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On characterization of Williams-Landel-Ferry equation for non-linear analysis

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A simple approach was developed for numerical evaluation of unknown parameters of Williams-Landel-Ferry equation used for non-linear analysis. The approach consists of an iterative process, where each iteration is reduced to a linear regression problem with respect to a specific set of parameters. The process continues until the required accuracy is satisfied. The approach accounts for the non-linearity of deformation, shows fast convergence, and offers high statistical reliability. Good correlation was found between predicted and measured magnitudes of storage modulus for an elastomer considered in this study.

1. Introduction

Visco-elastic properties of polymers and elastomeric materials are reported to be very sensitive to ambient temperature and frequency of loading (see, for example [1–5]). Empirical Williams-Landel-Ferry transformation [1] or a so-called WLF equation is widely used to predict the effect of temperature, T, and frequency, ϖ on material behavior. Shear modulus G, for example, may be written as

$$G = G(T, \varpi) = G(\varpi_r) \tag{1}$$

where ϖ_r is the reduced frequency and adjusted at a given temperature as [1]

$$\varpi_r = \varpi\alpha_T; \tag{2}$$

where

$$\alpha_T = \exp\left\{\frac{-A(T - T_0)}{B + (T - T_0)}\right\} \tag{3}$$

$A = 8.86$ and $B = 101.6\,^\circ$C are empirical material parameters and assumed to be absolute constants for any polymer [1]. T_0 is a reference temperature approximately 50 °C above the glass transition temperature of the polymer [1].

In literature, it is frequently shown (see, for example, reviews [3–5]) that the relation between $\log(G)$ and $\log(\varpi_r)$ is almost linear in the region of rubber-like behavior. Thus, $G(T, \varpi)$ may be approximated as

$$G(T, \varpi) = \Psi(T, \varpi)G_0 \tag{4}$$

where

$$\Psi(T, \varpi) = \left\{\frac{\varpi_r}{\varpi_0}\right\}^\beta = \left\{\left(\frac{\varpi}{\varpi_0}\right)\alpha_T\right\}^\beta \tag{5}$$

while β is the empirical material parameter; ϖ_0 is an arbitrary reference frequency; G_0 is the shear modulus at $T = T_0$ and $\varpi = \varpi_0$.

If G_0 is assumed to be a material constant at fixed temperature and frequency (i.e., not a function of load) phenomenological approximation of $\Psi(T, \varpi)$ may be carried out using a relevant statistical treatment, such as the method of least squares (MLS). However, visco-elastic properties of elastomeric materials depend on the stress-strain state due to significant levels of non-linearity. Therefore, in the domain of practical interest, shear modulus G should be expressed as $G = G(T, \varpi, \gamma)$, where γ is the loading characteristic (strain amplitude of cyclic loading). Function $G(T, \varpi, \gamma)$ is usually approximated in engineering applications as

$$G(T, \varpi, \gamma) = \Psi(T, \varpi)G_0(\gamma) \tag{6}$$

where the function $G_0(\gamma)$ reflects the non-linear response and may be written as a polynomial

$$G_0(\gamma) = \sum_{n=0}^{N} g_n\gamma^n \tag{7}$$

Characterization of $G(T, \varpi, \gamma)$ is much more difficult than evaluating $G(T, \varpi)$ for a linear analysis, since the non-linearity significantly complicates statistical treatment of the problem. The difficulty is associated with the fact that parameters A, B, and β, introduced in the classical linear analysis, have to reflect the non-linear nature of loading. If parameters of $G_0(\gamma)$ were approximated at specific values of T and ϖ, the predicted function $G_0(\gamma)$ would be valid for those conditions only. On the other hand, approximations for $\Psi(T, \varpi)$ can be developed exclusively at specific values of γ.

The purpose of this paper is to propose a simple approach for the characterization of parameters accounting for the non-linearity of material response.

