

A time- and temperature-dependent viscoelastic model based on the statistical compatibility condition

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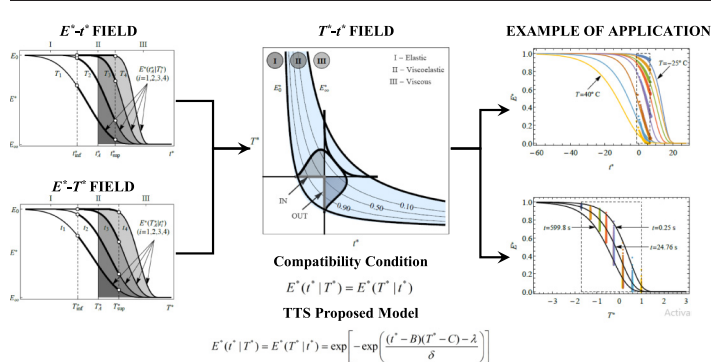
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HIGHLIGHTS

- The statistical compatibility condition is applied to derive the analytical expression of the temperature-time ($T-t$) field.
- The master curves on $E-t$ and $E-T$ fields are obtained in one step over the whole ranges of time and temperature.
- Time overlapping requirement of short-term recorded curves are avoided.
- The suitability of the methodology is confirmed by its application to experimental data of PVB at various temperatures.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper presents a novel methodology to characterize viscoelastic materials, allowing the limitations of current conventional models based on Time-Temperature-Superposition (TTS) principle to be avoided. It implies the definition of the temperature-time field, $T-t$, from short-term recorded relaxation curves at different temperatures by establishing the compatibility condition between the temperature dependent relaxation modulus at given time, $E(T; t)$, and the time dependent relaxation modulus for a given temperature, $E(t; T)$. The solution of the resulting functional equation allows the $T-t$ field to be analytically defined by assuming the normalized relaxation function to be a stochastic model properly identified as a survival cumulative distribution function of certain statistical families such as normal or Gumbel ones. As a result, the corresponding master curves in the $T-t$ field for both $E-t$ and $E-T$ functions are directly derived over the whole range of time and temperature, preventing user's influence on the definition of the classical shift factors and the minimum overlapping requirement over time on the short-term curves. The suitability of the proposed methodology is confirmed by its application to the experimental results from a campaign of relaxation tests on commercial PVB (polyvinyl butyral) at different temperatures.

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1. Introduction and motivation

Viscoelastic materials are nowadays extensively used in multiple engineering and scientific fields of application encompassing a heterogeneous variety of materials ranging from biological to polymeric materials (see for example Diani et al. [1], Zhang et al. [2], Bonning

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et al. [3] and Guo et al. [4]). The main characteristic is their time and frequency dependent properties, which influences all the phases of the engineering design, from manufacturing process (see Astrom [5]) to computational design (see Marques [6]). This process requires to require advanced mathematical methods for modelling their mechanical behaviour (see for example Christensen [7] and Drozdov [8]).

The viscoelastic characterization has been traditionally performed using two kind of strategies, encompassing relaxation and creep tests. In the former case, the viscoelastic specimen is subjected to an initial constant strain input, such as a step impulse, while then the stress is recorded along the time. In turn, in the creep test an initial constant stress is applied as input and the strain is measured along the time. Nevertheless, both strategies are impelled to be tested within a limited time interval, since both viscoelastic phenomena extend during several decades in time, which is not practically affordable. Consequently, alternative methods are required in order to predict the time-dependent properties of the viscoelastic materials beyond the limits of the experimental window, especially the limiting values of the viscoelastic modulus, i.e. the elastic and relaxed moduli. One of the widely used procedures consists in testing at various temperatures and to apply the well-known Time-Temperature Superposition (TTS) principle (or equivalently the Frequency-Temperature Superposition (FTSP) principle), empirically developed in previous works (see Ferry [9], Leaderman et al. [10] and Tobolsky and McLoughlin [11]) and formally stated and disseminated by Williams-Landel-Ferry work (see Williams et al. [12]). This principle, only valid for thermo-rheologically simple materials, assumes the existence of an equivalence between time and temperature by means of which test results at different temperatures are equivalent to those at different times.

Accordingly, the transformation of the relaxation modulus in uniaxial deformation along the time from a given temperature $E(t; T_i)$ to another $E(t; T_j)$ is defined, in accordance with the TTS principle, as follows (see Findley et al. [13] and Ferry [14]):

$$E(\log t; T_j) = E(\log t + \log a_T(T_j, T_i); T_i), \quad (1)$$

where $a_T(T_j, T_i)$ is called the *shift factor*. Despite of the large variety of models based on the TTS principle, proposed over the last decades (see Tschoegl et al. [15]), the Williams-Landel-Ferry proposal finds general acknowledgment to be applied in practical applications (see Williams et al. [12]):

$$\log a_T(T_j, T_i) = \frac{C_1^i(T_j - T_i)}{C_2^i + T_j - T_i}, \quad (2)$$

where C_1^i and C_2^i are constants, which turn out to be only valid for transformations referred to T_i (the superscript in constants indicates the origin of the transformation). In this sense, if the reference temperature is changed, the constants must be also modified according to the well-known symmetric relations (see Ferry [14]).

