On the Modeling of the Dynamic-Elastic Modulus for Polymer Materials under Isochronal Conditions

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ABSTRACT: A model based on the concept of fractional calculus is proposed for the description of the dynamic elastic modulus, $E^* = E' + iE''$, of polymer materials. This model takes into account three relaxation phenomena (α, β, and γ) under isochronal conditions. The differential equations obtained for this model have derivatives of fractional order between 0 and 1. Applying the Fourier transform to the fractional differential equations and associating each relaxation mode to cooperative or noncooperative movements, $E^*(i\omega,T)$ was evaluated. The isochronal diagrams of E' and E'' clearly show three relaxation phenomena, each of them is manifested by a decrease of E' when temperature increases. This decrease is associated with a maximum in $E''(T)$ diagram for each relaxation mode. The shape of the three peaks (three maxima in $E''(T)$ diagrams) depends of the fractional orders of this new fractional model. The mathematical description obtained of E^* corresponds to a nonexponential relaxation behavior often encountered in the dynamics of polymer systems having three relaxation phenomena. This model will enable us to analyze the viscoelastic behavior of polymers. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 657–670, 2004

Key words: modeling; viscoelastic properties; mechanical properties; relaxation; polymers

INTRODUCTION

Due to the long chain character of polymer molecules, polymeric materials can be completely amorphous or semicrystalline. In these complex structures, several relaxation phenomena can be found. These are usually designated by the letters α, β, γ, and so on. The origin of these relaxations is most often ascribed to rearrangements of segments or small portions of the polymer chains. Due to its sensitivity to molecular motion dynamics, the dynamic elastic modulus analysis, $E^* = E' + iE''$, is a convenient way to test the dynamic of the relaxation processes of polymer materials. The real part, E', called the storage modulus, defines the energy stored in the specimen when a force field is applied and the imaginary part, E'' called the loss modulus, defines the dissipation of energy. Identifying the modes of relaxation processes (α, β, and γ) with specific molecular motions will enhance our understanding of the structure–property relationships for polymers. The modeling of the dynamic elastic modulus by using differential equations with derivatives of fractional order (fractional calculus) provides a better description than the classical models formulated with integer-order derivatives.[1–7] It has been shown that constitutive equations employing derivatives of fractional order could be linked to molecular theories describing the macroscopic behavior of viscoelastic materials.[7,8]

Recent contributions in the modeling of the elastic modulus presents a fractional model analogous to the classical Zener model, but, in this one, the dashpot was replaced by a fractional rheological element called the spring-pot.[4,5,9–11] This fractional element combines the solid behavior (Hooke's law) with fluid behavior (Newton's law).

Applying the Fourier transform to the fractional model, a mathematical representation of the frequency dependence of $E^*(\omega)$, under isothermal conditions, could be obtained.[9–11] However, in practice, it is very useful to describe the analysis of the temperature dependence of $E^*(T)$ (isochronal conditions).

The aim of this work is to present a fractional model for the description of E^* in polymeric materials, taking into account three relaxation phenomena under isochronal conditions. This model could be used to study the molecular mobility phenomena in polymer materials, associating a molecular interpretation to parameters of our model.

The first relaxation at higher temperature, the α-relaxation, is associated with cooperative movements of chain segments by a configuration rearrangement of the entire chain, involving long chain segmental motion and reflecting the glass transition (T_g) in amorphous polymers. In the case of semicrystalline polymers, α-relaxation can be associated with cooperative movements at the interface between amorphous and crystalline regions.[12] The β-relaxation is the second relaxation phenomenon in the order of decreasing temperature. In the case of semicrystalline polymers, β-relaxation can, sometimes, be associated with glass transition,[12] while for amorphous polymers it is associated with less cooperative processes than α-movements, and they are localized motions of elements in macromolecular chains carried out at short distance, in regions where mobility is possible such that the polymer is far from T_g. The γ-relaxation is observed at a lower temperature than those of β-relaxation. It is related to movements that are very localized and of a noncooperative nature.

THE FRACTIONAL ZENER MODEL

A fractional Zener model (FZM) has been used as a first approximation for the description of the α-relaxation under isothermal conditions for amorphous polymers in a glassy state, having secondary relaxations far away from α-relaxation.[4,9–11] Figure 1 shows the proposed FZM obtained by replacing the dashpot by a spring-pot, element "a," in the classical Zener model.

Where σ is applied stress, ε is the strain, E_0 is the relaxed modulus corresponding to values of E' at low frequencies or high temperatures, E_U is the nonrelaxed modulus corresponding to values of E' at high frequencies or low temperatures, and $D_\tau^a \varepsilon_a$ is the fractional derivative of the strain with respect to time with an order a ($0 \leq a \leq 1$), the relaxation time, τ, characterizes the time required by a chain segment in movement for a complete reorganization and a full reorientation to a new structural equilibrium state. Hence τ also characterizes the nonlinearity of the relaxation process and it is dependent of relaxation mode (α, β,
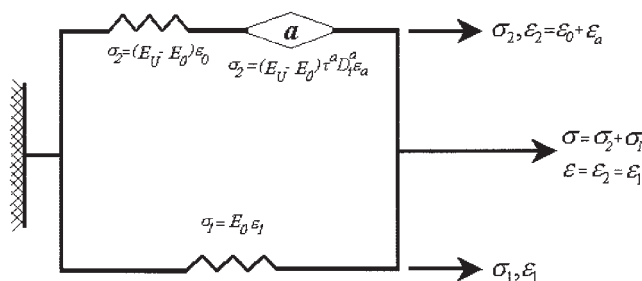
or γ). The stress–strain relationship for this model is:[4,9–11]

$$\sigma(t) + \tau^a D_t^a \sigma(t) = E_0 \varepsilon(t) + E_U \tau^a D_t^a \varepsilon(t) \quad (1)$$

According to Riemman-Liouville, the fractional derivative in eq. (1) is defined[1] by eq. (2) and the fractional integral defined between 0 and t can be defined by eq. (3)

$$D_t^a \varepsilon(t) = D \int_0^t \frac{(t-y)^{-a}}{\Gamma(1-a)} \varepsilon(y) dy \quad a \in (0,1) \quad (2)$$

$$D_t^{-a} \varepsilon(t) = \int_0^t \frac{(t-y)^{a-1}}{\Gamma(a)} \varepsilon(y) dy \quad a \in (0,\infty) \quad (3)$$

where Γ is the gamma function

$$\Gamma(m) = \int_0^\infty e^{-u} u^{m-1} du, \text{ with } m > 0 \quad (4)$$

Equation (1) provides us, after Fourier transformation, the dynamic modulus E^* as a function of frequency, ω. To obtain the temperature dependence, we need first to define the relationship between the relaxation time, τ, and temperature, T, which in turn depends on the cooperative and noncooperative nature of the molecular movements.

Due to the complex structure of the polymers, the molecular movements, associated to relaxation phenomena (α, β, and γ) can be cooperative or noncooperative processes. Cooperative movements are simultaneous motions at a time of segments of macromolecular chains due to the interference between neighboring segments-chains. If many segments of chain are involved in the cooperative process, the probability for that process is small, and the relaxation time is long; in addition, as the temperature is lowered, the polymer densifies, shortening the average intermacromolecular chain distance and, consequently, τ also increases and has and infinite value to the Kauzmann zero entropy temperature, T_0.[13] The α-relaxation is a typical example of cooperative movements, β-movements are less cooperative than α-movements, and the molecular motions associated with γ-relaxation are very localized, having a negligible cooperativity, and consequently can be considered as noncooperative movements. The relaxation time, τ, for noncooperative movements follows an Arrhenius law behavior:

Figure 1 The fractional Zener model with a spring-pot.

$$\tau = \tau_0 \exp\left(\frac{E_a}{kT}\right) \quad (5)$$

Where E_a is the activation energy corresponding to noncooperative processes. It could have values that are identifiable with real energy barriers,[14,15] k is the Boltzmann constant, T is the absolute temperature, and τ_0 is a preexponential factor with values within the range of 10^{-16} s $\leq \tau_0 \leq 10^{-13}$ s; values in the vicinity of the upper limit correspond to molecular vibrational times and those near the lower limit may be rationalized as additional entropy contributions.[14]

