,T_i}}{dx}$ and $\frac{dY_{x,T_{i+1}}}{dx}$. Fig. 1 illustrate the process to obtain the horizontal shifts. First, the horizontal shift of the curve closest to the one corresponding to the temperature at which the master curve is to be estimated is calculated. Then, we apply the shift resulting a master curve composed of the reference curve and one shifted curve that overlaps with the previous one. After, with respect to the master curve resulting from the first shift, we calculate how much we have to shift the second nearest curve and we shift it. This is done successively in an iterative process until all the curves have been shifted to form the master curve at a given temperature.

Once all a_T are applied, b_T can be necessary, thus, as shown in (10),

$$\log_{10} b_T = \frac{\sum_{i=1}^n \left| \frac{dY_{T_1}}{dx}(x_i) - \frac{dY_{T_2}}{dx}(x_i) \right|}{|x_n - x_1|} \tag{10}$$

Therefore, the master curve is estimated by superposition of the remaining curves, applying the shift factors corresponding to each curve to displace them.

The master curve estimated at T_0 by shifting the remaining viscoelastic curves is characterized by the presence of discontinuity. This proposes to obtain reliable estimates of the viscoelastic property. Consequently, this methodology also propose the application of a B-spline model to obtain a smooth and reliable estimation of the master curve, $\hat{\psi}_i(x, T_i) = a_1 B_1(X) + \dots + a_k B_k(X)$. The coefficients $a = a_0, \dots, a_k$ are estimated by minimizing the sum of penalized squared residuals $\sum_{j=1}^m (y_j - f(x_j))^2 + \lambda \int (f''(x))^2 dx$. In this specific case, $j = 1, 2, \dots, m$ is each knot of the curves, x_i the time or frequency for each knot, y is $Y(x_j, T_i)$, f is $\hat{\psi}_i(x, T_i)$, $\int (f''(x))^2 dx$ measures the degree of curvature of m , and λ is the penalization factor.

It is also important to note that the a_T and b_T shifts obtained by this methodology can be used, as initial solution, to fit parametric models such as Arrhenius and WLF.

Moreover, the TTS package also implements the calculation of confidence intervals for the master curve by applying bootstrap resampling. These intervals allow us to study the accuracy of the master curve estimate. The bootstrap procedure to obtain such intervals is briefly described below.

1. Calculate the mean ($\bar{\epsilon}$) and variance ($\hat{\sigma}_\epsilon^2$) of the residuals or differences between the estimated values of the master curve and the values obtained from the application of the TTS principle to the sample of experimental curves. Overall, we have $n \times m$ residuals, where m is the number of observations that define a curve and n the number of curves.
2. Then, generate B bootstrap samples analogous to the sample of $n \times m$ pairs observed from the application of the TTS principle to experimental curves. The B bootstrap samples are calculated by adding the $n \times m \hat{\epsilon}_{i,j}^*$ generated from the $N(\bar{\epsilon}, \hat{\sigma}_\epsilon^2)$ distribution.
3. For each x value, the $R_x^{*(k)} = \hat{\psi}^{*(k)}(x, T_0) - \hat{\psi}(x, T_0)$ estimate is obtained, with $k = 1, 2, \dots, B$. Each $\hat{\psi}^{*(k)}$ is estimated by B-splines in each resample, whereas $\hat{\psi}(x, T_0)$ is the estimated master curve.
4. The $R_x^{*(k)}$ bootstrap estimates are sorted for each x and the $R_x^{*[B(\alpha/2)]}$ and $R_x^{*[B(1-\alpha/2)]}$ quantiles are obtained.
5. Finally, for each x value, the confidence intervals are obtained as follows, $[\hat{\psi}(x, T_0) - R_x^{*[B(1-\alpha/2)]}, \hat{\psi}(x, T_0) + R_x^{*[B(\alpha/2)]}]$.

3.2. Implementation of Arrhenius and WLF parametric models

In this section, the process to obtain the parameters of the TTS parametric models is presented. It is important to note that the TTS library provides a new approach to obtain the Arrhenius and WLF parameters based on the estimation of an initial solution for a_T using the derivative shifting procedure.

The parameters of the WLF model are estimated from the linearized model:

$$\log_{10}(a_T) = -\frac{C_1(T - 150)}{C_2 + (T - 150)} \tag{11}$$

$$\frac{1}{\log_{10}(a_T)} = -\frac{1}{C_1} - \frac{C_2}{C_1(T - 150)} \tag{12}$$

In (11) and (12), the linearized equation corresponding to the estimation of the master curve at $T_0 = 150$ is presented. The $\log_{10}(a_T)$ values are the horizontal shifts obtained by the derivative shifting based on the method proposed in [5]. Afterward, a linear fitting is obtained, estimating $C_1 = 6.90799$ and $C_2 = 23.21744$ corresponding to the WLF model. Once the parameters C_1 and C_2 are estimated, the a_T factors corresponding to the WLF model can be straightforward obtained.

In the case of Arrhenius model, the estimation of the activation energy E_a is necessary to obtain a parametric relationship between a_T and the temperature. This is done by linearizing the Arrhenius equation as follows (13):

$$\log_{10}(a_T) = \frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \log_{10}(e) \tag{13}$$

where the $\log_{10}(a_T)$ are the horizontal shifts obtained by the derivative based method [5]. Thus, the linearized equation is $v = B \cdot u$, with $u = \frac{1}{T} - \frac{1}{T_0}$, $v = \log_{10}(a_T)$ and $B = \frac{E_a}{R} \log_{10}(e)$ is the constant to be determined (slope of the linear trend). Finally, a linear fitting is performed, obtaining an activation energy $E_a = 1007.817$. Once the parameter is estimated, the a_T factors corresponding to the Arrhenius method can be obtained.

4. Description and utilities of TTS package

4.1. Data

The TTS package includes three databases called PC, Epoxy and SBS. These datasets have been obtained by experimental procedures in laboratory, measuring the storage modulus or the compliance of different polymeric materials such as polycarbonate, and epoxy or styrene-butadiene-styrene based composites. Each one of the databases are briefly described below.

Epoxy and SBS datasets corresponds to data obtained in creep test. This experimental testing is defined by the application of a constant stress, σ , to a sample of material, measuring the strain, $\epsilon(t)$, or compliance, $J(t) = \epsilon(t)/\sigma$ as the response variable. The application of the TTS principle to creep tests is becoming more and more common. Creep test provides information about the deformation of a material subjected to a constant load. This test is in accordance with many real applications such as the performance of shoe insoles, structural materials, asphalt, etc. In this framework, TTS provides the degree of the deformation of the material at an extended range of times, when this material is subjected to a constant load. Therefore, TTS is becoming increasingly useful in studies of material degradation and lifetime estimation. The use of the TTS principle with creep tests usually provides smoother master curves since each curve is usually defined by a larger number of experimental observations than, for example, modulus curves as a function of frequency.

4.1.1. PC

PC is a database composed by the DMTA curves obtained from polycarbonate (PC) polymer samples, called PC.

Polycarbonate is a thermoplastic polymeric material obtained by the reaction of bisphenol A and phosgene, and characterized by the existence of carbonate groups in its structure [43]. Polycarbonate is commonly used in engineering due to its toughness, transparency and mechanical strength. In addition, it is a viscoelastic material that meets the TTS principle. Consequently, 7 different storage modulus curves of polycarbonate (E') defined at 7 different frequencies, have been obtained by a TA Instruments Q800 DMTA analyzer, and included in the PC database. A comprehensive description of the experimental setup to obtain the PC curves can be found in [5]. In short, each DMTA curve is composed by 7 pairs (E' , *frequency*), where the frequency varies between 0.3142 and 62.83 rad s⁻¹. The E' curves have been obtained in isothermal tests at temperatures between 147 and 153 °C.