Additionally to the classical definition of the TTS principle, several efforts were devoted to develop more complex formulations involving more than the horizontal shift factor a_T , such as those proposals based on vertical shift factors or in the combination of them, originally proposed by Honerkamp and Weese [16]. Special mention deserves when the TTS principle holds only approximately and the measurements can show significant scatter, such that the subjective manual shifting must be even more enhanced by objective methods (see Zhao et al. [17], Knauss [18] and Maiti [19]), as for instance those based on minimizing the sum of square errors in horizontal distances in the overlapping (see Honerkamp and Weese [16] and Buttlar et al. [20]), matching first derivatives (see Hermida and Povolito [21] and Naya et al. [22]), minimizing areas in the overlapping regions between two adjacent curves (see Gergesova et al. [23] and ISO 18437-6:2017 [24]) or minimizing the arc-length of the master curve in the complex modulus space (see Cho [25] and Bae et al. [26]). Finally, different numerical improvements

have been proposed, as for example those based on the application of neural networks (see Aulova et al. [27]), Bayesian techniques (see Hernandez et al. [28]) or uncertainty quantifications with statistical bootstrap method (see Maiti [19]).

As well known, the main limitations or inconsistencies of the classical Time-Temperature Superposition (TTS) principle formulations are the following:

1. Firstly, the resulting experimental shift factors from compounding the short-term curves recorded at different temperatures into the final master curve would be different depending on the experience of the user.
2. Secondly, the analytical definition of the shift factors with temperature ($a_T - T$) requires resorting at least to two different TTS models, being usually preferred the WLF and Arrhenius models.
3. Thirdly, current TTS methodologies require overlapping of short-term curves at different temperatures during at least one decade (see for example Gergesova et al. [23]). This implies, unavoidable discontinuity at the different overlapping regions, artificially enforced compatibility to derive the master curve by regression and practical restrains in the experimental campaign.
4. Fourthly, the parameter values and, therefore, the master curve definition depend on the reference temperature adopted. Even if the difference among the obtained results maintains under non-significant limits, it denotes the incongruity of the classical approach.
5. Fifthly, extrapolation using a classical model, such as Arrhenius or WLF, is only feasible towards one of the two limiting cases, $t \rightarrow 0$ or $t \rightarrow \infty$, respectively. The extrapolation to the other limiting case requires resorting to a complementary approach.

In the present work, an alternative methodology for viscoelastic characterization of materials is proposed by deriving the master curve at any reference temperature from the statistical compatibility condition between the distribution functions of viscoelastic moduli for either temperature or time in the T - t field. In this way, any additional assumption concerning the temperature-effect over the relaxation modulus is avoided. From such a compatibility condition, the analytical definition of the T - t field is achieved and, as a result, the master curve either in the E - t field or in the E - T field are directly obtained in one step over the whole range of time and temperature, respectively. As a result, the inconveniences due to the use of different TTS laws for defining analytically the shift factors are now avoided. Furthermore, the required minimum overlapping in the short-term curves during at least one decade, which is required by current methods, is also avoided.

To this aim, the paper is organized as follows. The proposed methodology is described in Section 2, indicating the derivation of the model based on different mathematical considerations. In Section 3, the applicability of the proposal is corroborated with experimental data from a uniaxial relaxation test program on a commercial polyvinyl butyral, commonly denoted as PVB, as referred in Álvarez-Vázquez et al. [29]. Finally, in Section 4 the advantages and limitations of the proposed methodology are discussed, and Section 5 summarizes the main conclusions of this work.

2. The methodology proposed

In what follows, the proposed methodology is sequentially described by establishing different statistical and mathematical conditions underlying the viscoelastic phenomena. Firstly, a dimensional analysis is applied for defining dimensionless variables to be considered in the viscoelastic characterization as an invariant selected system of units. Secondly, the conditional specification of viscoelastic characterization problem is presented, according to which the experimental data from a common relaxation or creep test only represents censored information of the viscoelastic behaviour of the material for a fixed reference value of the variable, this being either temperature or time. In statistical terms this allows the distributions of relaxation moduli to be

determined either for fixed temperature, thus defining the $E-t$ field, or for fixed time, thus defining the $E-T$ field. Thereafter, the compatibility condition between both distributions is applied, allowing the so-called $T-t$ field to be analytically defined as a new paradigm field for deriving the master curves of both fields $E-t$ and $E-T$ at any reference temperature or time, respectively.

