

MODELLING OF RELAXATION PHENOMENA IN ORGANIC DIELECTRIC MATERIALS. APPLICATION OF DIFFERENTIAL AND INTEGRAL OPERATORS OF FRACTIONAL ORDER

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In this work we have used differential and integral operators of fractional order (between 0 and 1) for modelling the real and imaginary parts of E^* and ε_r^* considering the three more important relaxation phenomena in semi-crystalline polymers. To justify the validity of the proposed models we have used measurements of E^* and ε_r^* under isochronal conditions of a semi-crystalline specimen of PEN in a broad temperature range.

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1. Introduction

The organic dielectric materials such as the semi-crystalline polymers have a significant place in industry, in particular in the field of electrical engineering. The excellent physicochemical properties of the semi-crystalline polymers give a satisfactory response to high demands of mechanical and electrical engineering requirements, for example in the miniaturization of electronic components or as film base for magnetic recording tapes [1,2]. These applications require, however, a wide knowledge of the viscoelastic behavior of polymers, for instance the relaxation phenomena that these materials can undergo. The relaxation phenomena are associated with molecular motions leading to a new structural equilibrium with lower energy content. The morphology of organic dielectric materials is very complex, it makes them very difficult to handle analytically. In this sense the use of differential and integral operators of fractional order (fractional calculus) is an alternative. Using these fractional operators we can model systems with partial energy dissipation, for instance the non-exponential relaxation phenomena (mechanical and dielectrical) in semi-crystalline polymers. The fractional order of a fractional integral can be considered to an indication of the remaining or preserved energy of a signal passing through a viscoelastic material [3]. Similarly, the fractional order of a derivative reflects the rate at which a portion of the energy has been lost in the system. Due to sensibility to molecular motions, the modelling of the complex modulus, $E^*=E'+iE''$, and the relative complex permittivity, $\varepsilon_r^*=\varepsilon_r'-i\varepsilon_r''$, is an alternative for studying the relaxation phenomena in polymeric materials. The dynamics of the relaxation process observed by dielectric and mechanical spectroscopies are in principle not the same. The dielectric spectroscopy monitors (ε_r^*) the fluctuating dipole moment of the polymer while the dynamic mechanical spectroscopy (E_r^*) follows the evolution of the shear stress. The spectra of real and imaginary parts of E^* and ε_r^* give complementary information about the molecular mobility of relaxation phenomena. In this work we have used fractional calculus for the mathematical description of E^* and ε_r^* , taking into account three relaxation phenomena. To test the validity of the proposed

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fractional models we have used measurements of E^* and ϵ_r^* under isochronal conditions of a semi-crystalline polymer, Poly(ethylene-2,6-naphthalene dicarboxylate) or PEN.

2. Modelling of mechanical and dielectrical manifestations of viscoelasticity

The differential and integral operators of fractional order provide an appropriate description of the mechanical and dielectrical manifestations of several relaxation phenomena present in polymeric materials. In this work we have used the Riemann-Liouville definition of a fractional integral which is a straightforward generalization to non integer values of Cauchy formula for repeated integration [4]:

$$D_t^{-a} f(t) = \int_0^t \frac{(t-y)^{a-1}}{\Gamma(a)} f(y) dy \quad \text{with } \Gamma(a) = \int_0^\infty e^{-u} u^{a-1} du \quad \text{and } a \in (0, \infty) \quad (1)$$

From Eq.1 one can also define a derivative of fractional order (between 0 and 1) by

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

In the following, we are also going to use the Fourier transform of a fractional differential operator, $D_t^a f(t)$, which can be written as a product of $(i\omega)^a$ and the Fourier transform of the function $f(t)$ [4].

Using Eq.2, we can obtain an intermediate behaviour between linear elasticity and Newtonian viscosity (spring-pot) [5-10], as well as that between an electric capacitor and Ohms law (cap-resistor).