Thus, the PC database is composed of 49 rows and 3 columns that are described in the following:

1. `log10.frequency` that accounts for 7 different frequencies (rad s⁻¹) in logarithmic scale for each temperature (overall 49).
2. `log10.module` that accounts for 7 different values of storage modulus, E' (Pa), in base-ten logarithmic scale for each temperature (overall 49).
3. `temperature` shows the temperatures at which E' is measured: 147, 148, 149, 150, 151, 152, and 153 °C. Each temperature accounts for 7 different values of frequency and storage modulus (overall 49).

This dataset can be called by typing PC, once TTS is loaded using the command `library(TTS)`.

4.1.2. Epoxy

The Epoxy dataset is composed of 273 rows and 3 columns that describes the performance of an epoxy resin based composite in a creep type test. These experimental tests are performed by DMTA, using a 3 point bending configuration with a 3-Point Bending clam, rectangular geometry, and samples with a length of 20 mm, width of 5.55 mm, and thickness of about 0.85 mm. One sample per testing temperature has been prepared and then testing by the same person, in a short interval of time, and using the same DMTA experimental instrument, reducing in this way the number of possible source of variation apart from those corresponding to the treatment [44].

This dataset is composed of the following columns:

1. `Log_time` that accounts for 39 different times from 2 s to 3600 s, in logarithmic scale for each one of the 7 studied temperatures (overall 273 observations).
2. `Log_Compliance`, defined by 39 different values for the compliance, J (MPa⁻¹), for each one of the 7 studied temperatures, in base-ten logarithmic scale.
3. `Temperature` is the variable that shows the temperature at which the measurements of compliance are experimentally obtained, namely 30, 40, 50, 60, 70, 80, and 90 °C.

The dataset includes the measurements of the compliance property depending on the time and corresponding to different specimens of an epoxy resin based composite. Its glass transition temperature is about 30 °C.

As in the case of PC, the Epoxy dataset can be called by typing Epoxy, once TTS package is loaded using the command `library(TTS)`.

4.1.3. SBS

SBS is a dataset composed of 234 rows and 3 columns that describes the performance in the framework of a creep test of a styrene-butadiene-styrene (SBS) composite. The experimental tests are made by DMTA technique, using a 3 point bending configuration with 3-Point Bending clamp, rectangular geometry, and sample size of 20 mm length, 5.54 mm width, and 3.87 mm thickness. One sample per testing temperature has been prepared and then testing by the same person, in a short interval of time, and using the same DMTA experimental instrument, reducing in this way the number of possible source of variation apart from those corresponding to the treatment [44].

This data frame is composed of the following variables:

1. `Log_time`: It accounts for 39 different times from 2 s to 3600 s, in logarithmic scale for each one of the 6 studied temperatures (overall 234 observations).

2. `Log_Compliance`: It accounts for 39 different values for the compliance, J (MPa^{-1}), for each one of the 6 studied temperatures, in base-ten logarithmic scale.
3. `Temperature`: It is the variable that shows the temperature at which the measurements of compliance are experimentally obtained, namely 30, 40, 50, 60, 70, and 80 °C.

As in the case of PC and Epoxy, the SBS dataset can be called by typing `SBS`, once TTS package is loaded using the command `library(TTS)`.

4.2. TTS function

As previously mentioned, the master curve at a specific temperature involves the variation of a specific viscoelastic property of the selected material depending on time or frequency. The TTS function is performed to estimate the master curve of a specific viscoelastic property at a constant temperature. The MNAT TTS method for estimating shift factors to obtain the master curve at a temperature chosen by the user is implemented [5] using the TTS function. It provides the horizontal and vertical shifts using the MNAT method. This function is composed by the following arguments:

1. `x`, that is the required data matrix or data frame. It should be composed of three columns: a numeric column vector with the experimental frequencies (in logarithmic scale, base-ten) or times, the base-ten logarithm of a specific viscoelastic property (E' , E'' , G' , G'' , among others), and the temperatures corresponding to each viscoelastic property observation.
2. `reference.temperature`, accounting for the reference temperature selected by the user to obtain the master curve of modulus or other viscoelastic property.
3. `n`, with the number of partitions in the frequency/time domain corresponding to the B-spline basis fitting (100 by default).
4. `nB` (100 by default) is the number of bootstrap replicates to estimate confidence intervals for the master curve fitting.
5. Finally, the `method` argument is a string vector composed of one of three options: `"derived"` (by default), `"WLF"` and `"Arrhenius"`. It accounts for the model that is applied to estimate the master curve. The `"derived"` option accounts for the procedure based on derivative curves shifting (e.g. $dE'/dx(x+aT) \rightarrow dE'/dx(x)$) combined with nonparametric B-spline basis fitting, the MNAT method. Moreover, the TTS function provides two alternative parametric options: the application of Arrhenius or WLF models to obtain the final a_T and b_T factors. It is important to note that, previously, it is necessary to provide an initial solution for the a_T . One of the goals of the implemented methodology is to provide an initial solution composed by the shifts obtained by the method of derivative shifting. The final a_T shifts are estimated by the WLF expression $\log_{10}(a_T) = -C_1(T - T_0)/(C_2 + (T - T_0))$ or, alternatively, with the Arrhenius equation $\log_{10}(a_T) = Ea[(1/T) - (1/T_0)] \log_{10}(2.718282)/R$. Finally, the resulting master curve is smoothed by B-spline and bootstrap resampling confidence intervals are estimated.

As a result, the TTS function is defined by the structure:

```
TTS(x, reference.temperature = 150, n = 100, nB = 100, method = c("derived", "WLF", "Arrhenius")).
```

It is important to stress that the `"derived"` method (MNAT) can be applied in a wider range of temperatures than the `"WLF"` and `"Arrhenius"` ones, thus the authors strongly recommend its use.

Once the a_T shifts are calculated by the first derivative based method, the vertical shifts, b_T , are calculated (if necessary) taking into account the vertical distance between the viscoelastic property curves (not the derivatives).

The TTS function provides the following values or outputs related to TTS analysis:

1. `data`, accounting for the input experimental data.
2. `aT` is a numerical vector composed of the horizontal shifts of the curves.
3. `bT` is the vector composed of the vertical shifts needed to obtain the master curve (of modulus, strain, among other mechanical properties) at a specific temperature.
4. `TTS.data` is the master curve data frame defined by three columns: `log10frequency`, `log10module` and `temperature`.
5. `ref.temp` is the parameter chosen by the user that accounts for the reference temperature, T_0 .
6. `TTS.gam` accounts for the data frame corresponding to the results of the generalized additive model (GAM) application. The GAM model uses B-spline smoothing regression (estimated using the `gam` function of the `mgcv` package [45]) to estimate of the master curve. This data frame contains two columns: `frequency` (or eventually time) and `Prediction`, with the predicted values of the viscoelastic property which are obtained by the application of the TTS model.
7. `I.lower` is the lower limit of the 95% confidence bands for the master curve, previously estimated by B-spline. It is obtained by the application of a parametric bootstrap resampling.
8. `I.upper` is the upper limit of 95% confidence bands for the master curve, previously estimated by B-spline. It is obtained by the application of a parametric bootstrap resampling.
9. `residuals` accounts for the B-spline semiparametric model residuals. They are the residuals of the master curve fitting.

