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SHORT COMMUNICATION

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Relaxation modulus in the fitting of polycarbonate and poly(vinyl chloride) viscoelastic polymers by a fractional Maxwell model

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Abstract The stress relaxation of two different polymers under a constant strain has been studied and approached by using a fractional Maxwell model in which the stress appears as a noninteger-order derivative of the strain. To obtain an accurate approximation of the experimental data for the model, two noninteger values for the derivative order are required. These values are related to two relaxation types. For short times, the derivative order is smaller and near zero, which indicates behavior close to the ideal elastic solid. For long times the derivative order is higher, showing more plastic behavior. In this work some classic models are revised and the fractional Maxwell model is used to fit the experimental data. Finally, the complex fractional modulus, the two derivative orders, and the relaxation times for samples of polycarbonate and poly(vinyl chloride) are obtained.

Keywords Relaxation modulus · Fractional calculus · Viscoelasticity

Introduction

The study of the viscoelastic behavior of a material by means of fractional calculus implies its modelization using differential equations with noninteger derivative order or transfer functions such as the quotient of polynomials in real powers of s. [1, 2].

These equations appear to be a natural extension of the classic models formulated with differential equations having integer-order derivatives. Several researchers have used fractional calculus to study and to control the dynamics of different systems: dielectric relaxation of polymers [3], rubbers [4], polymers with loads [5], polymeric gels, etc. An extensive review of the applications of fractional calculus in physics can be found in the book by Hilfer [6].

In general, this tool provides an appropriate description of the system behavior with fewer parameters. Numerous contributions relate the order of those derivatives in the differential equation to a fractal geometry of the system [7, 8], and the representation, through these fractional operators, of an infinite memory of the system regarding its past, which models its actual behavior [9].

In this work, first of all, a brief review is made of the classic models, which can be extended, to introduce a new model of fractional type with four parameters denominated the Maxwell fractional model. [6, 10]. The original contribution of this work is the presentation of experimental results of stress relaxation in several polymers and their good fitting by using the Maxwell model.

A viscoelastic material presents behavior that implies dissipation and storage of mechanical energy. Considering the response to an input step, $H(t)$, two types of analysis or test can be considered:

1. Creep analysis: this studies the material strain under a constant stress, $\sigma(t) = H(t)$. In the frequency domain $\sigma(s) = H(s) = 1/s$. In this case, the strain is $\varepsilon(t) = J(t)$ and is denominated creep compliance.
2. Relaxation analysis: this is the time variation of the stress for a constant strain, $\varepsilon(t) = H(t)$. The function representing the uniaxial effort, $\sigma(t) = G(t)$, is denominated the relaxation modulus.

In general, we can apply the Boltzmann overlapping principle and obtain an expression for the Stieltjes integral for the creep and relaxation phenomena:

$$\varepsilon(t) = \int_{-\infty}^{t} J(t-\tau)\mathrm{d}\sigma(t) \ ,$$

$$\sigma(t) = \int_{-\infty}^{t} G(t-\tau)\mathrm{d}\varepsilon(t) \ .$$

Using the Laplace transform in the previous expressions, we obtain

$$\varepsilon(s) = sJ(s)\sigma(s) \ ,$$

$$\sigma(s) = sG(s)\varepsilon(s) \ .$$

We can characterize the material behavior in the relaxation process by means of various classical and fractional models according to the previously defined function temporal relaxation modulus, $G(t)$.

Classic and fractional models

Classic models

Hooke's model

This model is used for ideal solids and is represented by an ideal spring. The system response to a unitary strain, $G(t)$, is a constant function as well as the response to an unitary stress, $J(t)$. This model cannot explain either the creep or the relaxation phenomenon:

$$\sigma(t) = E\varepsilon(t), \quad G(t) = E \ .$$

Newton's model

This is used for ideal fluids and is represented by means of a dashpot, which is the viscous element. In this model the deformation under a constant strain grows linearly with the time, $J(t) = (t/b)$, and the response to a constant strain is a δ function:

$$\sigma(t) = \eta\frac{\mathrm{d}\varepsilon(t)}{\mathrm{d}t}, \quad G(t) = \eta\delta(t) \ .$$