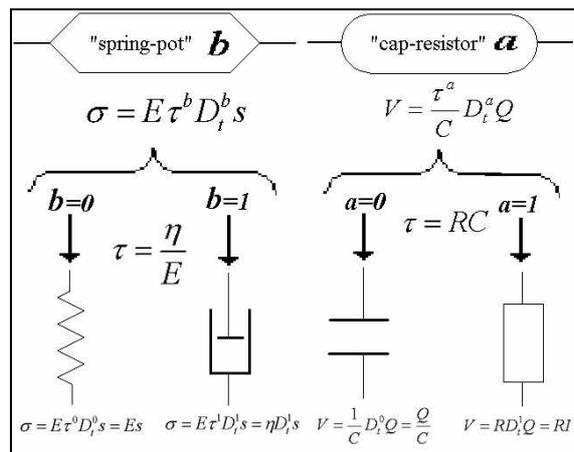


Fig. 1. The fractional elements obtained using fractional calculus.

In the fractional elements "spring-pot" and "cap-resistor", τ is a characteristic time called relaxed time, which could be associated to time required by chain segments in movement for a complete reorganization and a full reorientation to a new structural equilibrium state. Note that from a "spring-pot" one obtains the Hook's law when $b=0$ and when $b=1$, Newton's law is obtained. On the other hand, an electrical-resistor behaviour is obtained from a "cap-resistor" when $a=1$ and when $a=0$, the electric behaviour corresponds to that of a capacitor.

Using fractional elements of Fig. 1 we have obtained the mechanical and dielectric fractional models for modelling three relaxation phenomena. Fig. 2a and Fig. 2b show the proposed models.

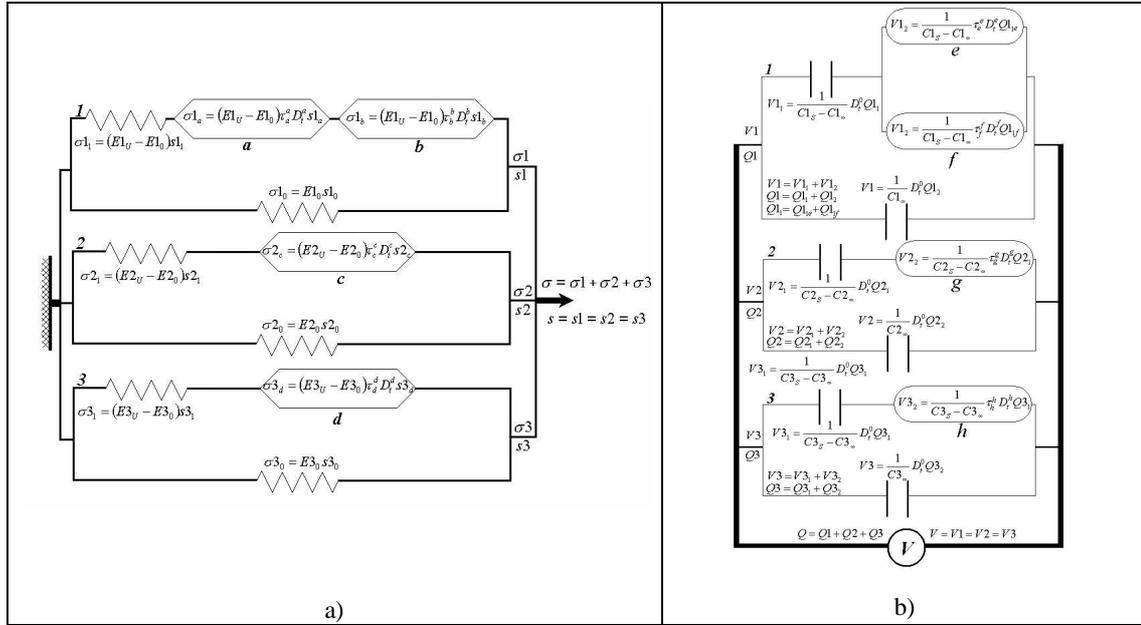


Fig. 2. Modelling of three relaxation phenomena. a) The Mechanic Fractional Model (MFM), b) The Dielectric Fractional Model (DFM).