2. Approach

In this study, parameters A and B are not considered as absolute constants, and evaluated therefore, as specific characteristics of a given material obtained using a statistical treatment. Thus, material parameters g_n ($n = 0, \ldots, N$), β, A, B may be evaluated using relevant experimental data obtained at different loading conditions, temperatures, and frequencies. If the experimental data set includes $T^{(k)}$, $\varpi^{(k)}$, $\gamma^{(k)}$, and $G^{(k)}$; $k = 1, \ldots, K$, where K is the number of experiments (population size), the unknown material parameters may be evaluated in principle using MLS as

$$\xi = \sqrt{\frac{1}{K}\sum_{k=1}^{K}\left\{G^{(k)} - G\big(\beta, A, B, g_n, T^{(k)}, \varpi^{(k)}, \gamma^{(k)}\big)\right\}^2} \rightarrow \min \tag{8}$$

where the objective is to minimize ξ and the analytical approximation $G(\beta, A, B, g_n, T, \varpi, \gamma)$ is given by Expression (6). It should be noted that direct solution of (8) with respect to g_n, β, A, B cannot be obtained through a system of linear equations due to the complex form of Equation 6. The solution is generally reduced to a multi-dimensional, multi-extremum problem, which is very difficult to solve numerically. The following iterative procedure is proposed to overcame this difficulty:

Step 1. Introduce initial (*rough approximations*) *magnitudes of parameters* β, A, B.
Step 2. Calculate refined magnitudes of parameters g_n. Here, Equation 6 is written according to approximation (7) as

$$G_0(\gamma) = \sum_{n=0}^{N} g_n\gamma^n \tag{9}$$

where

$$G_0(\gamma) = \frac{G}{\Psi(T, \varpi)} = \frac{G}{\left\{\left[\dfrac{\varpi}{\varpi_0}\right]\alpha_T[T]\right\}^{\beta}} \tag{10}$$

Statistical characterization of Equation 9 with respect to parameters g_n may be easily developed using classical MLS. For this simple statistical problem, the response $G_0^{(k)}$ corresponding to kth experimental point $\gamma^{(k)}$ is calculated as

$$G_0^{(k)} = \frac{G^{(k)}}{\left\{\left[\dfrac{\varpi^{(k)}}{\varpi_0}\right]\alpha_T\left[T^{(k)}\right]\right\}^{\beta}} \tag{11}$$

Step 3. Calculate refined magnitudes of parameters β, A, and B. These parameters are evaluated using g_n calculated in Step 2. In such a case, Equation 7 can be written as

$$\Psi(T, \varpi) = \left\{\left(\frac{\varpi}{\varpi_0}\right)\alpha_T(T)\right\}^{\beta}, \tag{12}$$

where experimental magnitudes of $\Psi^{(k)} = \Psi(T, \varpi)$ corresponding to kth observation are calculated as

$$\Psi^{(k)} = \frac{G^{(k)}}{G_0\big(\gamma^{(k)}\big)} = \frac{G^{(k)}}{\sum_{n=0}^{N} g_n\left[\gamma^{(k)}\right]^n}. \tag{13}$$

Taking the logarithm of both sides, Equation 12 can be presented as

$$\log[\Psi(T, \varpi)] = \beta\log\left[\frac{\varpi^{(k)}}{\omega_0}\right] + (AB\beta)\left[\frac{1}{B + T^{(k)} - T_0}\right] + (-A\beta), \tag{14}$$

or

$$y = c_1x_1 + c_2x_2 + c_0 \tag{15}$$

where

$$y = \log[\Psi(T, \varpi)]; \quad x_1 = \log\left[\frac{\varpi}{\varpi_0}\right]; \quad x_2 = \frac{1}{B + T - T_0}; \tag{16}$$

$$c_1 = \beta; \quad c_2 = AB\beta; \quad c_0 = -A\beta. \tag{17}$$

This problem of linear regression for Equation 15 may be easily solved using MLS. (Note that x_2 is calculated in Equation 16 using the initial (*rough*) magnitude introduced for B in Step 1). Unknown parameters can be calculated using Equation 17 as:

$$\beta = c_1; \quad A = -c_0/c_1; \quad B = -c_2/c_0. \tag{18}$$

Step 4. Convergence condition. If the difference between solutions (18) and the ones introduced in Step 1 are larger than the requested tolerance, *refined* solutions (18) are considered as the *rough* ones in Step 2 for the next iteration. Therefore, the required accuracy may be satisfied by increasing the number of iterations.