In the case of the cooperative relaxation phenomena, the probability that such an event happens is $P^{Z,}$ where $P \propto 1/\tau$ is the probability of an elementary movement of simultaneous motions at a time of segments of macromolecular chains; Z, depending of the polymer structure, can be considered to be the number of elementary movements participating on the cooperative processes. Therefore, relaxation times verify the next power law:[15,16]

$$\tau_{\text{cooperative}} = \tau_0 \left(\frac{\tau}{\tau_0}\right)^Z \quad T_0 \leq T \leq T^* \qquad (6)$$

Where τ is the relaxation time of the elementary or fastest molecular motion of cooperative movements, and it is defined by eq. (5). The Z exponent is calculated with the next equation:[13,15]

$$Z(T) = \frac{T\,T^* - T_0}{T^*\,T - T_0} \quad T_0 \leq T \leq T^* \qquad (7)$$

T^* is a crossover temperature above which cooperative and noncooperative movements merge together[15,16] and $Z = 1$. Below T^* the relaxation times of cooperative movements verify the empirical Vogel—Fulcher–Tammann equation, this temperature, T^*, being in the order of $1.3T_g$ for completely amorphous polymers. For semicrystalline polymers, T^* was found to be equal to the melting temperature.[15] T_0 is a temperature below T_g where both Z and $\tau_{\text{cooperative}}$ extrapolate to infinity.

Figure 2 shows that relaxation times of cooperative and noncooperative movements (Arrhenius law) merge together at a crossover point (τ^*, T^*) when the activation energy, E_a, of the single movements of the cooperative process is equal to the activation energy of noncooperative motions. This behavior has been reported for several polymers,[15] depending the crossover point of the nature of the polymer.

On the other hand the apparent activation energy for cooperative motions is temperature dependent according to following equation:

$$E_{a\text{ cooperative}} = ZE_{a\text{ elementary}-\text{movement}} \qquad (8)$$

This equation can be justified because, when the temperature decreases, there is a sharp reduction of mobility and, consequently, the corresponding apparent activation energy tends toward significant values.[17,18]
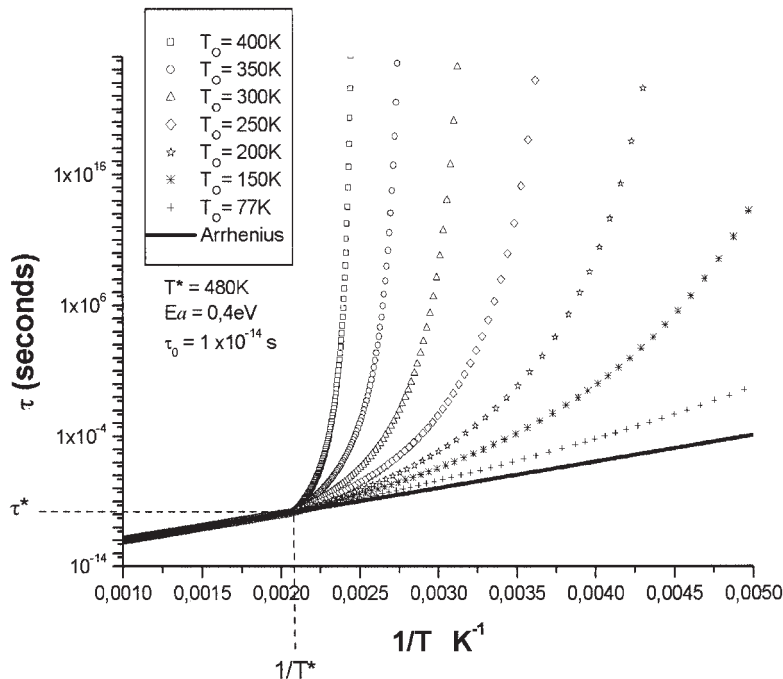

Figure 2 Relaxation times for several cooperative movements, eq. (6), in comparison with the relaxation times of noncooperative movements, eq. (5). $T_0 = 77$ K corresponding to liquid nitrogen temperature.

The dynamic-elastic modulus under isochronal conditions

In dynamical mechanical experiments, the specimen is subject to an alternating strain, measuring the resulting stress. For linear viscoelastic behavior, when equilibrium is reached, the stress and strain will both vary sinusoidally, but the strain lags behind the stress, thus we write the complex modulus as:

$$E^* = \frac{\sigma^*(i\omega,T)}{\varepsilon^*(i\omega,T)} = E'(\omega,T) + iE''(\omega,T) \qquad (9)$$

where ω is the angular frequency of alternating applied strain. The storage modulus, E', is in phase with the applied strain, and the loss modulus, E'', is $\pi/2$ out of phase with the strain. The phase lag, δ, between the strain and stress is defined as $\delta = \tan^{-1}(E''/E')$. .

The dynamic-elastic modulus under isochronal conditions for FZM (Fig. 1) was calculated applying the Fourier transform to eq. (1) and considering the temperature dependence of τ. The Fourier transform of the fractional differential operator, $D_t^a[\varepsilon_a(t)]$ can be written like a product of $(i\omega)^a$ and the Fourier transform of the function $\varepsilon_a(t)$.[1] The storage, E', and loss, E'', modulus obtained are

$$E'(T) = E_U - \frac{(E_U - E_0)\left[1 + [\omega\tau(T)]^a\cos\left(a\frac{\pi}{2}\right)\right]}{\left[1 + [\omega\tau(T)]^a\cos\left(a\frac{\pi}{2}\right)\right]^2 + \left[[\omega\tau(T)]^a\sin\left(a\frac{\pi}{2}\right)\right]^2}$$

$$E''(T) = \frac{(E_U - E_0)\left[[\omega\tau(T)]^a\sin\left(a\frac{\pi}{2}\right)\right]}{\left[1 + [\omega\tau(T)]^a\cos\left(a\frac{\pi}{2}\right)\right]^2 + \left[[\omega\tau(T)]^a\sin\left(a\frac{\pi}{2}\right)\right]^2}$$

Cooperative movements $\rightarrow \tau(T) = \tau0\left(\exp\left(\frac{E_a}{KT}\right)\right)^z$

Noncooperative movements $\rightarrow \tau(T) = \tau_0\exp\left(\frac{E_a}{kT}\right)$

$$(10)$$

Figures 3 and 4 show the storage and loss modulus considering cooperative movements for different values of the a parameter. Both E' and E'' are similar to the classical behavior of glass transition of viscoelastic amorphous materials having a secondary relaxation process far away from α-relaxation.

At lower and higher temperatures, the temperature dependence of E' and E'' is negligible, because the phase lag is very small. The intermediate region shows the typical mechanical relaxation processes manifested by a decrease of E' with increasing temperature (Fig. 3) associated with a maximum of E'' (see Fig. 4). E'' rises to a maximum value, close to the temperature at which E' is changing most rapidly with temperature in Figure 3. The maximum value of E'' increases when the a parameter increases. The temperature dependence of E' and E'' in the viscoelastic region is very large and also dependent of the a parameter. From Figure 3 we can also distinguish the three typical regions associated with glass transition: glassy behavior when E' is very close to the nonrelaxed modulus, E_U; viscoelastic behavior when $E' = f(T,a)$ and rubber-like behavior when E' is very close to relaxed modulus, E_0.

It is important to remark here that with this model it is not possible to describe the flow behavior in amorphous polymers or the cold-crystallization phenomenon in semicrystalline polymers;[17,18] these phenomena can appear after rubber-like behavior.

The values of E' and E'' can be combined in a single curve called the Cole-Cole diagram (E'' versus E': Fig. 5). These diagrams are symmetrical for different values of a. The angle of the slope in the region of high and low values of E' is constant and equal to $a\pi/2$.

Considering now noncooperative movements under FZM where τ is defined by eq. (5), the isochronal diagrams of E' and E'' are similar but not equal to Figs. 3 and 4, respectively, because the temperature dependence of τ is different, but the Cole-Cole diagrams will also be symmetrical for different values of the a parameter. However, it is well know that, for polymers in a glassy state, having a secondary β-relaxation that moves away from α-relaxation, the Cole-Cole diagrams are asymmetric.[4,5,9–11] The slope angles of the curves at low and high values of E' are different. This behavior is due to the different viscoelatic response at low or high temperatures (high or low frequency). In a Cole-Cole diagram low temperatures correspond to high values of E' and high temperatures correspond to low values of E'.