The Mechanical Fractional Model (MFM) and the Dielectric Fractional Model (DFM) are based on three elements arranged in parallel for modelling the three relaxation phenomena of PEN. The first elements of either MFM and DFM are mainly associated with α -relaxation, the second elements are associated with β^* -relaxation and the last elements are associated with the β -relaxation. In dynamical analysis, the polymer is subject to an alternating excitation (mechanical or electrical) and the response can be expressed as a complex variable. The real part corresponds to an instantaneous response, and the imaginary part corresponds to a delayed response associated with the partial energy dissipation. For a mechanical excitation, we can calculate the complex elastic modulus, $E^* = E' + iE''$ from the MFM and for an electric excitation, we obtain the relative complex permittivity, $\epsilon_r^* = \epsilon_r' - i\epsilon_r''$, from the DFM. Table 1 shows the fractional differential equations for each element of MFM and DFM. In either MFM or DFM the τ parameters have been associated with the relaxation times of molecular motions associated to each mechanical or dielectrical relaxation phenomenon.

Table 1. The fractional differential equations for the MFM and DFM.

Element	The fractional differential equations	
	MFM	DFM
1	$(E_{1v} - E_{1s})s(t) = [\sigma(t) - E_{1s}s(t)] + \tau_1^\alpha D_t^\alpha [\sigma(t) - E_{1s}s(t)] + \tau_1^\beta D_t^\beta [\sigma(t) - E_{1s}s(t)]$	$Q1 = C_{1\infty}V1 + (C_{1s} - C_{1\infty}) \left[\tau_1^\alpha D_t^\alpha \left(V1 - \frac{Q1 - C_{1\infty}V1}{C_{1s} - C_{1\infty}} \right) + \tau_1^\beta D_t^\beta \left(V1 - \frac{Q1 - C_{1\infty}V1}{C_{1s} - C_{1\infty}} \right) \right]$
2	$\sigma 2(t) + \tau_2^c D_t^c \sigma 2(t) = E_{20} s 2(t) + E_{2v} \tau_2^c D_t^c s 2(t)$	$V 2 = \frac{Q 2 - C_{2\infty} V 2}{C_{2s} - C_{2\infty}} + \frac{\tau_2^g}{C_{2s} - C_{2\infty}} D_t^g (Q 2 - C_{2\infty} V 2)$
3	$\sigma 3(t) + \tau_3^d D_t^d \sigma 3(t) = E_{30} s 3(t) + E_{3v} \tau_3^d D_t^d s 3(t)$	$V 3 = \frac{Q 3 - C_{3\infty} V 3}{C_{3s} - C_{3\infty}} + \frac{\tau_3^h}{C_{3s} - C_{3\infty}} D_t^h (Q 3 - C_{3\infty} V 3)$

Applying the Fourier transform to the fractional differential equations shown in Table 1, we have calculated E^* and ε_r^* , which could be expressed as a function of the corresponding complex modulus and complex permittivities of each element of the MFM and DFM.

$$E^* = E1^* + E2^* + E3^* = \frac{E1_U + E1_0 \left((i\omega\tau_a)^{-a} + (i\omega\tau_b)^{-b} \right)}{1 + (i\omega\tau_a)^{-a} + (i\omega\tau_b)^{-b}} + \frac{E2_0 + E2_U (i\omega\tau_c)^c}{1 + (i\omega\tau_c)^c} + \frac{E3_0 + E3_U (i\omega\tau_d)^d}{1 + (i\omega\tau_d)^d} \quad (3)$$