4.3. TTS_10 function

In the new version of the package, the `TTS_10` function is also defined. This function provides an estimate of the Master Curve in a similar way to the `TTS` function, with the difference that a thin plate spline fit is performed (instead the B-splines smoothing implemented in the `TTS_10` function), within the framework of the application of generalized additive models (GAM), as implemented in the `mgcv` package. The use of thin plate splines may be more appropriate than the application of B-splines when there are smooth curves defined by a relatively large number of observations. In fact, this prevents the interpolation of the curves, obtaining smoother fits of the starting curves and, therefore, smoother estimates of their derivatives. Specifically, this function is applicable when each of the experimental curves is composed of 10 or more points.

The arguments of the `TTS_10` function (and also its outputs) are the same that those corresponding to the `TTS` function, above described.

```
TTS_10(x, reference.temperature = 150, n = 100, nB = 100, method = c("derived", "WLF", "Arrhenius"))
```

4.4. PLOT.TTS function

Considering that one of the reasons of the TTS principle success is its very intuitive and informative graphical output, the ad-hoc `PLOT.TTS` function has been implemented in the `TTS` package. This function plots the experimental data, horizontal and vertical shifts, TTS data, and TTS master curve fitting using B-spline (with bootstrap confidence intervals). When the data matrix `x` is introduced as the only argument, the following outputs are provided:

1. `PLOT.data()` is the generic function plotting the experimental data.
2. `PLOT.aT()` is the generic function that shows the horizontal shifts corresponding to each curve of the experimentally retrieved viscoelastic property (e.g. modulus versus frequency).
3. `PLOT.bT()`, accounting for the generic function that plots the vertical shifts corresponding to each curve.
4. `PLOT.TTS.data()` is the generic function that shows the experimental data once they are horizontally and vertically shifted with respect to the curve at the reference temperature, T_0 .
5. `PLOT.TTS.gam()` provides the plot of the master curve obtained by B-spline estimation (with bootstrap confidence intervals at 95%).
6. Finally, `PLOT.res()` gives the residual plot corresponding to the master curve B-spline fitting.

5. Real data application

In this section, the application of the `TTS` library functions, to perform a TTS analysis and obtain the master curve, is illustrated and presented. For this purpose, real datasets are obtained and analyzed. The procedure to implement a TTS analysis is illustrated with two real case studies that correspond to the measurement of compliance depending on the time during a creep test of two different materials: an epoxy based (`Epoxy` dataset) and a styrene-butadiene-styrene based (`SBS` dataset) composites. As pointed out, creep is phenomena that consists in the deformation that some materials suffer when are subjected to a constant load. In this type of experiments, the TTS principle is applied to estimate the path of degradation of a material in real life conditions at a specific temperature, saving time and resources. The addition of these datasets obtained testing real samples in laboratory help us to evaluate our TTS methodology in a more complete way. Moreover, the performance of our model is also compared with standard procedures in the framework of laboratory work such as the manual fitting applied by skilled personnel, following the procedure pointed out in López-Paz et al. [40].

We analyze the hypothetical case study in which the usage conditions of a specific epoxy based composite correspond to 40 °C. This material will be subjected to continuous stress at this temperature of 40 °C during its service life, i.e it will suffer the creep phenomena. Therefore, we need to know the degree of deformation (directly related with its fail) of this material in a wide range of different times, in order to asses the material reliability depending on the specific application. Consequently, the aim is to estimate the master curve at 40 °C, to predict $J(t)$ (t =time) out of experimental range taking into account that the TTS principle can be applied, saving time and resources. In fact, the $J(t)$ at 40 °C can be estimated by applying the TTS principle from $J(t)$ obtained at lower and higher temperatures. Therefore, this is a particular case of an accelerated life testing. It is also important to note that the T_g of the epoxy based composite is around 30 °C, thus, this is a case where Arrhenius could not provide reliable results, taking into account that $T_g < T_0 = 40$ °C.

First, the J curves obtained by DMTA at different temperatures are imported by typing `data(Epoxy)`. Then, a TTS object, `x`, is developed by running the `TTS` function:

```
1 library(TTS)
2 data(Epoxy)
3 x <- TTS(Epoxy, method="derived")
```

Listing 1: Code for loading the `TTS` package and the `Epoxy` dataset included in the package, in addition to apply the `TTS` function to the `Epoxy` dataset, also assuming the application of the MNAT procedure.

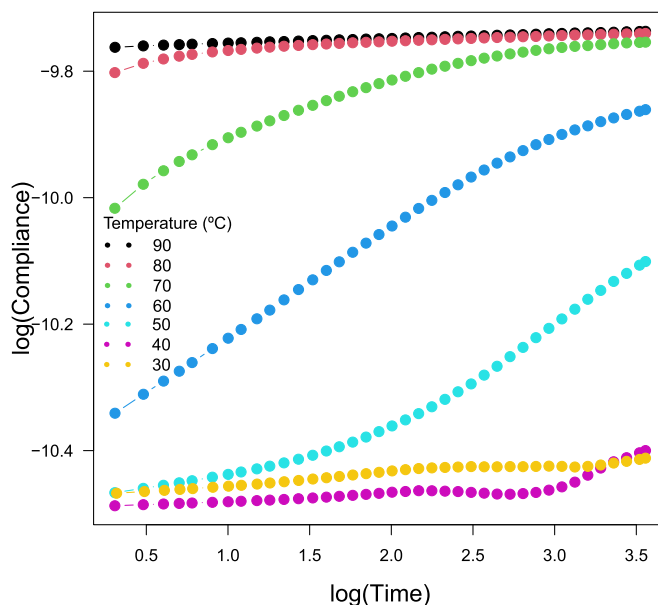


Fig. 2. $J(t)$ curves of the epoxy based composite obtained in a creep test.

It is important to stress that the datasets obtained by the researches can be imported by usual procedures in the framework of the R statistical software. In fact, the procedure to import an external dataset and subsequently apply the TTS or TTS_10 functions is shown below. We assume that the external dataset is the Epoxy dataset, in text format. The structure of this text file can serve as a guide to organize the researchers' own databases prior to the application of the TTS package functions.

```

1 library(TTS)
2 Epoxy <- read.table(Epoxy,header=TRUE) # Before, the folder where the dataset is included has to be selected
   as working directory
3 attach(Epoxy)
4 x <- TTS(Epoxy, method="derived")

```

Listing 2: Code for loading the TTS package and importing the Epoxy dataset as external data in txt format. The TTS function is applied to the Epoxy dataset. The application of the MNAT procedure has been selected.

Afterwards, the application of the PLOT.TTS function allows us to obtain the different TTS graphical outputs. Fig. 2 shows the J curves of the epoxy based composite obtained by DMTA (applying the PLOT.data generic function):

```

1 plot <- PLOT.TTS(x)
2 plot$PLOT.data(xlab="log(Time)", ylab="log(Compliance)", cex.lab=1.4)

```

Listing 3: Code to plot the original creep curves (compliance versus time) corresponding to the epoxy based composite.

Once the data are uploaded, a B-spline smoothing is applied to each curve and, then, their first derivatives are obtained by the application of cubic smoothing splines, by running the TTS function. The TTS package performs internally the estimation of the nonparametric fit of the original curves, as well as the estimation of the curves corresponding to the first derivative. Therefore, the TTS package does not automatically provide the corresponding graphical outputs. In any case, these can be obtained by using basic R code, mainly based on the application of the spline function of the R splines package, in addition to the gam function of the mgcv package (see supplementary material). The graphical outputs are shown in Fig. 3 and Fig. 4. Fig. 3 shows the smoothed curves obtained by fitting a B-spline basis.