To obtain the classical asymmetric response in Cole-Cole diagrams, it is necessary to add[4,5,9–11] a second spring-pot b to FZM (Fig. 6), where $D_t^b\varepsilon_b$ is the fractional derivative of the b order of the ε_b.

This model is characterized by three mechanisms. The first spring-pot, a, characterizes short times (τ_a) associated with viscoelastic behavior in the region at low temperature. The second spring-pot, b, character-

izes long times (τ_b) associated with viscoelastic behavior in the region at high temperature, and the last mechanism (spring) represents the elastic behavior of polymers.[4,5,9–11]

The stress–strain relationship obtained for this model (Fig. 6) is

$$(E_U - E_0)\varepsilon(t) = [\sigma(t) - E_0\varepsilon(t)] + \tau_a^{-a}D_t^{-a}[\sigma(t) - E_0\varepsilon(t)]$$
$$+ \tau_b^{-b}D_t^{-b}[\sigma(t) - E_0\varepsilon(t)] \quad (11)$$

The storage and loss moduli under isochronal conditions were calculated applying the Fourier transform to eq. (11), and considering cooperative movements for τ_a and τ_b parameters:

$$E' = E_0 + \frac{(E_U - E_0)\left[1 + [\omega\tau_b(T)]^{-b}\cos\left(b\frac{\pi}{2}\right) + [\omega\tau_a(T)]^{-a}\cos\left(a\frac{\pi}{2}\right)\right]}{\left[1 + [\omega\tau_b(T)]^{-b}\cos\left(b\frac{\pi}{2}\right) + [\omega\tau_a(T)]^{-a}\cos\left(a\frac{\pi}{2}\right)\right]^2 + \left[[\omega\tau_b(T)]^{-b}\sin\left(b\frac{\pi}{2}\right) + [\omega\tau_a(T)]^{-a}\sin\left(a\frac{\pi}{2}\right)\right]^2}$$

$$E'' = \frac{(E_U - E_0)\left[[\omega\tau_b(T)]^{-b}\sin\left(b\frac{\pi}{2}\right) + [\omega\tau_a(T)]^{-a}\sin\left(a\frac{\pi}{2}\right)\right]}{\left[1 + [\omega\tau_b(T)]^{-b}\cos\left(b\frac{\pi}{2}\right) + [\omega\tau_a(T)]^{-a}\cos\left(a\frac{\pi}{2}\right)\right]^2 + \left[[\omega\tau_b(T)]^{-b}\sin\left(b\frac{\pi}{2}\right) + [\omega\tau_a(T)]^{-a}\sin\left(a\frac{\pi}{2}\right)\right]^2} \quad (12)$$

The Cole-Cole diagrams shown in Figures 7 and 8 are the classical asymmetric response of the system, eq. (12). These figures confirm the fact that two spring-pot elements could reproduce the viscoelastic behavior of the system at low and high temperatures. The slope angle at low values of E' will be ($b\pi/2$) and on the region of high values of E' the angle will be ($a\pi/2$).

It could be seen that the FZM, even with two spring-pots, can only represent the viscoelastic behavior of polymers in the neighborhoods of one relaxation phenomenon. It should be noticed that this model cannot be used in the case of polymers having two important and close relaxations (α and β), because their effects are very related, modifying substantially the shape of the Cole-Cole diagram.[4,5,9–11]

The polymeric materials will, in general, possess several relaxation phenomena that can be attributed to molecular rearrangements and configurational changes. The most prominent of these for an amorphous polymer is the α-relaxation associated with glass transition, but this distinction cannot always be made for semicrystalline polymers.

We thus will present another fractional model with the aim of predicting the viscoelastic behavior of polymer materials on a very wide temperature range including three relaxation phenomena, α, β, and γ.

Modeling of three relaxation phenomena: α, β, and γ

For modeling the viscoelastic behavior of polymers showing three important relaxation phenomena, we developed a fractional model based on three FZM elements arranged in parallel (Fig. 9). The first one possesses two spring-pots: a and b, associated mainly with α-relaxation. The second FZM has only one spring-pot, c, and it is associated with β-relaxation. The last one also has only one spring-pot, d, associated with γ-relaxation.

The total stress is the result of the contributions of $\sigma 1$, $\sigma 2$, and $\sigma 3$:

$$\sigma = \sigma 1 + \sigma 2 + \sigma 3 \quad (13)$$

In addition the total deformation, ε, is equal to the individual deformations of elements 1, 2, and 3 of the model:

$$\varepsilon = \varepsilon 1 = \varepsilon 2 = \varepsilon 3 \quad (14)$$

Applying the Fourier transform to eq. (13) and using eq. (14) and the complex modulus definition we obtain

$$E^*(i\omega,T) = E1^*(i\omega,T) + E2^*(i\omega,T) + E3^*(i\omega,T) \quad (15)$$

The real (storage modulus) and imaginary (loss modulus) parts of the complex modulus could be expressed as a function of the corresponding modulus of each element of our model (Figure 9):

$$E'(\omega,T) = E1'(\omega,T) + E2'(\omega,T) + E3'(\omega,T)$$

$$E''(\omega,T) = E1''(\omega,T) + E2''(\omega,T) + E3''(\omega,T) \quad (16)$$

$E1'$ and $E1''$ on eq. (16) are the same as already defined by eq. (12), and, at this time, the temperature dependence of τ_a and τ_b are also defined by eq. (6), which means that element 1 is associated with cooperative
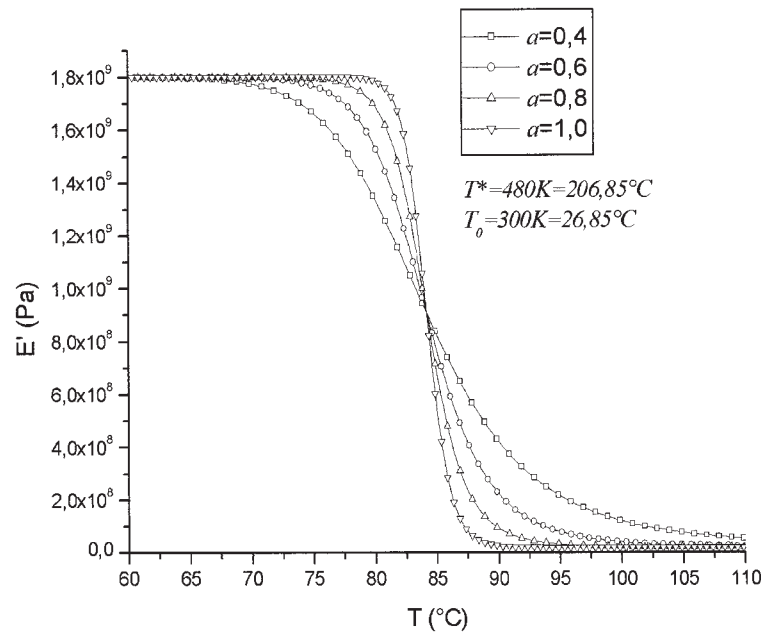
Figure 3 Storage modulus versus temperature for FZM with $E_a = 0.4$ eV, $\tau_0 = 1 \times 10^{-14}$s, $E_U = 1.8 \times 10^9$ Pa, $E_0 = 2 \times 10^7$ Pa, and a frequency of 1 Hz.

molecular motions, corresponding to the α-relaxation of polymers.

The second FZM element, related to β-relaxation, is equivalent to those defined by eq. (1) and the loss and storage modulus for this element, substituting first the corresponding parameters, will follow eq. (10). The chain motions on β-relaxation will also be considered as cooperatives, but at least to the extent that those occurred at α-relaxation. Then the relaxation time will also be defined by eq. (6).

The third FZM element is equivalent to the second one, with $E3'$ and $E3''$ also following eq. (10). In this case it is considered that the chain movements are very localized and of noncooperative nature. The relaxation time, τ_d, will be estimated using eq. (5).