2.1. Derivation of the model

2.1.1. Dimensional analysis

Accordingly to the principle of similitude of Buckingham and good-practice in the formulation of scientific laws (see Aczél [30] and Castillo et al. [31]), a reformulation of the variables involved in the viscoelastic characterization is required in order to provide consistent models from a dimensional point of view. Without loss of generality, any functional relation between the involved variables, i.e. temperature and time, influencing the relaxation modulus may be defined in this way:

$$f(t^*, T^*, E^*) = 0, \quad (3)$$

where

$$t^* = \log(t/t_0),$$

$$T^* = (T - T_g)/(T_r - T_g), \quad (4)$$

$$E^* = \log(E(t^*, T^*)/E_\infty) / \log(E_0/E_\infty),$$

and t_0 is a reference time (usually in seconds), E_∞ and E_0 are the limiting values of the relaxation modulus at $t = 0$ and $t \rightarrow \infty$, respectively, and T_r and T_g are two reference temperatures, such as the rubbery and glassy characteristic temperatures of the material, where $T_r > T_g$.

2.1.2. Conditional specification approach

When dealing with censored information related to a physical phenomenon, the conditional statistical specification concept arises in a natural manner. This is the case when considering the time evolution of the relaxation modulus for different given values of an external variable, either temperature or pressure. Indeed, in viscoelastic terms, experimental strategies usually consist in testing the relaxation of the viscoelastic modulus under relaxation conditions along the time, for different fixed values of temperature, providing the well-known $E-t$ field (isothermal relaxation curves). The evolution of the normalized viscoelastic modulus at a fixed reference temperature T_{ref}^* , i.e. $E^*(t^*; T_{ref}^*)$ can be identified as a cumulative distribution function, which, by definition, grows monotonically from zero to the unit value. Equivalently, the alternative field $E-T$ can be defined as well (isochronal relaxation curves). Consequently, the value of the viscoelastic modulus for a fixed reference time t_{ref}^* , i.e. $E^*(T^*; t_{ref}^*)$ can also be identified in statistical terms as a cumulative distribution function.

It is worth emphasizing that these both fields are also proposed in the literature as complementary information related to the viscoelastic behaviour (Stouffer and Wineman [32], Schwarzl [33], Tschoegl et al. [15] and Münstedt and Schwarzl [34]), since the turning point of the isochronal curves may be interpreted as the glass temperature (see Tschoegl et al. [15]).

2.1.3. Compatibility condition between $E^*(t^*; T^*)$ and $E^*(T^*; t^*)$

As a statistical interpretation, the previous distributions $E^*(t^*; T^*)$ and $E^*(T^*; t^*)$ can be contemplated as representing the probability of the viscoelastic modulus E^* being less or equal than some particular value E_A^* at a certain given time or temperature, that is, $E^*(t_A^*; T_i^*) = Pr(E_A^* \leq E^*(t_A^*) | T^* = T_i^*)$ and $E^*(T_A^*; t_i^*) = Pr(E_A^* \leq E^*(T_A^*) | t^* = t_i^*)$, respectively. In Fig. 1, both distributions are illustrated for different fixed values of temperature or time, the same as can be obtained in a typical relaxation test carried out in the time range with limiting times t_{inf}^* and t_{sup}^* for a temperature range between T_{inf}^* and T_{sup}^* (experimental

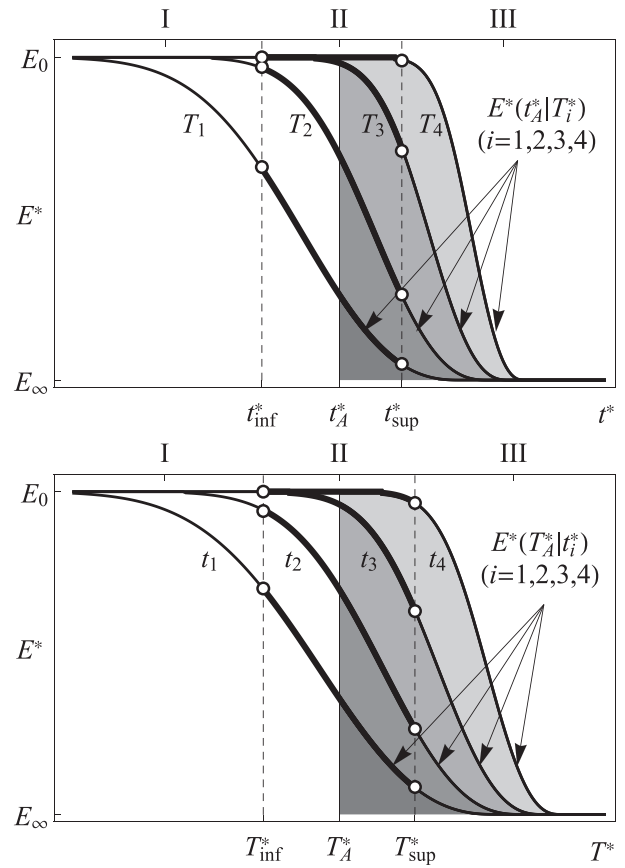


Fig. 1. Illustration of the $E-t$ field for different temperatures (above) and $E-T$ field for different times (below).

window), such that $T_{inf}^* \leq T_1^* < \dots < T_4^* \leq T_{sup}^*$ and $t_{inf}^* \leq t_1^* < \dots < t_4^* \leq t_{sup}^*$. As well-known, due to the limited duration of the relaxation test, zone II can be obtained experimentally while zones I and III must be derived by applying the suitable extrapolation method.