Maxwell's model

This is a series arrangement of the Hooke and Newton models: an ideal spring in series with a dashpot. This model proves to work badly if the strain is constant, since it implies a constant variation of the deformation as the time increases. The model presents a relaxation of exponential type. The parameter τ_σ is denominated the relaxation time:

$$\sigma(t) + a\frac{\mathrm{d}\sigma(t)}{\mathrm{d}t} = b\frac{\mathrm{d}\varepsilon(t)}{\mathrm{d}t}, \quad G(t) = \frac{b}{a}\exp(-t/\tau_\sigma) \ .$$

Voigt's model

This is a parallel arrangement of the Hooke and Newton models. In this model, a constant strain also implies a constant stress. The relaxation phenomenon is not taken into account and presents an exponential-type creep. The parameter τ_ε is denominated the delay time:

$$\sigma(t) = E\varepsilon(t) + \eta\frac{\mathrm{d}\varepsilon(t)}{\mathrm{d}t}, \quad G(t) = E + \eta\delta(t) \ .$$

Zener's model

This model, also denominated the standard linear solid model, consists of an elastic spring in series with the Voigt model or in parallel with the Maxwell model:

$$\left(1 + a\frac{\mathrm{d}}{\mathrm{d}t}\right)\sigma(t) = \left(m + b\frac{\mathrm{d}}{\mathrm{d}t}\right)\varepsilon(t), \ G(t) = G_\mathrm{e} + \beta\exp(-t/\tau_\sigma) \ ,$$

where $G_\mathrm{e} = m$, $\beta = \frac{b}{a} - m$, $\tau_\sigma = a$.

Fractional models

Modifications of classical models can be obtained by relating the strain to the stress through a differential equation of order q; considering that the response functions $J(t)$ and $G(t)$ are a linear combination of those found in the previous models. $J(t)$ and $G(t)$ are the summation of a constant value, a group of vanishing exponentials with different relaxation times, lineal functions and Dirac's deltas, as follows:

$$G(t) = G_\mathrm{e} + \sum_n G_n \exp(-t/\tau_{\sigma,n}) + G_{-}\delta(t) \ .$$

By performing the Laplace transform on the previous models we obtain

$$sG(s) = G_\mathrm{e} + \sum G_n - \sum \frac{G_n}{1 + s\tau_{\sigma,n}} + G_{-}s \ .$$

$sG(s)$ can be expressed as a rational function in the complex domain with real poles and zeros:

$$\frac{1}{sG(s)} = \frac{P(s)}{Q(s)}, \ \text{where } P(s) = 1 + \sum_{k=1}^{p} a_k s^k,$$

$$Q(s) = m + \sum_{k=1}^{p} b_k s^k \ .$$

The strain–stress behavior can be modeled by the following differential equation:

$$\left(1+\sum_{k=1}^{p} a_k \frac{\mathrm{d}^k}{\mathrm{d}t^k}\right)\sigma(t)=\left(m+\sum_{k=1}^{p} b_k \frac{\mathrm{d}^k}{\mathrm{d}t^k}\right)\varepsilon(t) \quad .$$

Formally, a fractional model extending the derivative order k in the last expression to noninteger values can be obtained. This implies the substitution of classic models with a finite distribution of delay and relaxation times, for models that involve a continuous distribution.

Maxwell fractional model

Mechanical models in fractional calculus use a model intermediate between ideal springs and dashpots denominated the Scott–Blair model, which is represented by a fractional derivative order. These elements can be built by means of structures in trees, cascades, lattices, etc., of discrete elements, springs, and dashpots.

The differential fractional equation corresponding to this element denominated the fractional Newton or Scott–Blair element is [11]

$$\sigma(t)=E\tau^{\alpha}\frac{\mathrm{d}^{\alpha}\varepsilon(t)}{\mathrm{d}t^{\alpha}}, \quad G(t)\approx\frac{E}{\Gamma(1-\alpha)}\left(\frac{t}{\tau}\right)^{-\alpha} \quad .$$

We need to consider a new fractional model that involves the association in series of two fractional Scott–Blair elements, denominated the generalized fractional Maxwell model, to fit the experimental data of the relaxation modulus in the two polymers studied in this work. [6, 12].