TESTING THE RESPONSE OF THE FRACTIONAL MODEL

To verify the behavior of the model defined by eqs. (13) and (15), we proceeded to vary systematically the
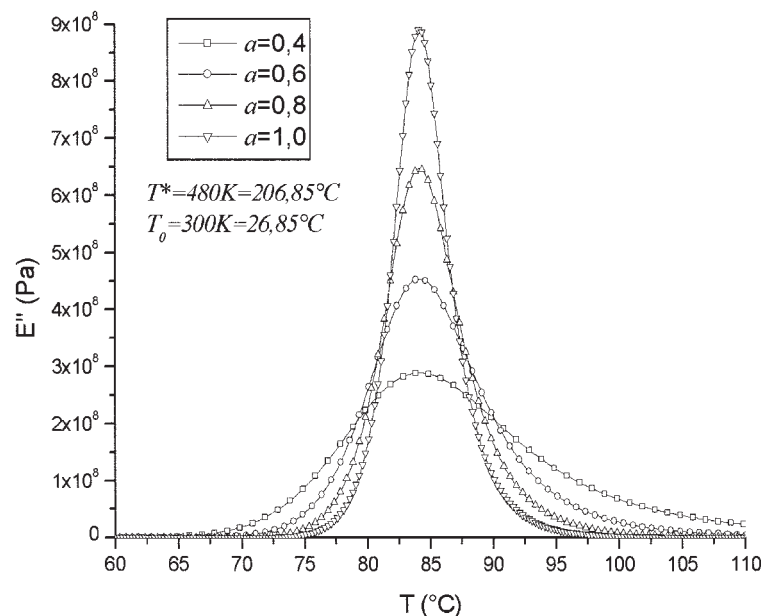
Figure 4 Loss modulus versus temperature for the fractional Zener model, with the same parameters as in Figure 3.
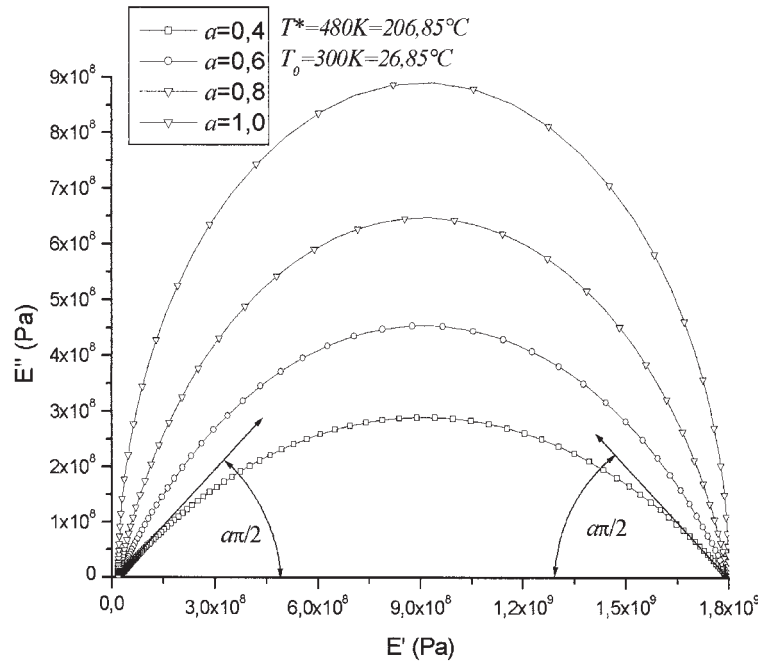
Figure 5 Cole-Cole diagram corresponding to Figures 3 and 4.

fractional order of spring-pots that constitutes the global model. It is important to point out that these parameters can only take values between 0 and 1.

Figures 10 and 11 show the predictions of the loss and storage modulus for different values of a, and remaining b, c, and d constants.

Figure 10, corresponding to $E''(T)$, shows how our model predicts the existence of three peaks corresponding, respectively, to the α, β, and γ relaxations. The peak at lower temperatures represents the γ-relaxation, the second peak is associated with the β-relaxation, and the last one at higher temperatures is associated with α-relaxation. We notice that the maximum of the α-relaxation increases as a increases; on the other hand a could be associated to the zone placed between α and β relaxations. This zone presents a minimum value of E'' that increases when a decreases.

Figure 11 shows the temperature dependence of E' for the same values of a, b, c, and d parameters of Figure 10. We can notice that, at very low temperatures, E' is equal to the global nonrelaxed modulus, E_U, calculated as follows:

$$E_U = E1_U + E2_U + E3_U \qquad (17)$$

On the other hand, at higher temperatures E' is equal to the global relaxed modulus, E_0, calculated as follows:

$$E_0 = E1_0 + E2_0 + E3_0 \qquad (18)$$

In the intermediate region between $E' = E_U$ and $E' = E_0$ (Fig. 11), E' is dependent of T and a, b, c, and d parameters, and we can identify three regions corresponding to the three peaks of Figure 10. At high temperatures, in the region of α-relaxation,
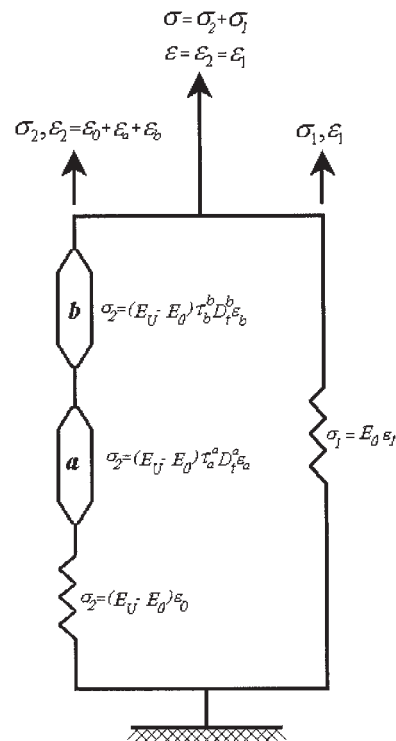

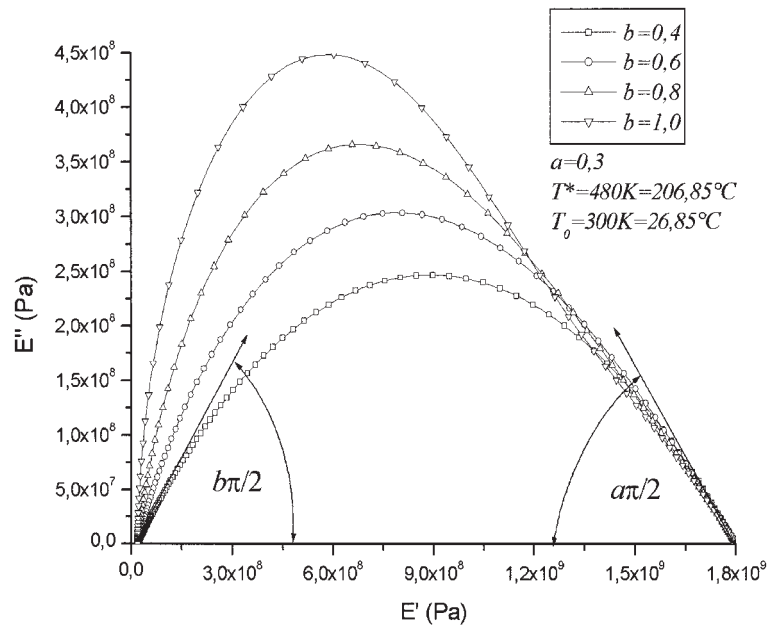**Figure 6** The fractional Zener model with two spring-pots.

Figure 7 The Cole-Cole diagram obtained from eq. (12) for a constant and different values of b, E_a = 0.4 eV, τ_0 = 1 × 10^{-14}s, $\tau_b(T)$ = $\tau_a(T)$, E_U = 1.8 × 10^9 Pa, E_0 = 2 × 10^7 Pa, and a frequency of 1 Hz.

there is a strong decrease of E' when temperature increases. The slope of the E' versus T curve is less pronounced for β and γ relaxation than for α-relaxation. The shape of the curve where α-relaxation starts is strongly dependent of the a parameter, while at the end of the curve (higher temperature) the parameter b determines the change rate of E' (see Fig. 12) and E'' (see also Fig. 13).