3. Numerical results

In this paper, storage shear modulus G will be considered to demonstrate the application of the proposed method. Consider a typical elastomeric material tested at three temperatures (30, 60, and 90 °C) and three frequencies (0.1; 1; and 10 Hz) under sinusoidal shear strain, γ, between 0 and 10%. The effect of loading on G is shown in Fig. 1a for different combinations of temperatures and frequencies. Each individual curve $G(\gamma)$ at specific T and ϖ may be approximated by a power series using classical MLS. Characterization of the master-curve for the entire set of experimental data, however, has to be done using the proposed method.

Table I lists the results of statistical iterative procedure for $T_0 = 25$ °C where the following initial values were used: $\beta = 0.01$; $A = 15$ °C; $B = 150$ °C. The parameters β and g_n are shown to converge quickly and an accuracy of three digits is guaranteed after 3–4 iterations (see, Table I). Even though, the parameters A and

TABLE I Convergence of the statistical parameters at $T_0 = 25\,^{\circ}\mathrm{C}$

L	β	A	B	g_0 (MPa)	g_1 (MPa)	g_2 (MPa)	g_3 (MPa)	ξ (MPa)
0	0.01	15.0	150.0	—	—	—	—	—
1	0.04936	13.76	172.1	1.926	0.00124	−50.29	−0.1658	0.17292
2	0.04934	16.91	177.4	2.071	0.00133	−53.81	−0.1770	0.11903
3	0.04934	17.72	178.5	2.114	0.00135	−54.89	−0.1805	0.11306
4	0.04934	17.91	178.5	2.125	0.00136	−55.18	−0.1815	0.11255
5	0.04934	17.94	178.1	2.128	0.00136	−55.25	−0.1817	0.11250
6	0.04934	17.92	177.7	2.129	0.00136	−55.27	−0.1818	0.11250
...	...	...	...	...	...	...	...	...
20	0.04934	17.48	171.8	2.130	0.00136	−55.29	−0.1819	0.11250

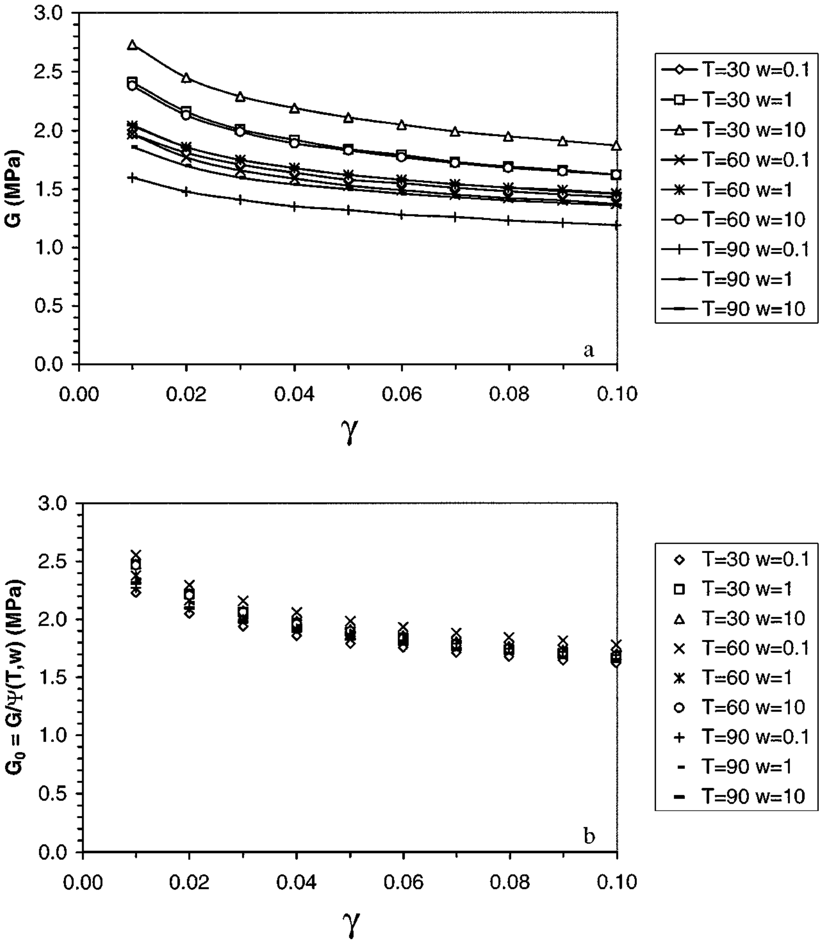

Figure 1 Dependency of storage shear modulus on temperature, frequency and amplitude strain (a) and respective master-curve (b).