$$\varepsilon_r^* = \varepsilon1_r^* + \varepsilon2_r^* + \varepsilon3_r^* = \frac{\varepsilon1_{r\infty} + \varepsilon1_{rs} \left((i\omega\tau_e)^{-e} + (i\omega\tau_f)^{-f} \right)}{1 + (i\omega\tau_e)^{-e} + (i\omega\tau_f)^{-f}} + \frac{\varepsilon2_{rs} + \varepsilon2_{r\infty} (i\omega\tau_g)^g}{1 + (i\omega\tau_g)^g} + \frac{\varepsilon3_{rs} + \varepsilon3_{r\infty} (i\omega\tau_h)^h}{1 + (i\omega\tau_h)^h} \quad (4)$$

From Eq. 3 and Eq. 4 we can obtain the temperature dependence of the real and imaginary parts of E^* and ε_r^* . However, at first we need to define the relationship between the relaxation time and temperature, which in turn depends on cooperative or non-cooperative nature of the molecular motions. The cooperative movements are simultaneous motions of segment-chains due to the interference of neighbouring segment-chains. In a non-cooperative process the segment-chains are able to move without being interfered by their neighbours because they are very localized movements. In the case of PEN, the molecular motions of α -relaxation are cooperative movements, β^* -relaxation is associated with partial cooperative movements and β -relaxation represents very localized motions having a negligible cooperativity, consequently they can be considered as non-cooperative movements [11].

The relaxation time, $\tau(T)$, for non-cooperative motions follows an Arrhenius law behaviour:

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

were the apparent activation energy, E_a , could be in the range of a real energy barrier, k_B is the Boltzman constant, T the absolute temperature, and τ_0 the pre-exponential factor, typically it falls within the range $10^{-16} s \leq \tau_0 \leq 10^{-13} s$. Values of τ_0 in the vicinity of the upper limit correspond to molecular vibrational times and the lower limit may be rationalized by an additional entropy contribution [12].

On the other hand, cooperative motions involve simultaneous movements of chain segments. The probability of success for cooperative motions is P^Z , $P \propto \frac{1}{\tau}$ is the probability of a single elementary movement. The Z exponent can be considered as the number of elementary movements, consequently, $\tau_{cooperative}$ represents a power law [13,14].

$$\tau_{cooperative}(T) = \tau_0 \left(\frac{\tau}{\tau_0}\right)^Z = \tau_0 \left[\exp\left(\frac{E_{a \text{ single movement}}}{k_B T}\right) \right]^Z \quad (6)$$

where τ is the relaxation time of the elementary movement defined by an Arrhenius behavior. Z exponent is dependent of the polymer structure and is calculated from the next equation [13,14]:

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

Above a cross-over temperature, T^* , cooperative and non-cooperative movements merge together [14] and $Z=1$. Below T^* the relaxation times of cooperative movements verify the empirical Vogel-Fulcher-Tammann equation. T^* is of the order of $1.3T_g$ in amorphous polymers whereas it corresponds to the melting temperature in semi-crystalline polymers [14]. T_0 is a temperature below T_g where $Z \rightarrow \infty$ and also $\tau_{cooperative} \rightarrow \infty$.

In order to verify the isochronal behaviour of the MFM and DFM we proceeded to vary systematically the fractional order of “spring-pots” and “cap-resistors”. It is important to point out that these parameters can only take values between 0 and 1. Fig. 3a and Fig. 3b show respectively the isochronal descriptions obtained from the MFM and DFM. In this case, we have considered different values of b and a , c , and d remain constants for the MFM. For the DFM, we have considered different values of f and remaining e , g , and h constants. For both MFM and DFM, cooperative movements have been considered for α -relaxation; partial cooperative movements for β^* -relaxation and non-cooperative motions for β -relaxation.