In Figure 13 it can be seen that the maximum value of E'' increases when the b parameter also increases.

From Figures 10 to 13 it can be concluded that the a and b parameters are associated mainly with α-relaxation mechanisms.

The effect of the c parameter on storage and loss modulus is presented in Figures 14 and 15, remaining the rest of parameters constants (a = 0.3; b = 0.8; d =
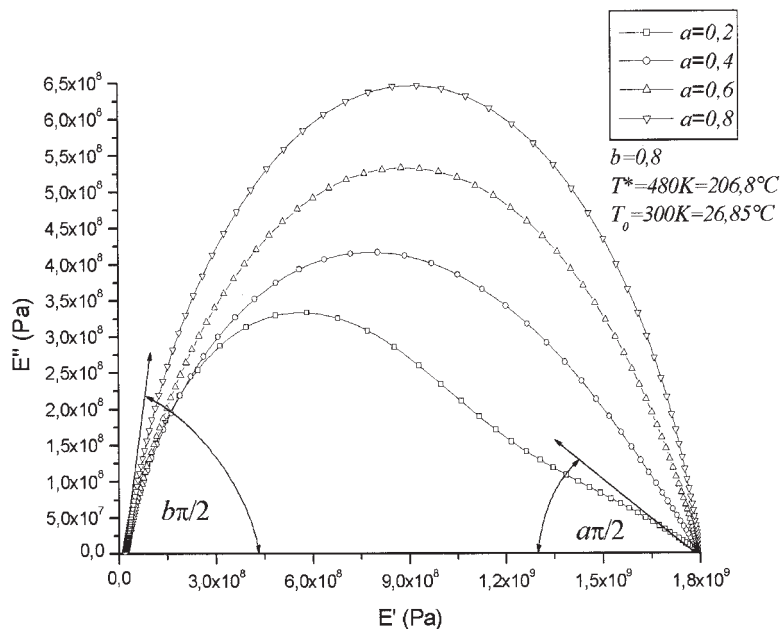

Figure 8 The Cole-Cole diagram obtained from eq. (12), for b constant and different values of a, with the same values of: E_a, τ_b, τ_a, T^*, T_0, E_U, E_0, and frequency, corresponding to Figure 7.
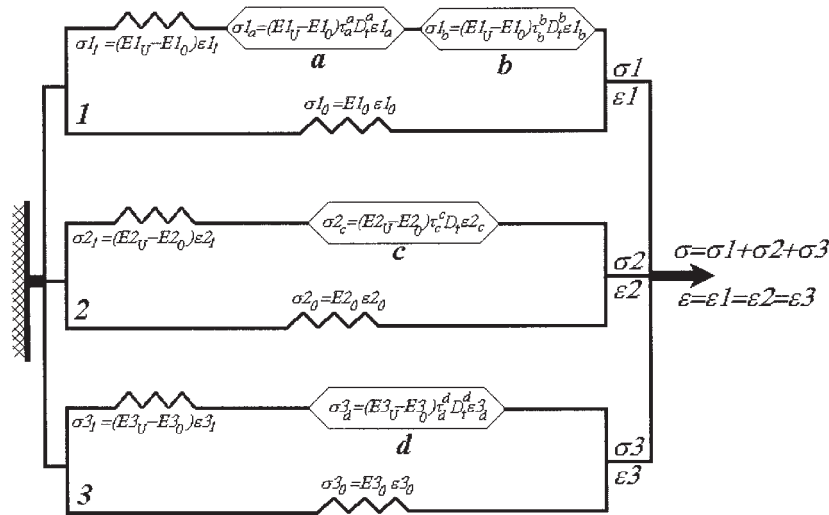
Figure 9 Fractional model for α, β, and γ relaxations. 1, FZM accounts for α relaxation; 2, FZM accounts for β relaxation; and 3, FZM accounts for γ relaxation.

0.3). Figure 14 shows that, at higher values of c, the slope of the E' curve is more pronounced, being practically vertical at values of c closest to one. Figure 15 shows the temperature dependence of E''; the maxi-