Though $E-T$ and $E-t$ are the most significant fields, the $T^* - t^*$ field is also feasible to be defined as already suggested in literature (see Schwarzl [33] and Münstedt and Schwarzl [34]). Each point in this field, given as (t_i^*, T_j^*) , represents an experimental record corresponding to a particular value of time and temperature, as obtained directly from relaxation test results. Accordingly, the results for a given temperature T^* , i.e. the distribution function $E^*(t^*; T^*)$ are identified as a set of points along the t^* -axis at the corresponding temperature ordinate. In the same way, the results for a given time t^* , i.e. the distribution function $E^*(T^*; t^*)$, are represented by a set of points along the T^* -axis at the corresponding x -coordinate. Fig. 2 shows a schematic representation of $T^* - t^*$ field pointing out the experimental short-term relaxation curves located at different temperatures coordinates within the experimental time window between t_{inf}^* and t_{sup}^* .

Once the $T^* - t^*$ field is established, the practical interest lies on the analytical derivation of the relaxation iso-modulus curves (also known as iso-*timics* in Tschoegl et al. [15]), which represent the same value of the viscoelastic modulus for any combination of time and temperature. To this purpose, Castillo and Fernández-Canteli [35] established originally the statistical compatibility condition concept in an equivalent field concerning with the fatigue lifetime prediction problem, namely, with the S-N field. Indeed, both fatigue and viscoelastic phenomena have in common to be similar examples of accelerated lifetime testing strategies. The physical interpretation of the compatibility condition in $T^* - t^*$ field consists in the fact that the same number of iso-modulus curves crossing the horizontal line for a fixed value of temperature

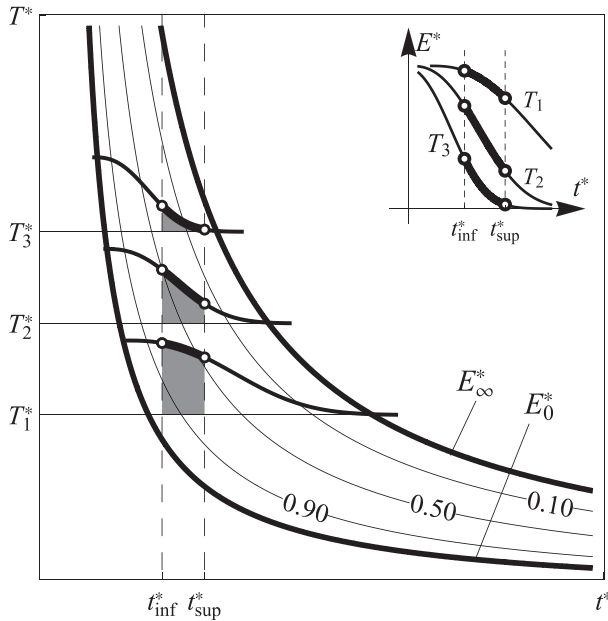


Fig. 2. Schematic illustration of short-term curves for relaxation modulus from the experimental campaign on the $T^* - t^*$ field pointing out the iso-modulus curves ($E^* = 0.0, 0.10, 0.50, 0.90, 1$).

must also intersect the corresponding vertical line for a given value of time (see the iso-modulus curves for $E^* = \{E_0^*, 0.90, 0.50\}$ crossing the gray lines in Fig. 3), that is, both distributions for given values of time or temperature must be the same and, consequently, their implied areas must be equal, as can be seen in Fig. 3. This condition leads to the following functional equation between the distributions for a given temperature and for a given time, originally developed by Castillo and Fernández-Canteli [35]:

$$E^*(t^*; T^*) = E^*(T^*; t^*), \tag{5}$$

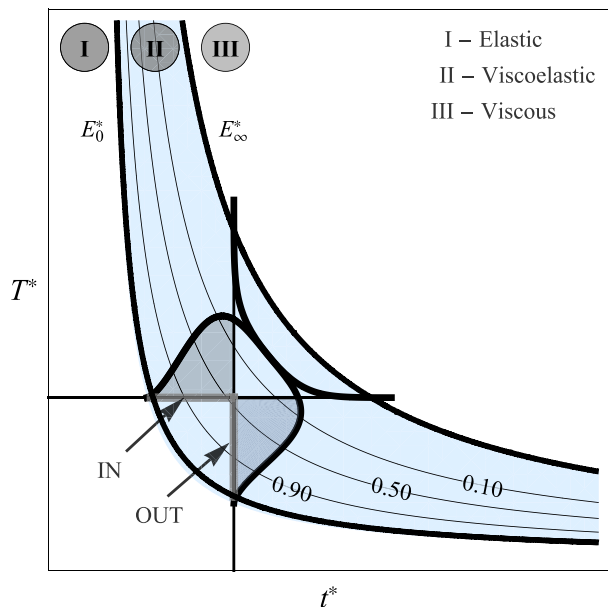


Fig. 3. Illustration of the compatibility between both distributions for a given temperature and time allowing three areas bounding the viscoelastic behaviour to be distinguished.

whose solution provides the unique possible analytical definition of the $T^* - t^*$ field, depending on the particular statistical distribution to which the relaxation modulus is assumed to belong.