In Maxwell's fractional model the total strain is the sum of the partial strains of each Scott–Blair element, with the same stress for both elements:

$$\varepsilon_1(t)=E_1^{-1}\tau_1^{-\alpha}\frac{\mathrm{d}^{-\alpha}\sigma(t)}{\mathrm{d}t^{-\alpha}} \quad ,$$

$$\varepsilon_2(t)=E_2^{-1}\tau_2^{-\alpha}\frac{\mathrm{d}^{-\alpha}\sigma(t)}{\mathrm{d}t^{-\alpha}} \quad .$$

By adding both expressions and performing the α-order derivative, the differential fractional equation for Maxwell's fractional model is obtained:

$$\sigma(t)+\tau^{\alpha-\beta}\frac{\mathrm{d}^{\alpha-\beta}\sigma(t)}{\mathrm{d}t^{\alpha-\beta}}=E\tau^{\alpha}\frac{\mathrm{d}^{\alpha}\varepsilon(t)}{\mathrm{d}t^{\alpha}} \quad .$$

By the Fourier transform we can obtain the complex modulus for this model and using the properties of the Mellin transform and the Fox integral [12] the time relaxation modulus is obtained as follows:

$$G(t)=E\left(\frac{t}{\tau}\right)^{\beta}, \quad E_{\alpha-\beta,1-\beta}\left[-\left(\frac{t}{\tau}\right)^{\alpha-\beta}\right] \quad , \qquad (1)$$

where $E_{\mathrm{k},\mu}$ is the generalized Mittag–Leffler function defined by [13]

$$E_{k,\mu}(x)=\sum_{n=0}^{\infty}\frac{z^n}{\Gamma(kn+\mu)} \quad .$$

The time relaxation modulus approaches, for different ranges of time, two negative power functions of the time. This fact is related to two types of relaxation: one for short times in which $t \ll \tau$ and the other one for long times where $t \gg \tau$ as can be seen in the experimental results.

$$t \ll \tau \rightarrow G(t)\approx\frac{E}{\Gamma(1-\beta)}\left(\frac{t}{\tau}\right)^{-\beta},$$

$$t \gg \tau \rightarrow G(t)\approx\frac{E}{\Gamma(1-\alpha)}\left(\frac{t}{\tau}\right)^{-\alpha}.$$

Over the deformation process of a viscoelastic material, a part of the deformation work is dissipated in the form of heat owing to viscoelastic losses and another part is stored as the energy of elastic deformation.

For classic models, the elastic part of the deformation work corresponds to the different springs and the loss part to the dashpots. In contrast, in fractional models we have both energy types (stored and dissipated) and in any part of the material they cannot be assigned separately to different springs and dashpots. Therefore the fractional model cannot be substituted for a finite arrangement of classic models.

Experimental

Two different types of commercial grade polymers samples from Dupont [polycarbonate, poly(vinyl chloride)] were used in this work and the stress relaxation test was achieved using a HOYTOM HM-20-D tensile machine.

Normalized test samples of dimensions 100 mm × 25 mm × 3 mm were used and deformed with a crosshead speed of 3 mm/min, until a total deformation of a 5% was reached. At that moment the crosshead was been stopped, keeping it in a constant position, and the values of the load, $F(t)$, that acts on the samples were obtained over the time. From $F(t)$, the stress, σ, can be obtained by dividing it by the normal section of the sample, S, and finally dividing by the constant strain of the sample, $\varepsilon_0 = 0.05$, the time relaxation modulus function is obtained:

$$G(t)=\frac{F(t)}{S\varepsilon_0} \quad .$$

Results

The experimental results of the relaxation modulus for the two samples are shown in Fig. 1. The experimental data cannot be fitted by means of classic models (Hooke, Newton, Maxwell, Voigt, etc.). Nevertheless, the fractional Maxwell model gives a very good fit of the experimental data.