mum of E'' corresponding to β-relaxation increases as c increases. This parameter thus affects on the one hand the maximum of β-relaxation and on the other hand both minima, one located between α and β re-
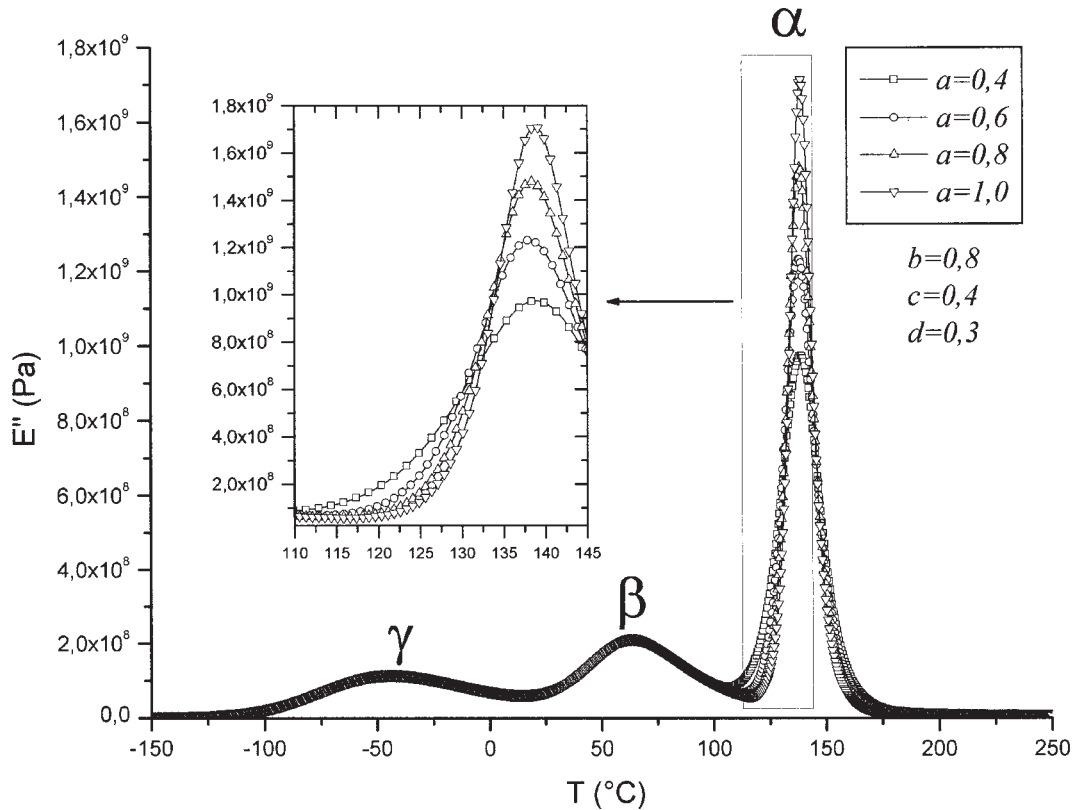
Figure 10 Loss modulus under isochronal conditions to a frequency of 1 Hz, for different values of a. Parameters for α-relaxation: $E_U = 4 \times 10^9$ Pa, $E_0 = 1 \times 10^7$ Pa, $E_a = 0{,}75$ eV, $\tau_0 = 1 \times 10^{-14}$s, $\tau_b(T) = \tau_a(T)$, $T^* = 500$ K, $T_0 = 300$ K; parameters of β-relaxation: $E_U = 1.2 \times 10^9$ Pa, $E_0 = 4 \times 10^7$ Pa, $E_a = 0.7$ eV, $\tau_0 = 1 \times 10^{-14}$ s, $T^* = 500$ K, $T_0 = 150$ K; parameters for γ-relaxation: $E_U = 1 \times 10^9$ Pa, $E_0 = 6 \times 10^7$ Pa, $E_a = 0.6$ eV, $\tau_0 = 1 \times 10^{-14}$ s.
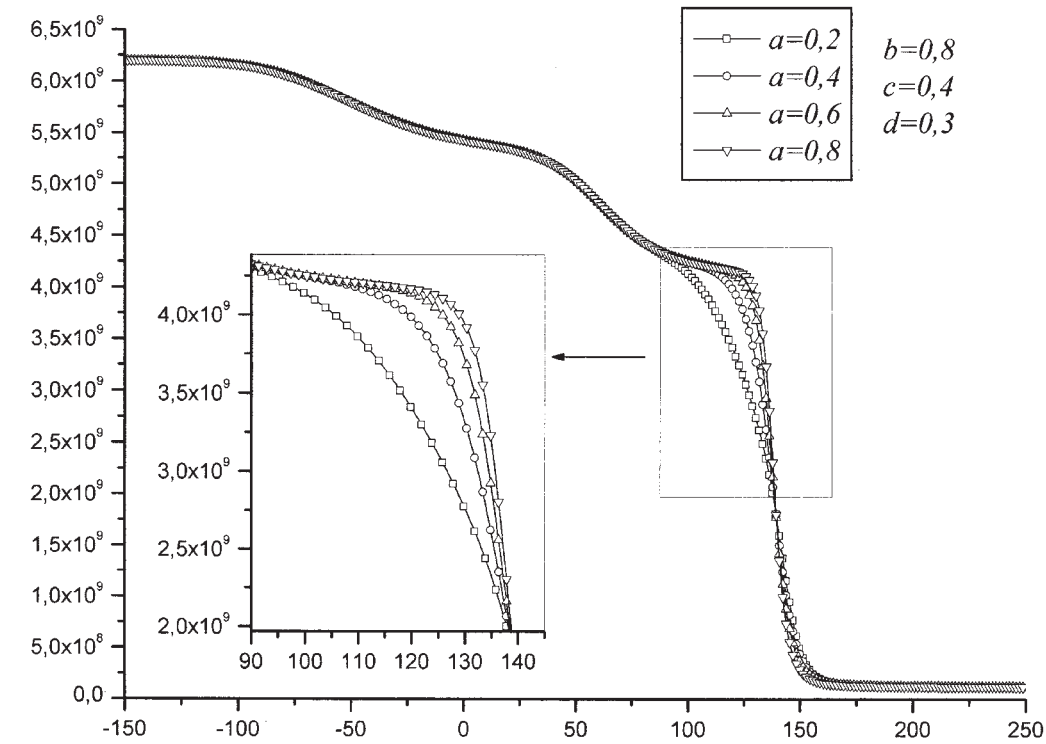
Figure 11 Storage modulus under isochronal conditions for different values of a, and the same values of parameters corresponding to Figure 10.
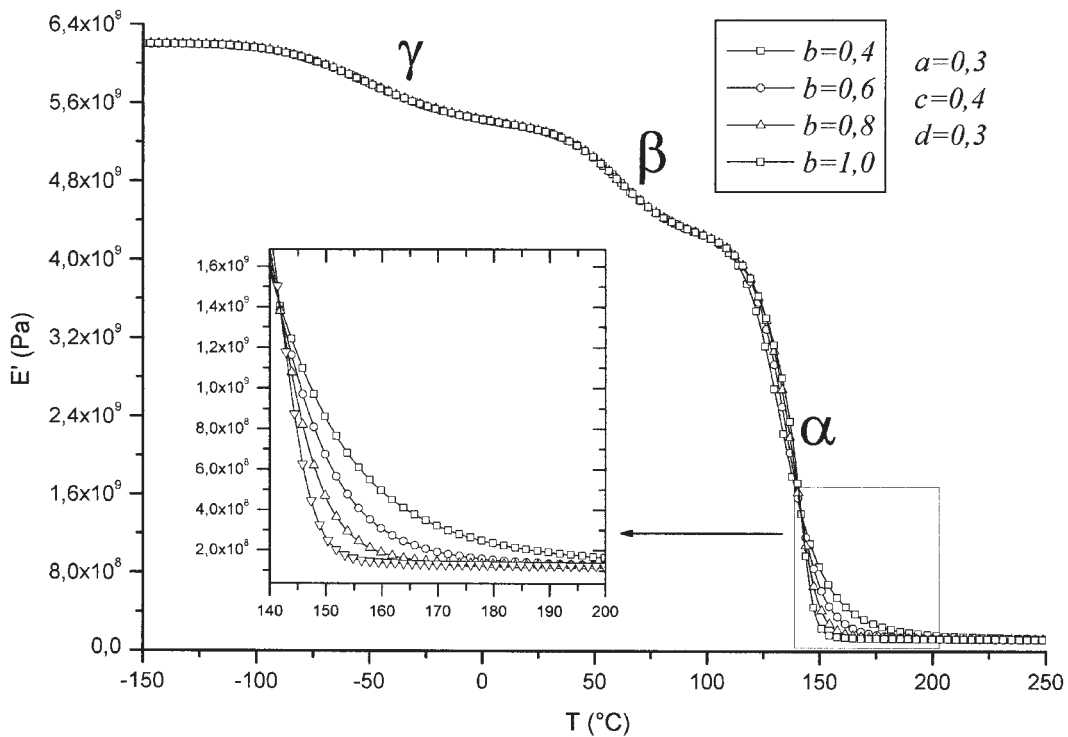

Figure 12 The temperature dependence of storage modulus for different values of b, and the same values of parameters corresponding to Figure 10.
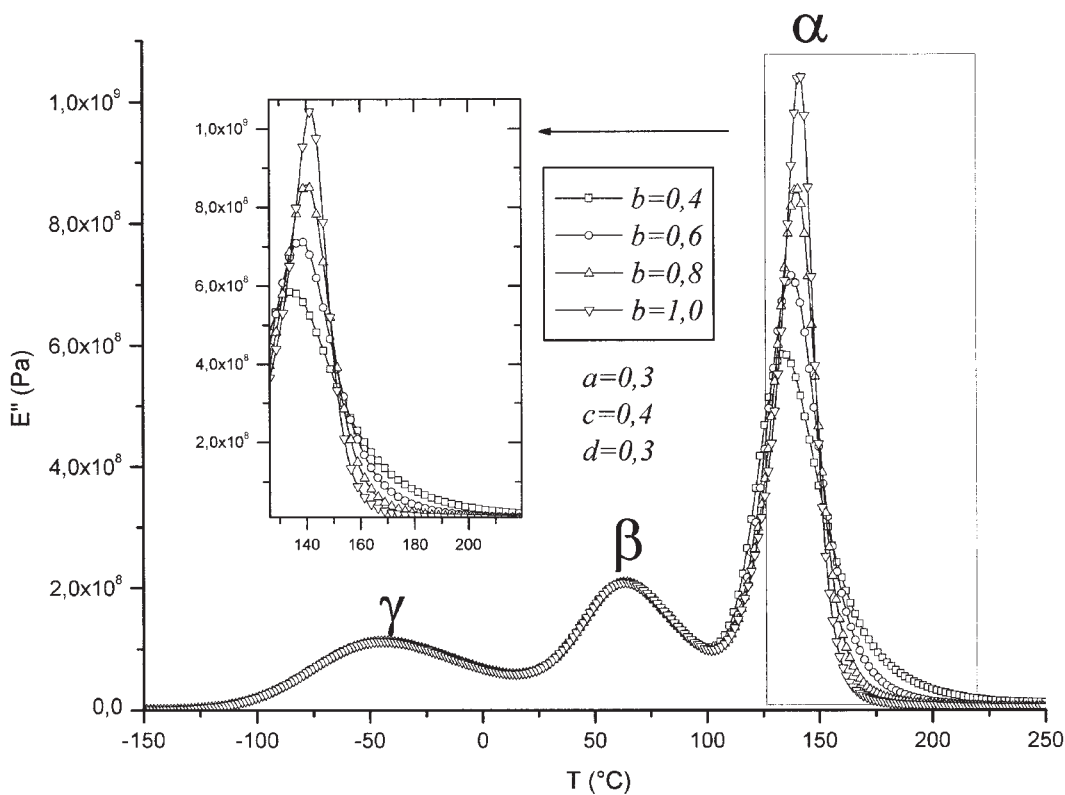
Figure 13 Loss modulus under isochronal conditions for different values of b, and the same values of parameters corresponding to Figure 10.
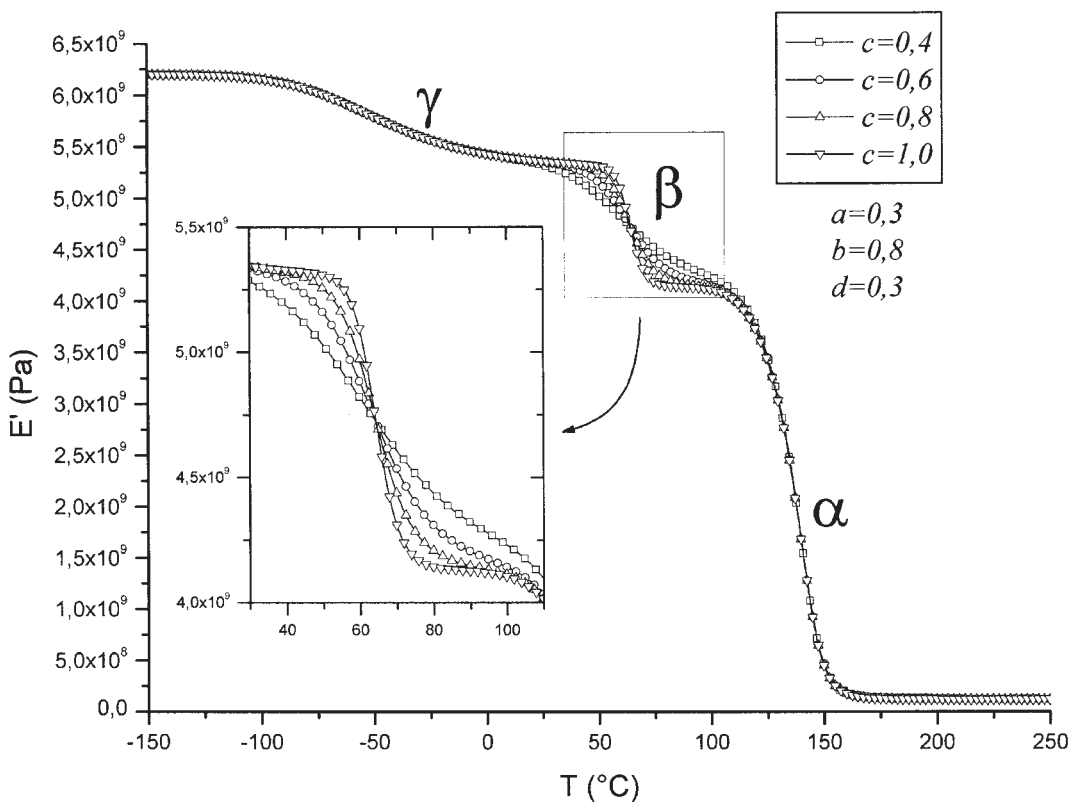