The first derivative of each interpolated curve (Fig. 4) is obtained by the application of the D1SS R function of sfsmisc package [42]. It implements the fitting of cubic smoothing splines [46] specially developed (in terms of smoothing parameter) to estimate the first derivative of the curves (see Fig. 4). The code to obtain this graphical output is also available in the supplementary material.

The derivative displacements over the J curve corresponding to $T_0 = 40$ °C is also performed by the application of TTS function. Fig. 4 shows the shift direction of each curve to construct the master curve.

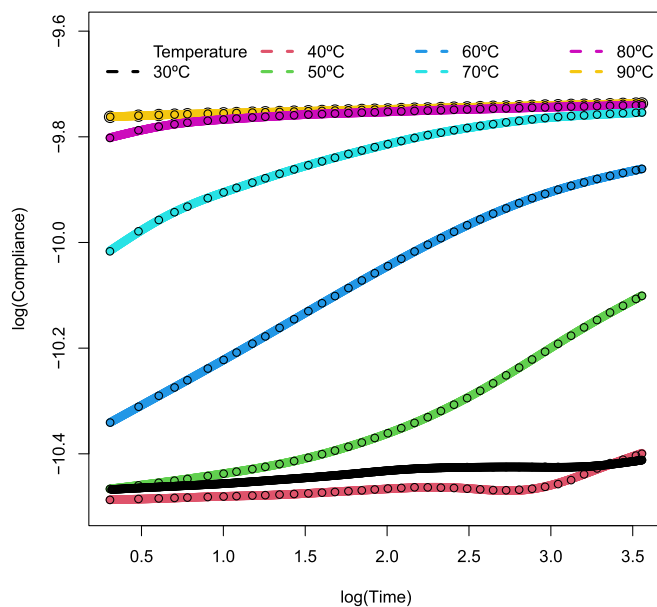


Fig. 3. Smoothed J curves of the epoxy based composite obtained by using cubic interpolation splines.

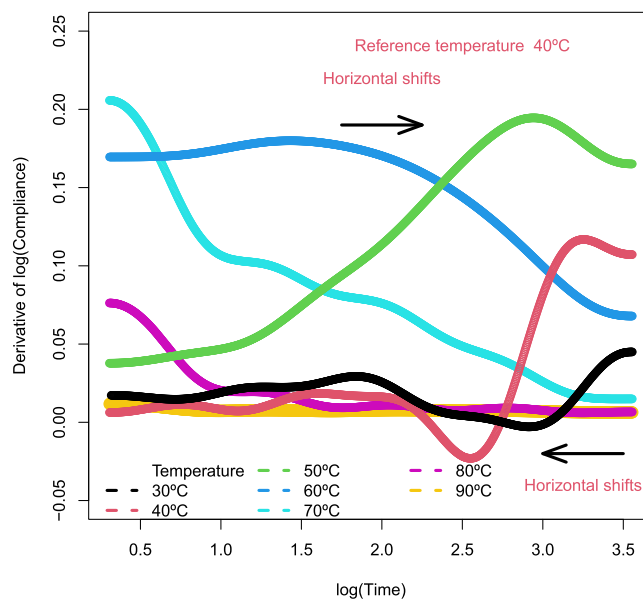


Fig. 4. First derivative of smoothed J curves obtained by the application of smoothing splines.

Considering the relatively high amount of observations in each original J curve, the TTS_{10} can be used instead the TTS function. The application procedure and the values or outputs are the same for both functions. Consequently, from here on, the results of the application of the TTS_{10} function will be shown. Thus, TTS object is again obtained by applying the TTS_{10} function as follows.

```
1 x <- TTS_(Epoxy, method="derived")
2 plot <- PLOT.TTS(x)
```

Listing 4: The TTS_{10} function is applied to the Epoxy dataset to obtain the x TTS object. The MNAT procedure has been selected by `method="derived"`. The corresponding graphical outputs are then also obtained and assigned to the `plot` object by means of the `PLOT.TTS` function.

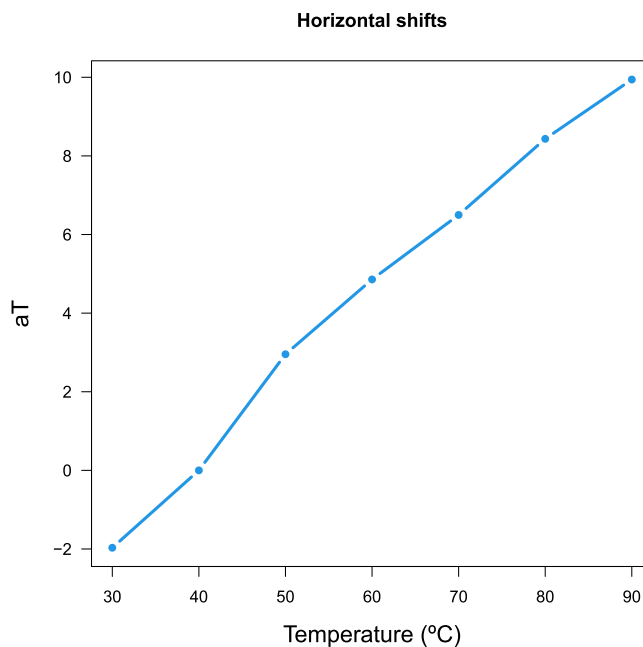


Fig. 5. Horizontal shifts obtained by the MNAT method in order to estimate the master curve of the epoxy composite at 40°C.

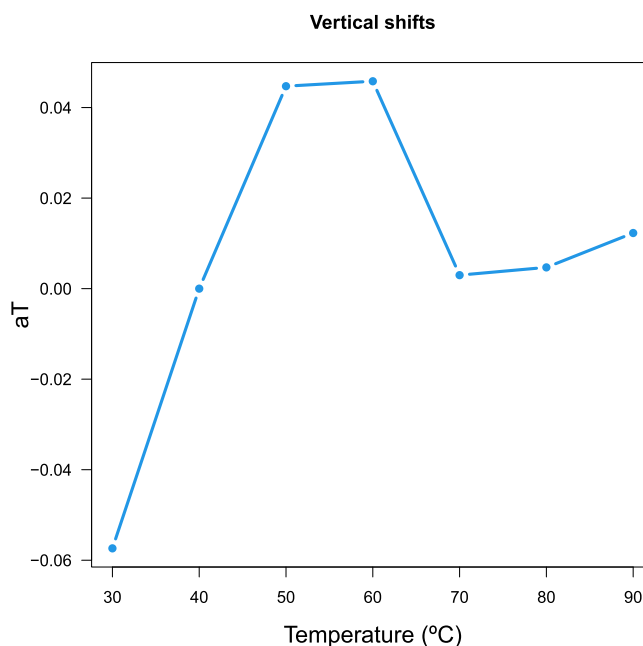


Fig. 6. Vertical shifts obtained by the MNAT method in order to estimate the master curve of the epoxy composite at 40°C.

The a_T shifts are obtained by the "derived" or MNAT method, i.e. by derivative shifting, by applying `PLOT$aT`. The graphical outputs are shown in Figs. 5-6. Alternatively, if `x <- TTS_10(Epoxy, method = "Arrhenius")` or `x <- TTS_(Epoxy, method = "WLF")` were run, the a_T shifts corresponding to Arrhenius or WLF models would be estimated from the aT obtained applying the MNAT method.

```
1 plot$aT(main="Horizontal shifts",cex.lab=1.4,xlab="Temperature (C)", ylab="aT")
```

Listing 5: Obtaining the horizontal shifts for the epoxy composite compliance curves in order to estimate the master curve at 40 Celsius degrees.