Really, if the fractional viscoelastic Maxwell model is correct we should obtain, by drawing the Naperian

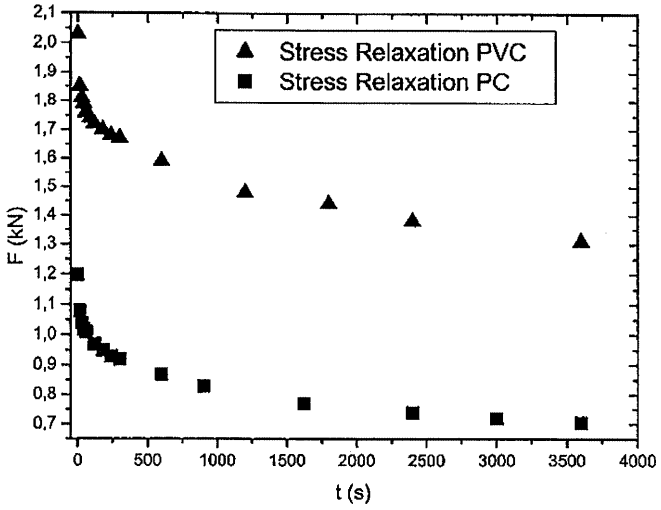

Fig. 1 Experimental load with time for polycarbonate (*PC*) and poly(vinyl chloride) (*PVC*) samples

logarithm of the relaxation modulus in front of the Naperian logarithm of the time, two straight lines whose slope is, in fact, the orders of the fractional derivative:

$$t \ll \tau \;\rightarrow \log G(t) = \log\frac{E}{\Gamma(1-\beta)} - \beta\log\left(\frac{t}{\tau}\right) = \log\frac{E\tau^{\beta}}{\Gamma(1-\beta)} - \beta\log t = \log k_1 - \beta\log t,$$

$$t \gg \tau \;\rightarrow \log G(t) = \log\frac{E}{\Gamma(1-\alpha)} - \alpha\log\left(\frac{t}{\tau}\right) = \log\frac{E\tau^{\alpha}}{\Gamma(1-\beta)} - \alpha\log t = \log k_2 - \alpha\log t \;.$$

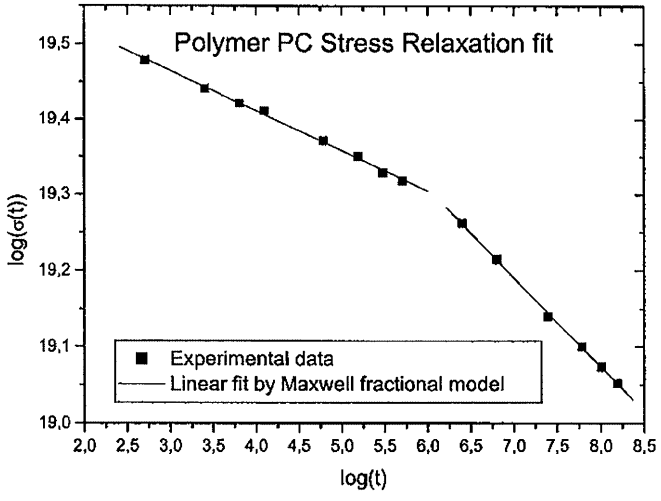

Fig. 2 PC stress relaxation fit

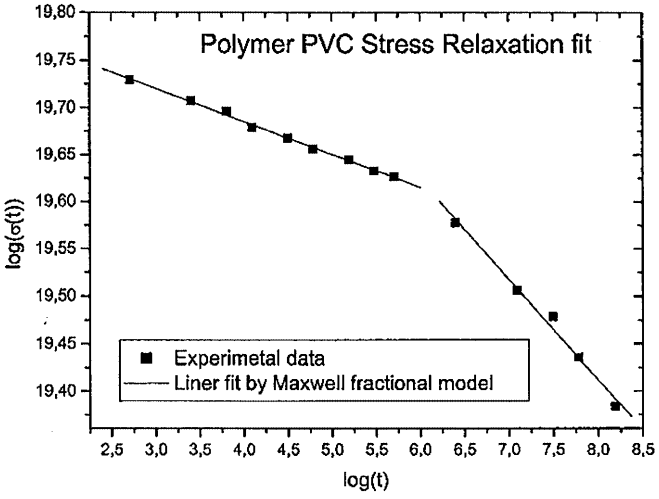

Fig. 3 PVC stress relaxation fit

The fitting is shown for the two samples in Figs. 2 and 3. It can be seen that four parameters are necessary for fitting each sample: k_1 and β for the first straight line and k_2 and α for the second line. This fact indicates that there are two types of stress relaxation in each polymer, a short time one and a long time one. The values obtained for the order of the fractional derivatives in the two polymers and their ordinates at the origin are shown in Table 1.