Figure 14 Storage modulus under isochronal conditions for different values of c, and the same values of parameters corresponding to Figure 10.
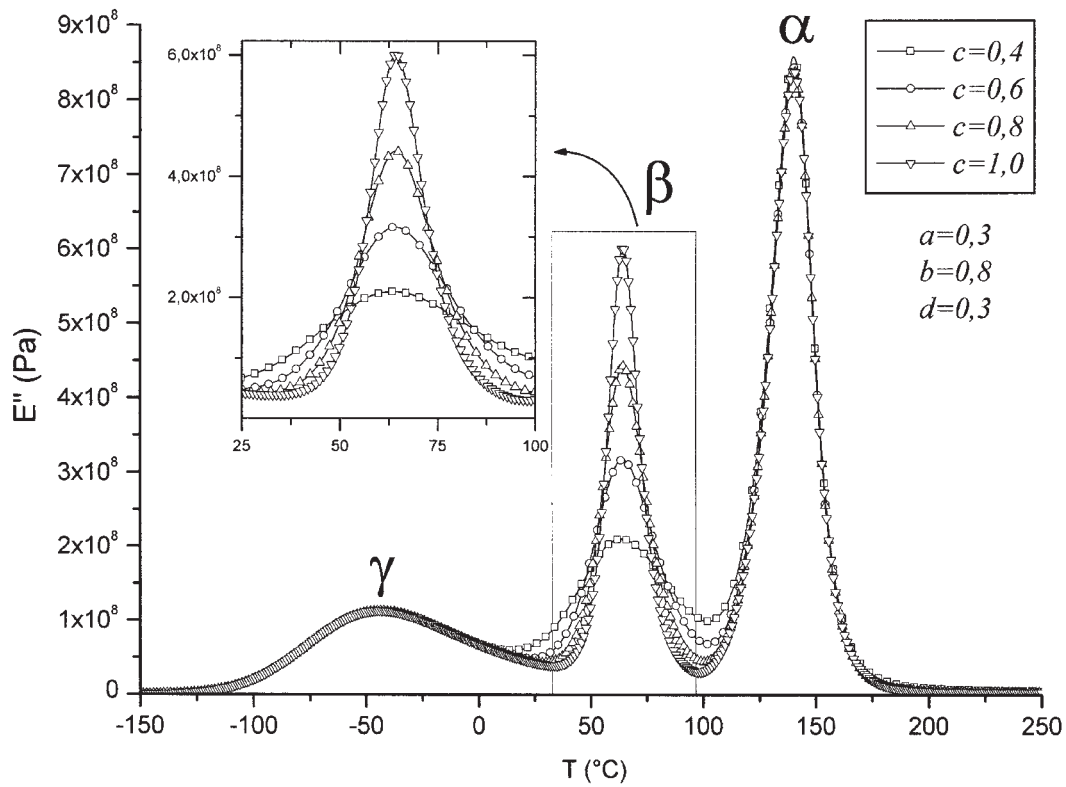
Figure 15 Loss modulus under isochronal conditions for different values of *c,* and the same values of parameters corresponding to Figure 10.
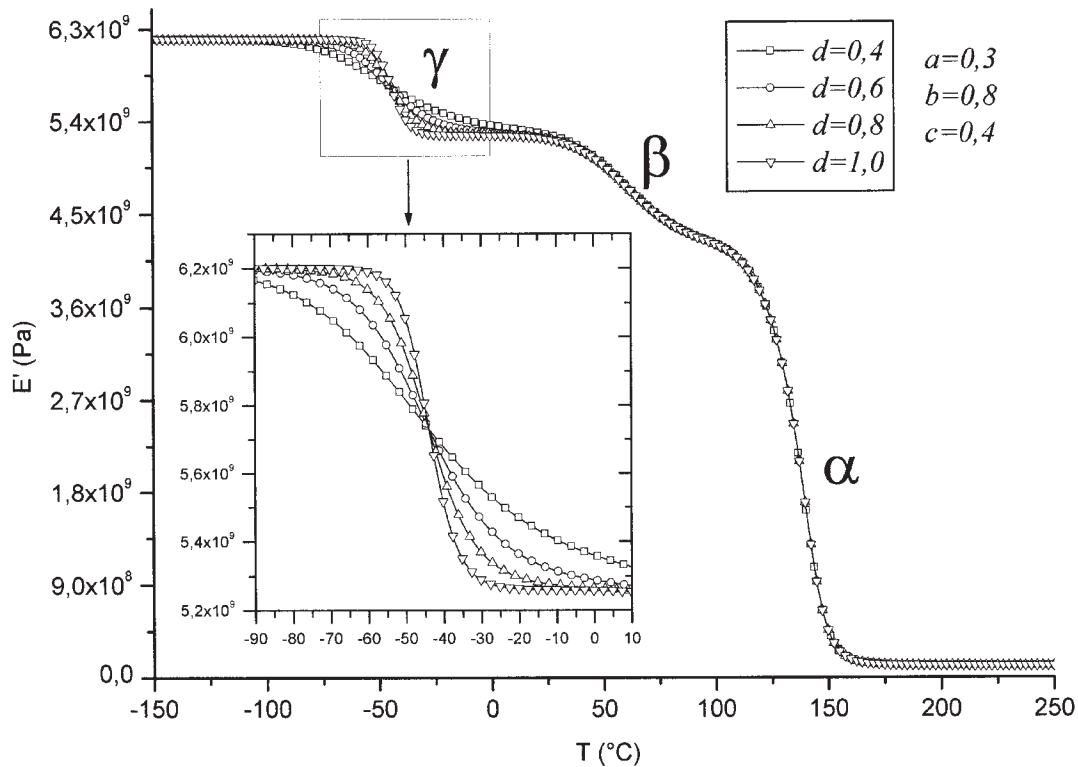