B do not converge fast, characteristics of dispersion ξ, calculated by Equation 8, is practically the same for $L \geq 3-4$, where L is the number of iterations. In other words, the same accuracy of prediction may be guaranteed at different combinations of A and B. Although, in this study the magnitudes of A and B at $L = 20$ were used, the prediction using values of A and B at $L = 4$ would have been equally good from the viewpoint of engineering applications. The process of convergence practically does not depend on initial values, if they are positive and $B + T^{(k)} - T_0 > 0$. Results presented in Table II show it on example of the effect of initially introduced rough parameter $\beta_{L=0}$. While there is certain discrepancy in parameters A and B, it practically does not affect the accuracy of prediction since variation in ξ is less than 1%.

Generally speaking, parameter T_0 may be considered as an unknown value as well, since the Williams-Landel-Ferry equation is an empirical approximation and the physical meaning of T_0 is ignored. To generalize the iterative approach, the residual parameter ξ, may be calculated as a function of T_0 according to Equation 8. Then, minimization of $\xi(T_0)$, a one-parameter convex function, can be performed using classical min-max techniques. Parameter T_0, providing the lowest value for ξ, can be used in the analysis. Effect of initial temperature, T_0, on ξ is illustrated in Table III. The variation in ξ was less than 1% when T_0 was increased from 0

TABLE II Statistical parameters at $L = 20$ ($T_0 = 25\,^\circ$C)

$\beta_{L=0}$	β	A	B	g_0 (MPa)	g_1 (MPa)	g_2 (MPa)	g_3 (MPa)	ξ (MPa)
0.01	0.04934	17.48	171.8	2.130	0.00136	−55.29	−0.1819	0.11250
0.05	0.04936	15.35	143.0	2.132	0.00136	−55.37	−0.1821	0.11301
0.10	0.04940	12.88	109.8	2.137	0.00137	−55.49	−0.1825	0.11382

TABLE III Dependence of the statistical parameters on T_0 at $L = 20$ ($\beta_{L=0} = 0.05$)

T_0	β	A	B	g_0 (MPa)	g_1 (MPa)	g_2 (MPa)	g_3 (MPa)	ξ (MPa)
0	0.04933	21.44	161.5	2.452	0.00157	−63.67	−0.2094	0.1124
20	0.04936	16.49	146.1	2.190	0.00140	−56.85	−0.1870	0.1129
40	0.04958	12.45	139.2	1.982	0.00127	−51.47	−0.1693	0.1134
60	0.04941	9.681	143.7	1.832	0.00117	−47.58	−0.1565	0.1139
80	0.04939	9.133	172.1	1.728	0.00111	−44.87	−0.1476	0.1136

to 80 °C. While β is practically independent on T_0, parameters A, B, and g_n were found to be affected by the initial temperature. Consequently, in engineering applications, parameter T_0 may be chosen arbitrarily in the 0–80 °C range.

A relevant master-curve (i.e., entire population of experimental data at different temperatures and frequencies together) may be constructed as a one-parameter dependence $G_0 = G_0(\gamma)$. Here, magnitudes of $G_0^{(k)}$ are calculated using Equation 11 for each kth observation. Transformation from initial functions $G(\gamma)$ to "shifted" master-curve $G_0(\gamma)$ is shown in Fig. 1b. The narrow domain of "shifted" points suggests a good conformation for the method in general. Certain variability in experimental data presented in Fig. 1b may be explained by the statistical deviation.

4. Conclusion

An iterative procedure, accounting for the non-linearity of deformation, is proposed to evaluate parameters of the Williams-Landel-Ferry equation. Experimental data at different loading conditions, temperatures, and frequencies are analyzed together until requested conditions of convergence are satisfied. Since the entire experimental population is treated simultaneously, results obtained possess high statistical reliability. Desired accuracy may be obtained by 3–4 iterations. The statistical method was experimentally verified for a typical elastomer at three temperatures and three frequencies, and the effect of non-linearity was shown.

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