As has been mentioned in previous section, the limiting values of the viscoelastic modulus are of great practical importance in the engineering design. In other words, the interest may be focused on two different scenarios: a) extrapolation to the elastic modulus E_0 , or, equivalently, to the viscoelastic modulus for very short time values, and b) extrapolation to the relaxed modulus E_∞ , or, equivalently, to the viscoelastic modulus for very large time values. Accordingly to the Extreme Value Theory, both cases can be conveniently dealt by assuming the distributions $E^*(t^*; T^*)$ and $E^*(T^*; t^*)$ as cumulative distribution functions of the generalized extreme value (GEV) family of distributions. Thus, if the first case of minimal values is concerned, two survival minimal laws for both variables time $t^* | T^*$ and temperature $T^* | t^*$ must be considered as a family of location and scale parameters, that is,

$$1 - q_{\min} \left(\frac{t^* - \lambda_{t^*}(T^*)}{\delta_{t^*}(T^*)} \right) = 1 - q_{\min} \left(\frac{T^* - \lambda_{T^*}(t^*)}{\delta_{T^*}(t^*)} \right), \tag{6}$$

where $q_{\min}(x)$ represents a distribution for minima, such that the survival function is defined as $S(x) = 1 - q_{\min}(x)$, with $\lambda_{t^*}(T^*)$ and $\lambda_{T^*}(t^*)$ as location parameters and $\delta_{t^*}(T^*)$ and $\delta_{T^*}(t^*)$, depending on temperature T^* and time t^* , respectively. Particularly, Gumbel is found to be suitable candidate for modelling the relaxation phenomenon, with possible extension to the Weibull distribution, as described in the following section.

2.2. The proposed Gumbel-Gumbel model

If both time and temperature variables are assumed to be represented by Gumbel distribution, $q_{\min}(x) = 1 - \exp[-\exp(x)]$, which after substitution in Eq. (6), results as:

$$E^*(t^*; T^*) = \exp \left[- \exp \left(\frac{t^* - \lambda_{t^*}(T^*)}{\delta_{t^*}(T^*)} \right) \right]; -\infty \leq t^* \leq \infty, \tag{7}$$

$$E^*(T^*; t^*) = \exp \left[- \exp \left(\frac{T^* - \lambda_{T^*}(t^*)}{\delta_{T^*}(t^*)} \right) \right]; -\infty \leq T^* \leq \infty, \tag{8}$$

Replacing Eqs. (7) and (8) into Eq. (5), leads to a functional equation with 4 unknown functions, providing the solution of the Gumbel survival model for relaxation modulus (see Castillo and Fernández-Canteli [35] and Arnold et al. [36]):

$$E^*(t^*; T^*) = E^*(T^*; t^*) = \exp \left[- \exp \left(\frac{(t^* - B)(T^* - C) - \lambda}{\delta} \right) \right], \tag{9}$$

such that $t^* > B$ and $T^* > C$. The product $V^* = (t^* - B)(T^* - C)$ represents a normalizing variable that allows the experimental data (T^*, t^*) pertaining to the $T^* - t^*$ field to be pooled as a single Gumbel cumulative distribution function with λ as location parameter, related with $E^* = 0.632$, and δ as scale parameter, related with the sample size. Fig. 4 illustrates the resulting $T^* - t^*$ field from the Gumbel-Gumbel compatible model. Note the practical consequences from the existence of either time (B) and temperature (C) asymptotes. The first asymptote of the model provides a time value below which the material shows elastic behaviour, independently of temperature. The second asymptote of the model ensures a temperature value below which the material exhibit linear-elastic behaviour independently of the exposure time, proving that the relaxation phenomenon does not take place below this temperature.

2.3. Parameter estimation

The parameter estimation of the model is based on the solution originally proposed by Castillo and Fernández-Canteli [35] by analyzing the

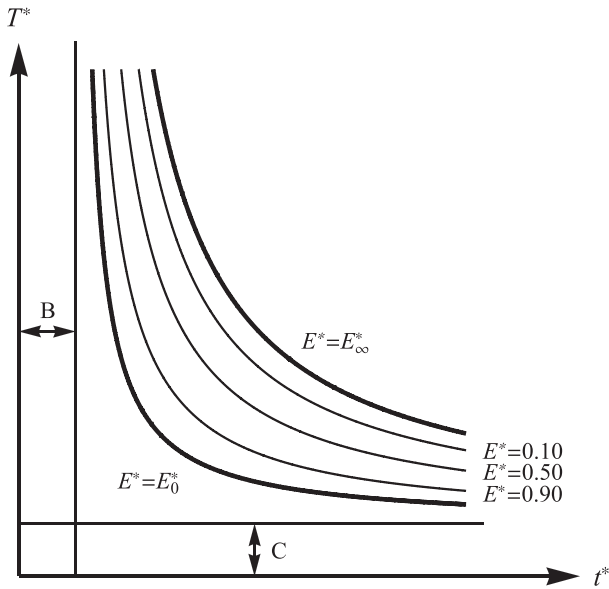


Fig. 4. Iso-modulus curves representing the relationship between the temperature and time in the $T^* - t^*$ field for the Gumbel-Gumbel model.