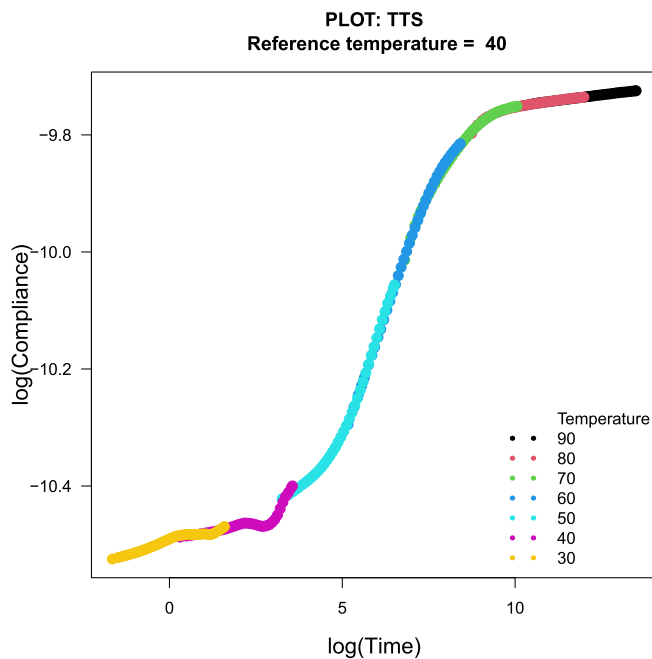


Fig. 7. Master curve at 40 °C corresponding to the epoxy based composite, after shifting of the original J curves by the MNAT method.

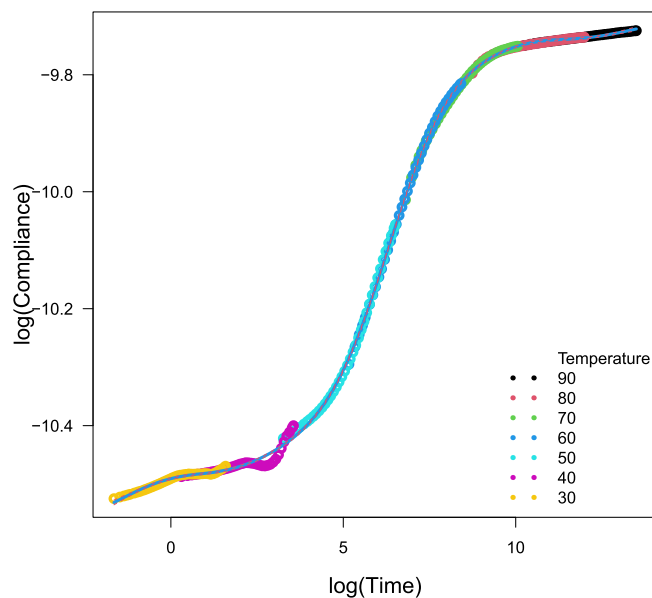


Fig. 8. Master curve at 40 °C corresponding to the epoxy based composite, after shifting of the original J curves by the MNAT method. A B-spline fitting is included (in black) in addition to the corresponding bootstrap intervals (in red).

Additionally, the b_T shifts can be obtained by running `!PLOT$PLOT.bT}! :`

```
1 plot$PLOT.bT(main="Vertical shifts",cex.lab=1.4,xlab="Temperature (C)", ylab="bT")
```

Listing 6: Obtaining the vertical shifts for the epoxy composite compliance curves in order to estimate the master curve at 40 Celsius degrees.

The TTS package also provides both the master curve of J (or, alternatively, other mechanical property such as E') without (Fig. 7) and with B-spline smoothing (Fig. 8) by running the `PLOT$PLOT.TTS.data` and the `PLOT$PLOT.TTS.gam` functions,

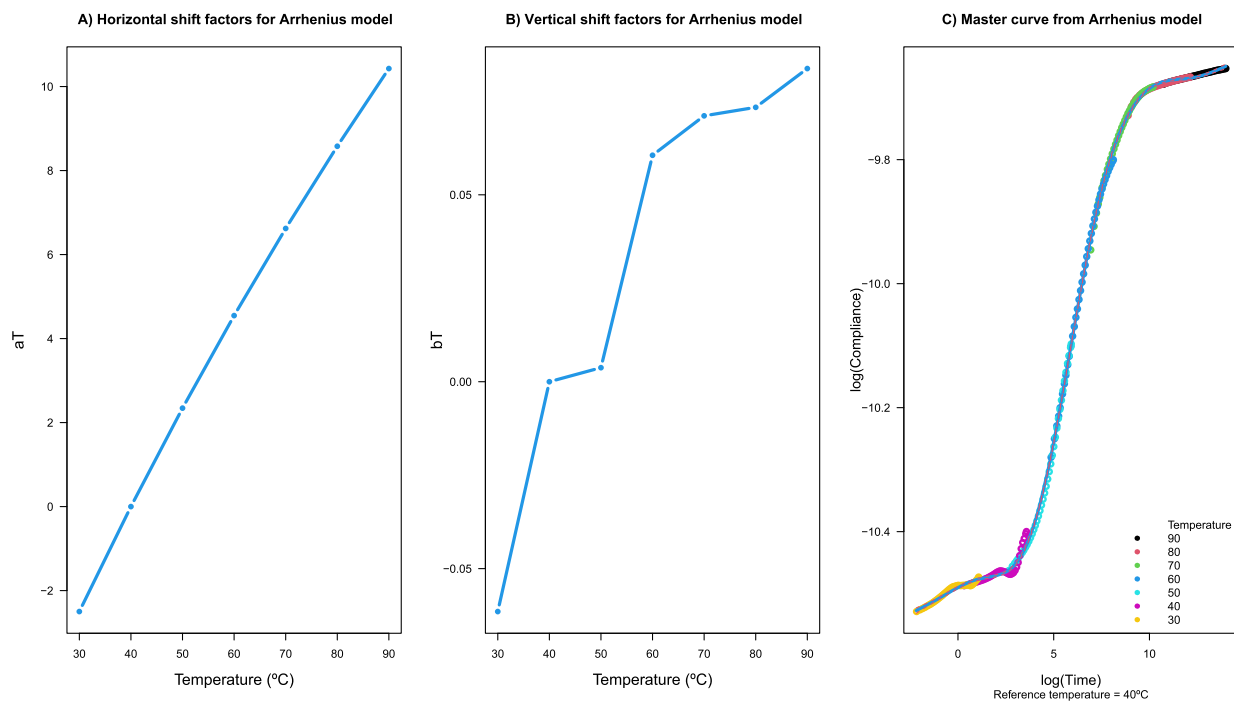


Fig. 9. The horizontal (panel A) and vertical (panel B) shifts to estimate the master curve at a 40 Celsius degrees, assuming the Arrhenius model, are shown. In addition, the corresponding smoothed master curve for the epoxy based composite is also included (panel C).

respectively:

```
1 plot$PLOT.TTS.data(xlab="log(Time)", ylab="log(Compliance)", cex.lab=1.3)
```

Listing 7: Code to obtain the master curve for the epoxy based composite at a 40 Celsius degrees.

```
1 plot$PLOT.TTS.gam(xlab="log(Time)", ylab="log(Compliance)", cex.lab=1.3)
```

Listing 8: Code to obtain the smoothed master curve for the epoxy based composite at a 40 Celsius degrees, assuming the MNAT method. B-splines fitting is applied and bootstrap confidence intervals are also provided.