From the values of the two constants we can obtain the fractional elastic modulus, E, and the average relaxation time, τ, of each material, keeping in mind that

$$k_1 = \frac{E}{\Gamma(1-\beta)}\tau^{\beta} \quad \text{and} \quad k_2 = \frac{E}{\Gamma(1-\alpha)}\tau^{\alpha} \;.$$

Therefore,

$$\tau = \left(\frac{k_2\Gamma(1-\alpha)}{k_1\Gamma(1-\beta)}\right)^{\frac{1}{\alpha-\beta}} \quad \text{and} \quad E = k_2\frac{\Gamma(1-\alpha)}{\tau^{\alpha}} \;.$$

The values for the two polymers are shown in Table 2. For each polymer, both exponents and orders of derivation are between 0 and 1, what represents the behavior of a material intermediate between a purely

Table 1 Numerical values from fractional derivative orders

Polymer	β	α	$\log k_1$	$\log k_2$
Polycarbonate	0.0533	0.1174	19.6245	20.0123
Poly(vinyl chloride)	0.0349	0.1058	19.8249	20.2584

Table 2 Fractional elastic modulus and average relaxation time

Polymer	k_1	k_2	E	τ (s)
Polycarbonate	3.33×10^8	4.91×10^8	2.40×10^8	884
Poly(vinyl chloride)	4.07×10^8	6.28×10^8	3.28×10^8	913

elastic material and a pure fluid, respectively. It can be proved that in all cases the values of β and α are $0 \le \beta < \alpha \le 1$; this is not in contradiction with the theoretical expectations of the fractional Maxwell model.

Once the good agreement of the model with the experimental data is obtained, we can obtain for each material their complex relaxation modulus by making the Fourier transform in Eq. (1) and we obtain

$$G(w) = \frac{E(iw\tau)^{\alpha}}{1 + (iw\tau)^{\alpha-\beta}} \quad .$$

In this expression we can see that for high frequencies, $(iw\tau)^{\alpha-\beta} \gg 1$, the complex relaxation modulus approaches $G(w) \approx E(iw\tau)^{\beta}$, and it presents a slope of 20β dB/decade with a phase of $\beta(\pi/2)$ in its Bode diagram. For low frequencies, $(iw\tau)^{\alpha-\beta} \ll 1$, the complex modulus approaches $G(w) \approx E(iw\tau)^{\alpha}$, with slope of 20α dB/decade and phase $\alpha(\pi/2)$.

In the two polymers β is much smaller that α. Since β is the exponent that governs the relaxation for short times, we can conclude that in the three materials there is first a stress relaxation closer to an ideal elastic solid (that does not have relaxation) and later the relaxation of plastic type takes place.

Studies of the relationship between the value of these exponents and the internal structure and conformation of the polymer, the influences of the temperature and the calculation of the free energy of activation will be the subject of more extensive work.

Conclusions

The study of stress relaxation under constant strain, in two commercial polymers, shows that the classic models that use integer-order differential equations, using springs and dashpots (Hooke, Newton, Maxwell, Voigt, etc.), do not reflect appropriately the behavior of these materials. Indeed, it is necessary to use models involving differential equations of noninteger order which relate the stress and strain of these materials.

In this work we obtained a good fit with the fractional Maxwell model for the experimental results of the relaxation modulus. As shown in Refs. [14–16], this model is like an infinite distribution of discrete elements (cascade, branch, etc.), implying the existence of a distribution function for the relaxation times instead of a finite number of discrete relaxation times, which are obtained when using classic models. The fractional derivative operators take into account the complete history of the system to obtain the derivative in a particular instant. The viscoelastic materials have infinite memory, i.e., their actual mechanical response is modulated by their whole past.

Likewise, the interesting fact of needing two straight lines and, therefore, two orders of the fractional derivative shows two models of relaxation in these materials: a short time one with quasielastic behavior and a long time one in which the material moves away from the behavior of an elastic solid.

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