fatigue problem, which only requires the direct substitution of the $\Delta\sigma^* - N^*$ field by the equivalent $T^* - t^*$ field to be applied in the present viscoelastic problem. These authors define the following steps:

1. Estimation of B and C values. The asymptotes of the Gumbel-Gumbel model can be estimated by minimizing the following equation:

$$Q(B, C, \mu) = \sum_{k=1}^K \sum_{i=1}^N \left(t_{ik}^* - B + \frac{\mu}{T_k^* - C} \right)^2, \quad (10)$$

in which μ represents the mean value of the time variable, while t_{ik}^* represents the i -th time for the k -th temperature T_k^* .

2. Calculation of the V^* values. Once the values of the two asymptotes, B and C are estimated, the normalization variable V^* results can be straightforwardly obtained according to Eq. (9), that is,

$$V_{ik}^* = (t_{ik}^* - B)(T_{ik}^* - C), \quad (11)$$

3. Estimation of the Gumbel parameters. The resulting experimental values of the normalization variable V_{ik}^* must be crossed one-by-one with the decreasing experimental normalized relaxation modulus values E_{ik}^* , allowing all of the data to be pooled into one single Gumbel survival cdf of Gumbel distribution representing the $E^* - V^*$ field. Then, the estimation of the Gumbel parameters λ and δ can be performed according to one of the standard methods for estimating the extreme value family of distributions (see Castillo et al. [37]), such as that based on the probability paper.

Further details about the derivation of this parameter estimation method can be found in the original works of Castillo and Fernández-Canteli [35].

3. Example of practical application

In this section, the proposed methodology is applied to the results of an experimental campaign performed by the authors (see Álvarez-

Vázquez et al. [29]) on a commercial polyvinyl butyral (PVB), widely used in a large variety of applications, such as solar panels, structural laminated glass elements, among others. Firstly, a brief description of the experimental campaign is presented. Secondly, the proposed Gumbel-Gumbel model is applied to the experimental data to obtain the $E^* - t^*$ and $E^* - T^*$ fields as a direct result from the $T^* - t^*$ field estimation.

3.1. Description of experimental data

The experimental campaign consisted in a set of relaxation tests under uniaxial deformation carried out with the DMA RSA3 equipment of T. A. Instruments on Polyvinyl Butyral (PVB) specimens at eight different temperatures ($m = 8$). The characteristic temperatures used for dimensional purposes are those corresponding with the rubbery ($T_r = 40^\circ\text{C}$) and the glassy ($T_g = 16^\circ\text{C}$) states for PVB, according to Eq. (4). Similarly, the limiting values E_0 and E_∞ are directly obtained from the experimental campaign as the maximum ($E_0 = 1.29 \times 10^9$ MPa) and minimum ($E_\infty = 8.94 \times 10^5$ MPa) values reached, respectively. Fig. 5 illustrates the relaxation short-term isothermal curves, or $E-t$ field, and the same information this time viewed from the corresponding $E-T$ field, showing some isochronal curves at three different times t_1 , t_2 and t_3 from a total number of $n = 1200$ recorded times in the interval $[0.25, 599.80]$ seconds. Further details about the experimental campaign can be found in Álvarez-Vázquez et al. [29].

3.2. Application of Gumbel-Gumbel model

As mentioned in the preceding sections, the proposed methodology aims at estimating the $T^* - t^*$ field from the experimental data at

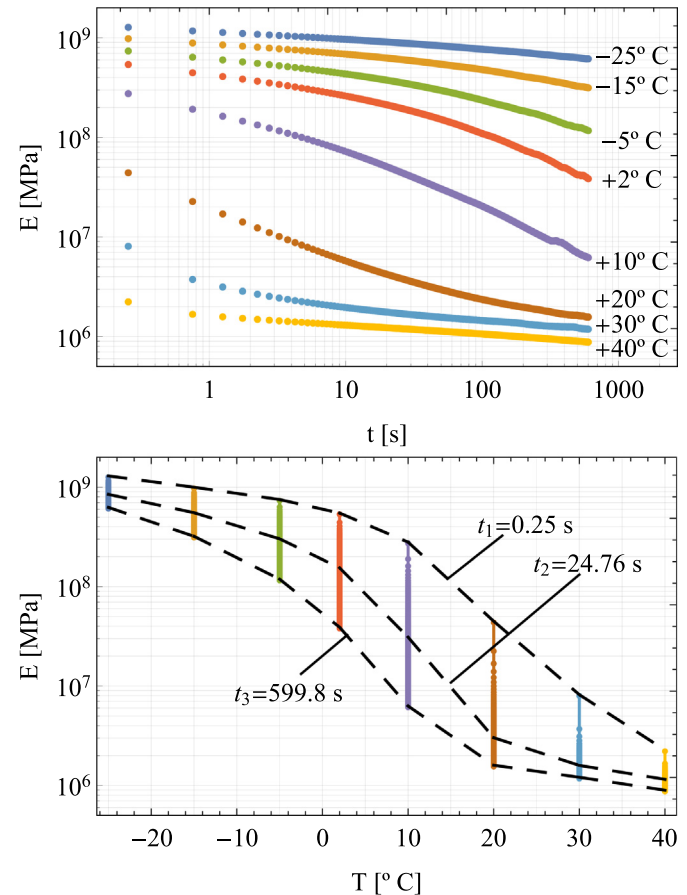


Fig. 5. Experimental relaxation $E-t$ field at eight different temperatures (above) and $E-T$ field (below) for experimental data from Álvarez-Vázquez et al. [29] at eight different temperatures.