If the master curves obtained by the application of Arrhenius and WLF methods are required, they can be estimated by replacing `method="derived"` by `method="Arrhenius"` or `method="WLF"` in the `TTS` or `TTS_10` functions, respectively (see Fig. 9). As pointed out in [5], the master curves obtained by the flexible method based on derivative shifting and B-spline fitting are smoother and accurate. Moreover, the implementation of an initial solution for a_T based on the derivative shifting method, can improve the fitting of Arrhenius and WLF models. In fact, a very similar solution for the master curve (and also similar precision) has been obtained. In the following lines, the code corresponding to the application of the Arrhenius method (and the corresponding graphical outputs) is shown. Thus, firstly the `plot_A` TTS object is obtained:

```
1 pc_A <- TTS_10(Epoxy, reference.temperature = 40, n = 1000, nB = 1000, method = "Arrhenius")
2 plot_A <- PLOT.TTS(pc_A)
```

Listing 9: R Code to obtain the master curve by the application of TTS principle, at a 40 Celsius degrees and assuming the Arrhenius model.

The second step is to plot the a_T and b_T shift factors of the Arrhenius model, obtained from the initial solution corresponding to the shift factors computed using the MNAT procedure (see Fig. 9). The master curve is estimated using the a_T and b_T shift factors obtained from the Arrhenius model. Then, the master curve is smoothed by B-spline fitting and the bootstrap confidence intervals are included.

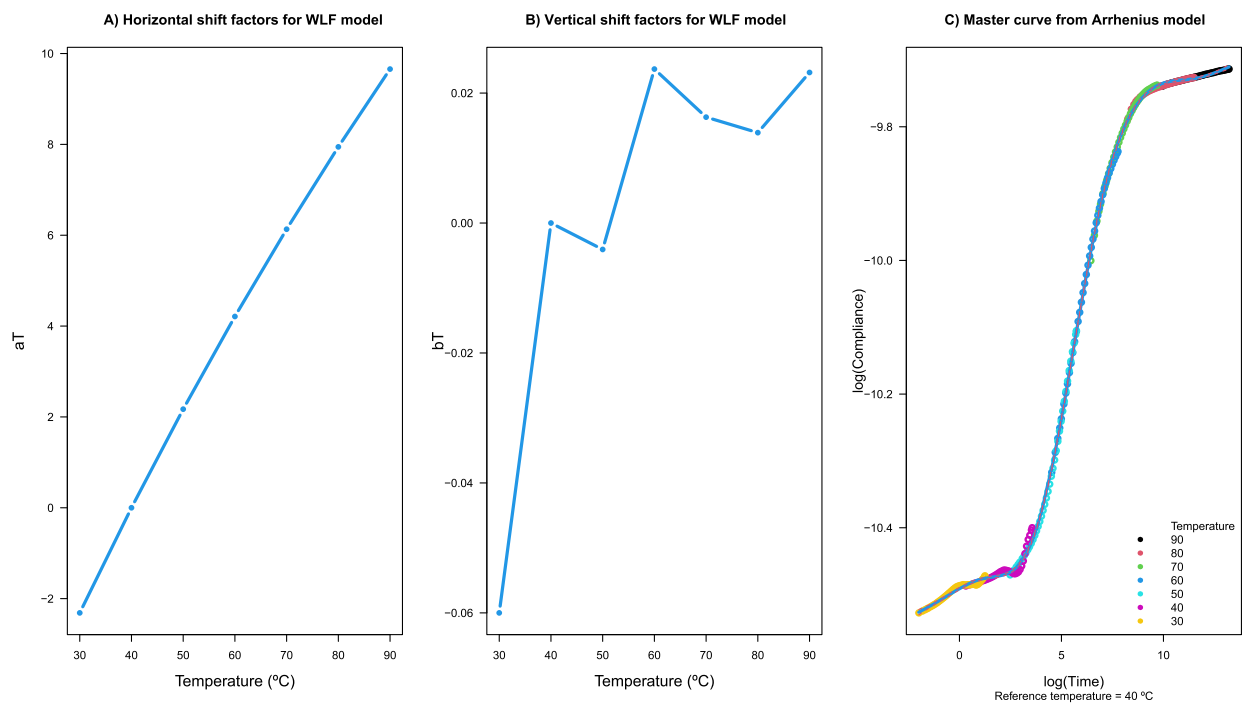


Fig. 10. Horizontal shifts (panel A), vertical shifts (panel B), and smoothed master curve (panel C) obtained by B-spline fitting from WLF shifts, including 95% bootstrap confidence bands with.

```

1 op <- par(mfrow=c(1,3))
2 plot_A$PLOT.aT(main="Horizontal shift factors for Arrhenius model", cex.lab=1.4,xlab="Temperature (C)", ylab="aT")
3 plot_A$PLOT.bT(main="Vertical shift factors for Arrhenius model", cex.lab=1.4, xlab="Temperature (C)", ylab="bT")
4 plot_A$PLOT.TTS.gam(xlab="log(Time)",ylab="log(Compliance)", main = "Master curve from Arrhenius model", sub = "Reference temperature = 40 C",cex.lab=1.3)
5 par(op)

```

Listing 10: R Code to obtain the horizontal and vertical shifts to estimate the master curve at a 40 Celsius degrees, assuming the Arrhenius model. In addition, the corresponding smoothed master curve for the epoxy based composite is also performed in the fourth line of code.

Fig. 10 also shows the smoothed master curve obtained from the WLF shifts. The corresponding R routine is analogous to the Arrhenius one, only replacing `method="Arrhenius"` by `method="WLF"` in the TTS function such as follows.

```

1 pc_W <- TTS_10(Epoxy, reference.temperature = 40, n = 1000, nB = 1000, method = "WLF")
2 plot_W <- PLOT.TTS(pc_A)
3 op <- par(mfrow=c(1,3))
4 plot_W$PLOT.aT(main="Horizontal shift factors for WLF model", cex.lab=1.4,xlab="Temperature (C)", ylab="aT")
5 plot_W$PLOT.bT(main="Vertical shift factors for WLF model", cex.lab=1.4, xlab="Temperature (C)", ylab="bT")
6 plot_W$PLOT.TTS.gam(xlab="log(Time)",ylab="log(Compliance)", main = "Master curve from Arrhenius model", sub = "Reference temperature = 40 C",cex.lab=1.3)
7 par(op)

```

Listing 11: R Code to obtain the horizontal and vertical shifts to estimate the master curve at a 40 Celsius degrees, assuming the WLF model. In addition, the corresponding smoothed master curve for the epoxy based composite is also performed in the sixth line of code.

In Figs. 8, 9, and 10, the estimates for J at $T_0 = 40^\circ\text{C}$ have been expanded to a significant broader range of times, from (2.028, 3600) s to (0, $3.155 \cdot 10^{13}$) s, in the time domain. Using the function `summary`, the different quantiles and the frequency mean in the logarithmic scale are obtained (before and after estimating the master curve).

```

1 summary(data.frame("Logarithm Real Time"=x$data$Log10_time, "Logarithm Extended Time"=x$TTS.gam$frequency))
2
3 Logarithm.Real.Time Logarithm.Extended.Time
4 Min. :0.3071 Min. :-1.651
5 1st Qu.:1.2561 1st Qu.: 2.885
6 Median :2.0865 Median : 6.861
7 Mean :2.0583 Mean : 6.446
8 3rd Qu.:2.8853 3rd Qu.: 9.938

```

Listing 12: Obtaining the ranges of time (in logarithmic scale) in which the $J(t)$ curve for $T=40^{\circ}\text{C}$ before and after the application of the TTS principle.