Figure 16 Storage modulus under isochronal conditions for different values of *d,* and the same values of parameters corresponding to Figure 10.
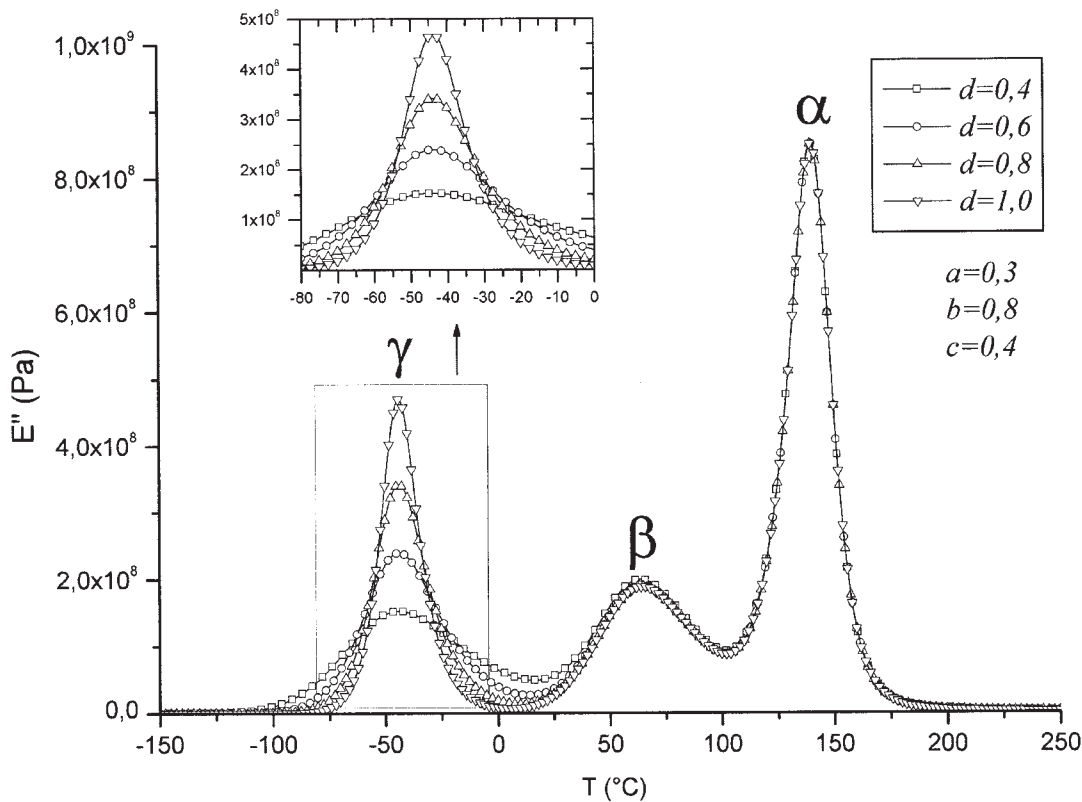
Figure 17 Loss modulus under isochronal conditions for different values of d, and the same values of parameters corresponding to Figure 10.

laxations, and the other located between β and γ relaxations. Both minima increase as c decreases.

Finally, Figures 16 and 17 show the effect of the d parameter on storage and loss moduli; in this case a, b, and c parameters are constants. Figure 16 shows how the shape of $E'(T)$ curves in the region corresponding to γ-relaxation is dependent of d. In this case the curves corresponding to α and β relaxations are superposed because a, b, and c parameters are constants.

Figure 17 shows how, when d parameter increases, the maximum associated with γ-relaxation also increases, and on the other hand d also affects to minimum located between β and γ peaks, the value of this minimum increases as d decreases.

From Figures 11, 12, 14, and 16 we can see that the shape of the $E'(T)$ curves shows five regions: glass behavior where $E' \approx E_U$; γ-relaxation where E' is mainly a function of T and d; β-relaxations where E' is mainly a function of T and c; α-relaxation where E' is mainly a function of T, b, and a; and, finally, rubber-like behavior where $E' \approx E_0$. Each relaxation phenomenon corresponds to a stretched exponential behavior of $E'(T)$, deviating from the classical exponential Debye behavior. In many cases experimentally observed relaxation functions exhibit a stretched exponential decay.[1–7]

We can note from Figures 10 to 17, the coupled effect of parameters a and c in the region between α and β relaxations and the coupled effect of parameters c and d in the region between β and γ relaxations.

The flow behavior and/or cold crystallization phenomenon[14] that could appear after rubber-like behavior with increasing temperature are not described for this fractional model.

CONCLUSION

This model takes into account the fractal intrinsic to polymers through the fractional calculus operators that appear in the governing equations; this enabled us to develop a model that returns accounts of a viscoelastic behavior in polymeric materials having three important relaxation phenomena: α, β, and γ.

Choosing in an arbitrary way the values of fractional order of our model, we have calculated for a sinusoidal request the storage and loss modulus of the dynamical elastic modulus, E^*. These diagrams enabled us to analyze the effect of the parameters of the model on α, β, and γ relaxations. We noted that a and b parameters are associated mainly with α-relaxation, c with β-relaxation, and d with γ-relaxation. The transition zone between α and β relaxation, and β and γ

relaxations, are associated to parameters *a* and *c*, and *c* and *d*, respectively. These transition zones are very important because they are very sensitive to the phenomena of physical aging.[8]

In the continuation of our work, we will analyze the experimental isochronal viscoelastic behavior of polymers having three important relaxation phenomena. This will enable us to associate a molecular interpretation to parameters of our model.

References

1. Schiessel, H.; Metzler, R.; Blumen, A.; Nonnenmacher; T. F. J Phys A: Math Gen 1995, 28, 6567.
2. Le Méhuaté Alain, A.; Nigmatullin, R. R.; Nivane, L. Flèches du temps et géométrie fractale; Editorial Hermès: Paris, 1998; 2nd ed.
3. Blumen, A.; Gurtovenko, A. A.; Jespersen, S. J Non-Cryst Solids 2002, 305, 71.
4. Alcoutlabi, M.; Martinez-Vega, J. J. Polymer 1998, 39, 6269.
5. Alcoutlabi, M.; Martinez-Vega, J. J. J Mater Sci 1999, 34, 2361.
6. Carpintieri, A.; Corneti, P. Chaos, Solitons and Fractals 2002, 13, 85.
7. Bagley, R. L.; Torvik, P. J. J Rheol 1986, 30, 133.
8. Schiessel, H.; Blumen, A. J Phys A: Math Gen 1993, 26, 5057.
9. Alcoutlabi, M.; Martinez-Vega, J. J. J Macromol Sci Phys1999, 38, 991.
10. Reyes-Melo, E.; Martinez-Vega, J.; Guerrero-Salazar, C.; Ortiz-Mendez, U. Modélisation de la viscoélasticité des polymères à l'état solide. Application du calcul fractionnaire; Revue des Composites et de Matériaux Avancés, Hermes Science Publications: Paris, 2002; vol. 12, pp. 337–359.
11. Reyes-Melo, M. E.; Martinez-Vega, J. J.; Guerrero-Salazar, C.; Ortiz-Mendez, U. Application du calcul fractionnaire à la modélisation du comportement en fréquence des diélectriques organiques; Colloque sur les Matériaux du Génie Electrique; Grenoble, France; 2–3 April 2003.
12. Martinez-Vega, J. J.; Lacabanne, C. Thermochim Acta 1993, 226, 51.
13. Matsuoka, S. J Res Natl Inst Stand Technol 1997, 102, 213.
14. Ngai, K. L. J Chem Phys 1998, 109, 6982.
15. Rault, J. J Non-Cryst Solids 2000, 271, 177.
16. Gauthier, C.; Pelletier, J. M.; David, L.; Vigier, G.; Perez, J. J Non-Cryst Solids 2000, 274, 181.
17. Zouzou, N. Thesis; Universite Paul Sabatier: Toulouse, France, 2002.
18. Martinez-Vega, J. J.; Zouzou, N.; Boudou, L.; Guastavino, J. IEEE Trans Dielectrics Electrical Insul 2001, 8, 776.