different temperatures and, as a result, predicting both fields $E^* - t^*$ and $E^* - T^*$ to be predicted over the whole range of time and temperature. Thus, the parameter estimation method from Section 2.3 with the experimental data from Álvarez-Vázquez et al. [29] provides the following expression for the Gumbel-Gumbel compatible model:

$$E^*(t^*; T^*) = \exp \left[- \exp \left(\frac{(t^* + 16.37)(T^* + 2.90) - 55.06}{9.86} \right) \right]. \quad (12)$$

The practical significance of the resulting asymptotes from the Gumbel-Gumbel model must be emphasized. On the one hand, the horizontal asymptote C indicates that this viscoelastic material does not show relaxation process for temperatures below $C = -2.90$ (or accordingly to Eq. (4), for -53.6°C) independently of the duration implied in the test. On the other hand, the value $B = -16.37$ of the vertical asymptote indicates that the relaxation process will not occur for shorter values than 7.8×10^{-8} s, according to Eq. (4), independently of the temperature at which the specimen is tested. Fig. 6 (above) illustrates the $T^* - t^*$ field from Eq. (12) resulting from the estimation of the experimental data. As an additional relevant advantage of the proposed methodology, all experimental data can be pooled together in one single cdf pertaining to the Gumbel distribution, acting as a general master curve, as can be seen in Fig. 6 (below).

Fig. 7 illustrates the prediction of both fields $E^* - t^*$ and $E^* - T^*$ provided by the Gumbel-Gumbel compatible model according to Eq. (12) for the whole time range and the master curve at a reference temperature of 20°C obtained from conventional use of the Arrhenius model for $T < T_g$ range and the WLF model for $T > T_g$ range. An acceptable

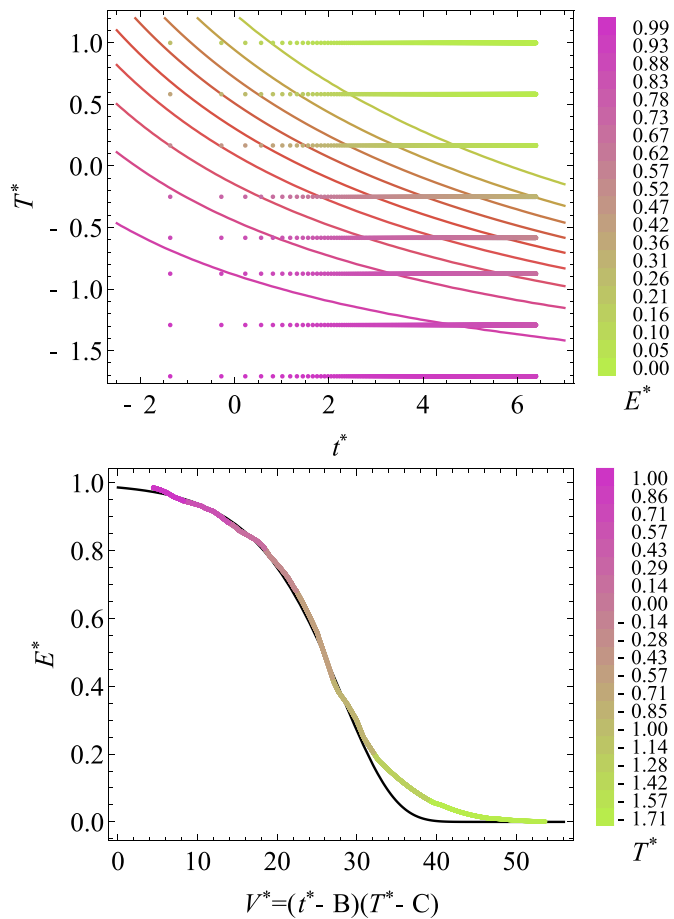


Fig. 6. Experimental data for $T^* - t^*$ field from Álvarez-Vázquez et al. [29] with iso-modulus curves (above) and the corresponding cdf for normalization variable V^* according to Gumbel-Gumbel model (below).