As a general comment, it is important to highlight that the MNAT method combined with the smoothed B-spline master curve is a nonparametric method that could be applied to estimate the master curve at temperatures above or below the glass transition temperature. This is a goal with respect to the parametric methods, taking into account that the Arrhenius model can be applied below the T_g and the WLF should be used in those cases where the master curve is required at temperatures above the T_g .

Next, the master curve estimate obtained using the present proposal is compared with the estimate obtained by manually shifting the curves by expert and qualified personnel. For this purpose, two different case studies are used, on the one hand, the Epoxy dataset and, on the other hand, the SBS database. Before showing the results, it is important to note that the curves of the SBS database are less smooth than those of the Epoxy database. The smoother the original curves (and the more points or observations that define them), the easier it will be to manually shift curves.

The next code shows how to perform the comparison of the TTS application using the MNAT automatic methodology and the manual shifting procedure (data and complete code are included as supplementary material). The manually shifted original curves have been provided as a text document called Epoxy_Manual.

```

1 # Importing the manually obtained master curve
2 Epoxy_Manual <- read.table("Epoxy_manual2.txt", header=TRUE)
3 # Smoothing of the manually obtained master curve by fitting a thin plate splines basis.
4 model_manual=gam(Log_Compl_Despl~s(Log_timeDespl), data=Epoxy_Manual)
5 op <- par(mfrow=c(1,2))
6 # Manual shifting:
7 plot(subset(Epoxy_Manual, Temperature==30)[,1:2], xlim=c(-0.25, 12.4), col=7,
8      ylim=c(-10.5, -9.725), xlab="log(Time)", ylab="log(Compliance)",
9      main="Master curve obtained by manual shifting", cex=1.5, cex.lab=1.3,
10     sub="Reference temperature = 40 Celsius degrees")
11 lines(subset(Epoxy_Manual, Temperature==40)[,1:2], type="p", col=6, cex=1.5)
12 lines(subset(Epoxy_Manual, Temperature==50)[,1:2], type="p", col=5, cex=1.5)
13 lines(subset(Epoxy_Manual, Temperature==60)[,1:2], type="p", col=4, cex=1.5)
14 lines(subset(Epoxy_Manual, Temperature==70)[,1:2], type="p", col=3, cex=1.5)
15 lines(subset(Epoxy_Manual, Temperature==80)[,1:2], type="p", col=2, cex=1.5)
16 lines(subset(Epoxy_Manual, Temperature==90)[,1:2], type="p", col=1, cex=1.5)
17 legend("bottomright", c("Temperature", "90", "80", "70", "60", "50", "40", "30"),
18      lty = rep(3,8), col=c(0,1:7), lwd=rep(4,8), bty="n")
19 ii=order(Epoxy_Manual$Log_timeDespl)
20 lines(Epoxy_Manual$Log_timeDespl[ii], as.vector(predict(model_manual))[ii], type="l", col=1, lwd=2)
21 # Automatic MNAT shifting:
22 plot$PLOT.TTS.gam(xlab="log(Time)", ylab="log(Compliance)", main="Master curve obtained by MNAT method", cex
23 .lab=1.3)
23 par(op)

```

Listing 13: Epoxy dataset: This code allow us to estimate and plot the master curve at 40 Celsius degrees using the MNAT method and compare it with the master curve obtained by manual shifting (in the dataset called Epoxy_Manual).

The master curve estimates obtained by MNAT and manual methods are shown in Fig. 11. We can observe that the results are very similar. The two results are compared in terms of how smooth (or rough) is the resulting master curve. For this purpose, a thin plate spline fitting is performed to estimate the two master curves and the Mean Squared Error (MSE) is calculated for the two approaches. As a result, the MSE corresponding to the master curve obtained by MNAT method is $MSE_{MNAT} = 2.199 \cdot 10^{-5}$, whereas the MSE of the master curve obtained by manual shifting is $MSE_{Manual} = 1.945 \cdot 10^{-5}$, almost the same value. Therefore, it is observed that the proposed automatic method is able to provide results comparable to those provided by an experienced and qualified expert.

The other case study to be studied is that of the SBS database, also provided in this R package. The time-compliance curves are not as smooth as those corresponding to the Epoxy database, so that manual shifting, even when performed by expert personnel, is more difficult and laborious. The code to obtain the master curve at 40°C using the MNAT procedure is shown below.

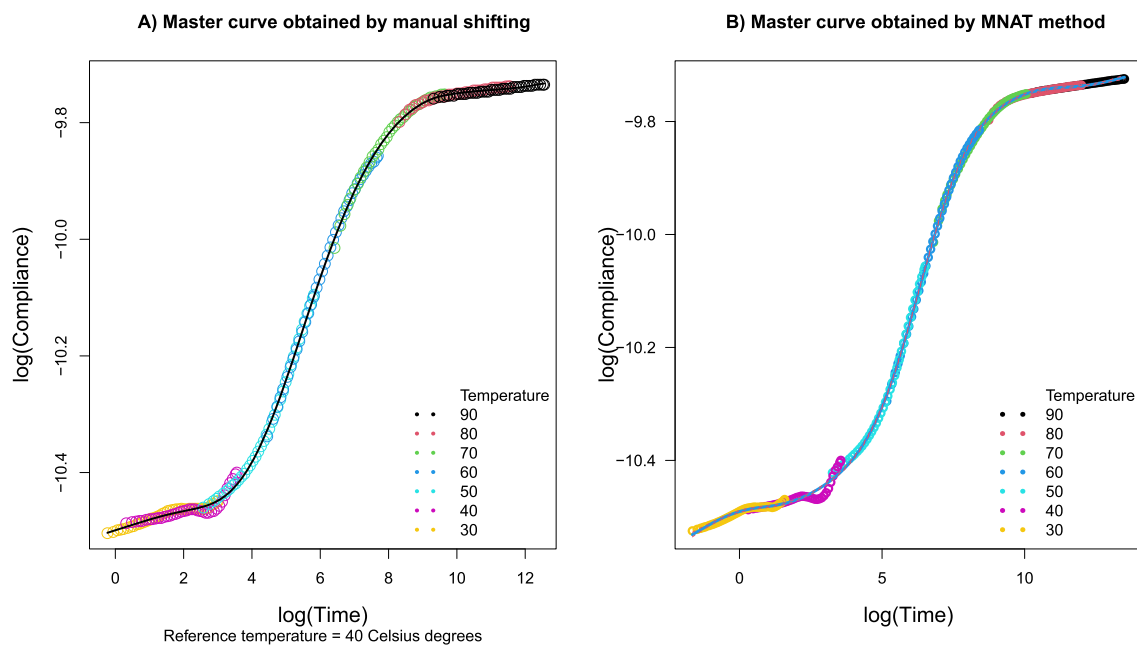


Fig. 11. Master curves for the epoxy based component corresponding to 40°C. They were obtained by the automatic MNAT method (panel B) and the manual procedure performed by skilled personnel (panel A).

```

1 SBS <- read.table("SBS.txt",header=TRUE)
2 y <- TTS_10(SBS,reference.temperature=40, method="derived")
3 PLOT <- PLOT.TTS(y)