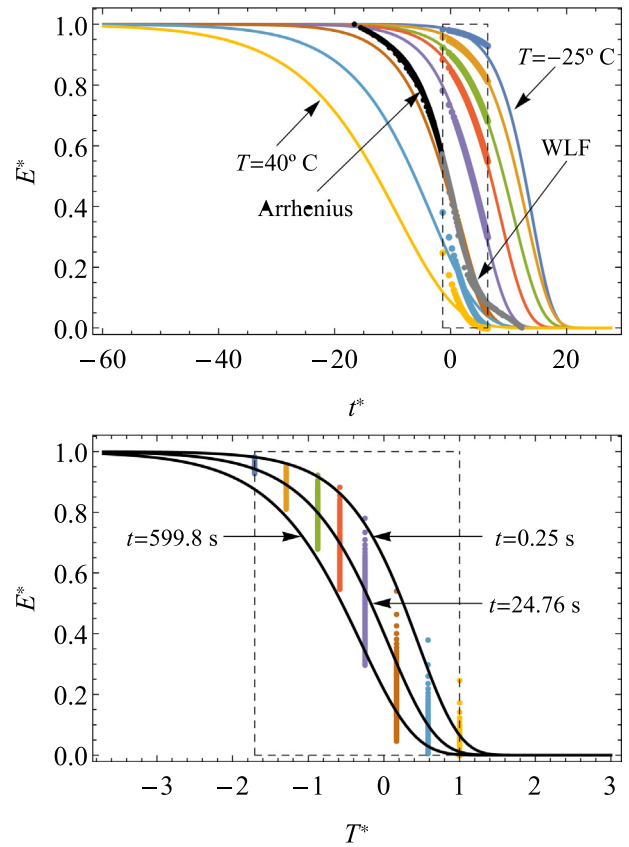


Fig. 7. Experimental data for the $E^* - t^*$ field and master curve at a reference temperature of 20°C obtained from WLF + Arrhenius (above) and $E^* - T^*$ field (below) with the corresponding iso-thermal and isochronal curves provided by the Gumbel-Gumbel model for experimental data from Álvarez-Vázquez et al. [29].

agreement between the experimental short-term curves and theoretical curves is corroborated for both fields. Due to the analytical definition of both fields in Eq. (12), the prediction of the viscoelastic properties under time and temperature conditions other than considered here can be also performed. Note also that the proposed methodology allows any master curve at both fields to be directly obtained in a unique step. In turn, current TTS methodologies are based on the combined use of at least two different models, such as Arrhenius and WLF ones, in order to define analytically the shift factors over the whole range of temperatures of interest, which is one of the greatest limitations avoided with the proposal in this work.

4. Discussion

In summary, the proposed methodology for viscoelastic characterization shows the following advantages in comparison with current TTS models:

- (a) Dimensional consistency. A dimensional analysis is firstly performed in order to derive models dealing with non-dimensional variables, being insensitive to the system of units selected.
- (b) Conditional statistical specification approach of the relaxation phenomenon. The relaxation phenomenon is handled using a statistical approach, indicating that traditional experimental strategies of testing at a fixed value of an external variable, such as temperature or pressure, represents a conditional information, which can be conveniently contemplated from a statistical perspective based on the compatibility condition between $E^* - t^*$ and $E^* - T^*$ fields.

- (c) Simultaneous derivation of $E^* - t^*$ and $E^* - T^*$ field. The estimation of the $T^* - t^*$ field allows the other fields $E^* - t^*$ and $E^* - T^*$ to be directly derived for any time or temperature by establishing the statistical compatibility condition between $E^*(t^*; T^*)$ and $E^*(T^*; t^*)$.
- (d) Simultaneous derivation of master curves. Any master curve in $E^* - t^*$ and $E^* - T^*$ field can be simultaneously derived from the estimation of the $T^* - t^*$ field over the whole range of time and temperature, respectively.
- (e) Free-assumptions. The proposed methodology is derived without resorting to any arbitrary assumption related to the temperature-effect on the viscoelastic modulus, providing a robust model with strong mathematical and physical justifications.
- (f) Full applicability in temperature range. Current TTS models are only applicable over a limited range of temperatures and, consequently so that, at least, two different models must be considered. On the contrary, the proposed methodology is valid for the whole range of temperatures.
- (g) Non-overlapping constraint. Another important limitation of the current TTS methodologies is the so-called “rule of thumb” by which the short-term relaxation curves must be overlapped at least during a decade in order to provide suitable matching in the master curve. In the proposed methodology any overlapping in these short-term curves is required.

5. Conclusions

- The proposed methodology allows the analytical definition of the relaxation modulus $E(t)$ to be achieved from experimental campaigns with short-term curves at different temperatures through the estimation of the $T^* - t^*$ field.
- The analytical definition of the $T^* - t^*$ field is derived from establishing the statistical compatibility condition for the distribution of viscoelastic modulus when either time or temperature are fixed. The use of the Gumbel distribution is proposed for time and temperature variables, with possible extension to the Weibull and extended Normal ones attending to phenomenological and statistical reasons.
- The proposed methodology allows to summarize the whole experimental data from short-term curves at different temperatures in one single cdf, acting as a general master curve, from which any other master curve in both fields, $E^* - t^*$ and $E^* - T^*$, can be obtained.
- This proposal avoids any arbitrary assumption concerning the temperature effect, thus constituting a more robust model.
- The suitability of the proposal is corroborated by practical data from an experimental campaign on a commercial polyvinyl butyral (PVB) tested at various temperatures.

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.

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