```

Listing 14: Code to obtain the master curve at 40°C by applying the MNAT procedure.

```

1 # Importing the manually obtained master curve
2 SBS_Manual=read.table("SBS_manuall.txt",header=TRUE)
3 # Smoothing of the manually obtained master curve by fitting a thin plate splines basis
4 model_manual2=gam(Log_Compl_Despl~s(Log_timeDespl),data=SBS_Manual)
5 op <- par(mfrow=c(1,2))
6 # Manual shifting:
7 plot(subset(SBS_Manual,Temperature==40)[,1:2],xlim=c(0.2,6.2),col=5, ylim=c(-9.83,-9.52), xlab="log(Time)",
8      ylab="log(Compliance)", main = "Master curve obtained by manual shifting",cex=1.5,cex.lab=1.3, sub = "
9      Reference temperature = 40 Celsius degrees")
10 lines(subset(SBS_Manual,Temperature==50)[,1:2],type="p",col=4,cex=1.2,lwd=3)
11 lines(subset(SBS_Manual,Temperature==60)[,1:2],type="p",col=3,cex=1.2,lwd=3)
12 lines(subset(SBS_Manual,Temperature==70)[,1:2],type="p",col=2,cex=1.2,lwd=3)
13 lines(subset(SBS_Manual,Temperature==80)[,1:2],type="p",col=1,cex=1.2,lwd=3)
14 legend("bottomright",c("Temperature","80","70","60","50","40"),
15      lty = rep(3,6),col=c(0,1:5),lwd=rep(4,6),bty="n")
16 iii=order(SBS_Manual$Log_timeDespl)
17 lines(SBS_Manual$Log_timeDespl[iii], as.vector(predict(model_manual2)[iii],type="l",col=6,lwd=2))
18 # Automatic MNAT shifting:
19 PLOT$PLOT.TTS.gam(xlab="log(Time)", ylab="log(Compliance)", cex.lab=1.3, main = "Master curve obtained by
20 MNAT method", sub = "Reference temperature = 40 Celsius degrees")
21 par(op)

```

Listing 15: SBS dataset: This code allow us to estimate and plot the master curve at 40 Celsius degrees using the MNAT method and compare it with the master curve obtained by manual shifting (in the dataset called SBS_Manual).

Next, the comparison between the estimation of the master curve by the two methods is performed in an illustrative way through the code block 15.

The SBS master curve estimates obtained by MNAT and manual methods are shown in Fig. 12. The two curves are compared in terms of roughness of the resulting master curve. For this purpose, a thin plate spline fitting is performed to estimate the two

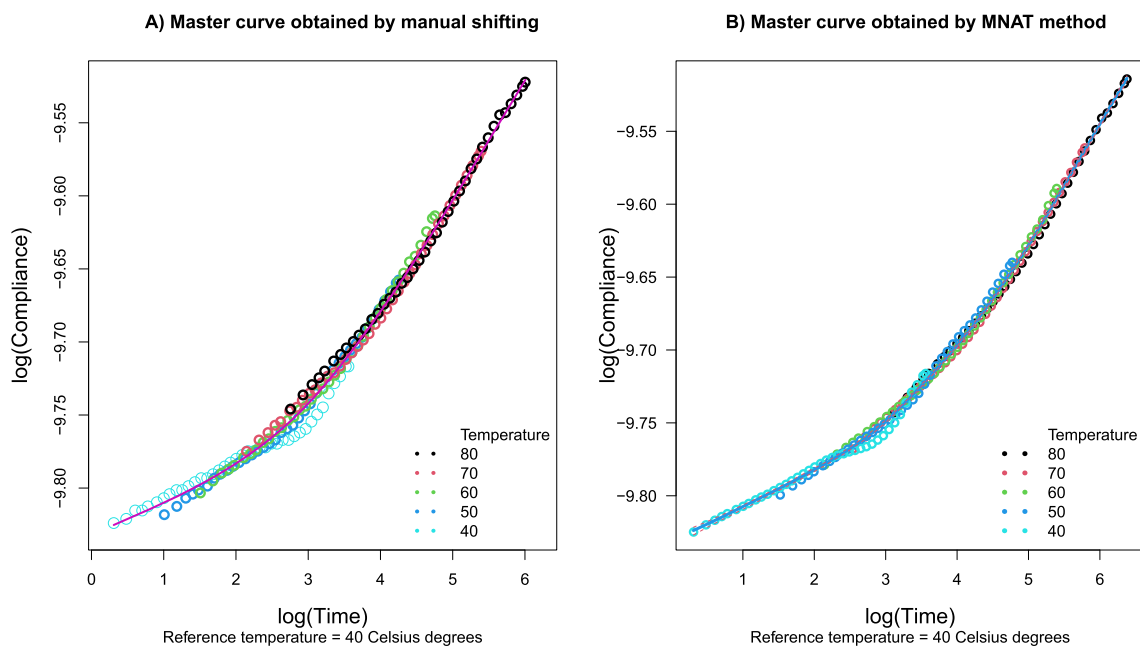


Fig. 12. Master curves for the SBS based component corresponding to 40 °C. They were obtained by the automatic MNAT method (panel B) and the manual procedure performed by skilled personnel (panel A).

master curves from the shifted original curves. Subsequently, the Mean Squared Error (MSE) is calculated for the two approaches. $MSE_{MNAT} = 8.1899 \cdot 10^{-6}$, whereas $MSE_{Manual} = 2.1009 \cdot 10^{-5}$. Thus, the MNAT method provides a smoother master curve (also observed in Fig. 12) than the manual shifting method. This is evidence of the potential usefulness of the proposed method.

6. Conclusions

The increasing demand of free software utilities in material science and material reliability justify to implement new R packages that perform traditional techniques and their recent improvements. At this regard, the TTS package has been developed to perform TTS analysis and to obtain master curves of viscoelastic materials (that meet the TTS principle). It is the first library in R dealing with the TTS principle, physical-based and related to accelerated life testing and reliability. The functions of TTS package provide tools to estimate the mechanical properties, such as storage modulus, of an amorphous polymeric materials out of the experimental time/frequency interval.

In the TTS library, the MNAT nonparametric method has been implemented to obtain smoother master curves and more accurate mechanical properties. It is based on shifting the first derivative curves of viscoelastic properties and employing the L_1 metric. Moreover, the estimation of the Arrhenius and the WLF model parameters has been improved by the addition of an initial solution obtained by the new derivative-based flexible method.

It is important to note that the MNAT methodology could be used to estimate the master curves at temperatures below and above the glass transition temperature, considering its nonparametric nature. This is an advantage with respect to Arrhenius and WLF parametric models.

The case studies shown in this work, dealing with Epoxy and SBS based composites, illustrate the utilities of the TTS package. The master curve can be estimated in a smooth way by using B-spline fitting and the Arrhenius and WLF parametric methods. All the master curve estimates are provided jointly with parametric bootstrap confidence bands, that allows to determine their accuracy and precision.

The automatic procedure for master curve estimation implemented by the TTS package has been compared with the manual curve shifting procedure performed by specialized and qualified personnel. When the original curves are relatively smooth and defined by a high number of points, which is the most favorable case for the manual shifting method, the MNAT procedure implemented in R provides similar results in terms of MSE. This is the case for the application to the Epoxy database, obtaining $MSE_{MNAT} = 2.199 \cdot 10^{-5}$ and $MSE_{Manual} = 1.945 \cdot 10^{-5}$. When the curves are not so smooth, as is the case for the SBS database, the MNAT method provides smoother master curve ($MSE_{MNAT} = 8.1899 \cdot 10^{-6}$) estimates than the manual method ($MSE_{Manual} = 2.1009 \cdot 10^{-5}$).

CRedit authorship contribution statement

Antonio Meneses: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Salvador Naya: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.
 Mario Francisco-Fernández: Analyzed and interpreted the data; Wrote the paper.
 Jorge López-Beceiro; Carlos Gracia-Fernández: Performed the experiments; Contributed reagents, materials, analysis tools or data.
 Javier Tarrío-Saavedra: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data associated with this study has been deposited at <https://cran.r-project.org/web/packages/TTS/index.html>.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.heliyon.2023.e15816>.

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