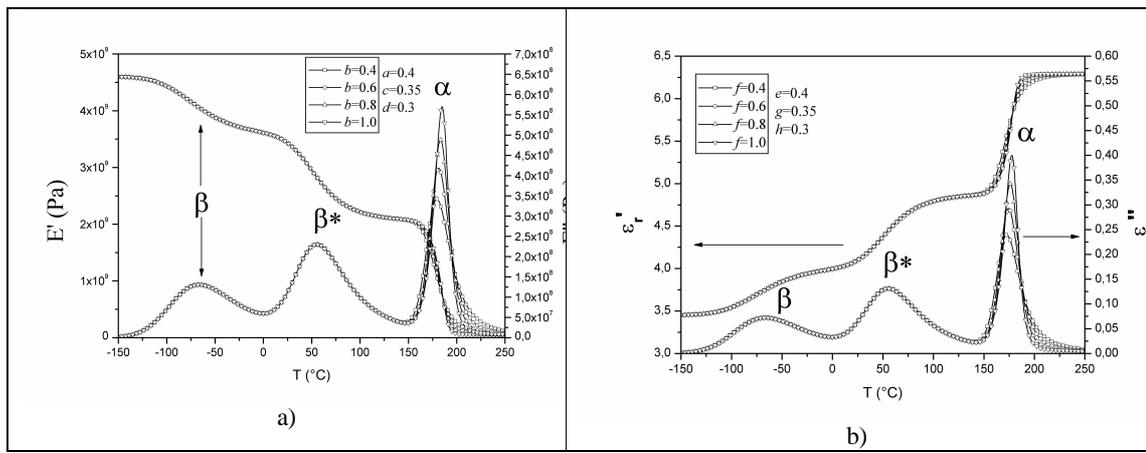


Fig. 3. The effect of fractional orders of spring-pots and cap-resistors of the MFM and DFM.
a) The real and imaginary parts of E^* , b) The real and imaginary parts of ϵ_r^* .

Each relaxation mode manifests by an increase of ϵ_r' and a decrease of E' with increasing temperature. These behaviours are associated with the three peak values in ϵ_r'' and E'' diagrams, the peak at low temperatures corresponds to β -relaxation, the second peak is associated with β^* -relaxation and the last one at higher temperatures with α -relaxation. In Fig.3a, the shape of the isochronal curves E' and E'' at the point where α -relaxation starts when the temperature decreases is strongly dependent on b , while at the end of the curves, a determines the change in E' and E'' . For the dielectric manifestation of α -relaxation (Fig. 3b), the shape of the curves ϵ_r' and ϵ_r'' are strongly depends on f when the temperature decreases, while at the end of the curves, e determines the change in ϵ_r' and ϵ_r'' . The parameters b and a are associated with the mechanical manifestation of α -relaxation, and the dielectric manifestation of α with e and f parameters. For β^* -relaxation, the mechanical manifestation is associated with c , and the dielectric manifestation with g . For β -relaxation, the mechanical manifestation is associated with d , and the dielectric manifestation with h . In the next section, we compare the theoretical predictions of the MFM and DFM with experimental measurements of E^* and ϵ_r^* , for a semi-crystalline specimen of PEN. For mechanical measurements, we have used 70 μ m-thick films, the measurements were made using a mechanical analyzer (DMA2980-TA Instruments). For dielectric measurements, we used 45 μ m-thick films and the metallization with gold was carried out on each of the two faces of the sample to guarantee a better contact with the electrodes of the dielectric analyzer used (DEA2970-TA Instruments).

3. Comparison between theoretical predictions and experimental results

In order to validate the MFM and DFM, we compared the theoretical predictions with the experimental results of real and imaginary parts of E^* and ϵ_r^* , obtained under isochronal conditions at a frequency of 10 Hz. Fig. 4a and Fig. 4b show a good agreement between theoretical and experimental isochronal spectra of the mechanical and dielectric manifestations of viscoelasticity of PEN. In the case of dielectric spectra (Fig. 4b) at $T > 160^\circ\text{C}$, $\epsilon_r''(T)$ increases with increase in

temperature, this behaviour is associated with the conductivity phenomenon and is not predicted by our DFM.

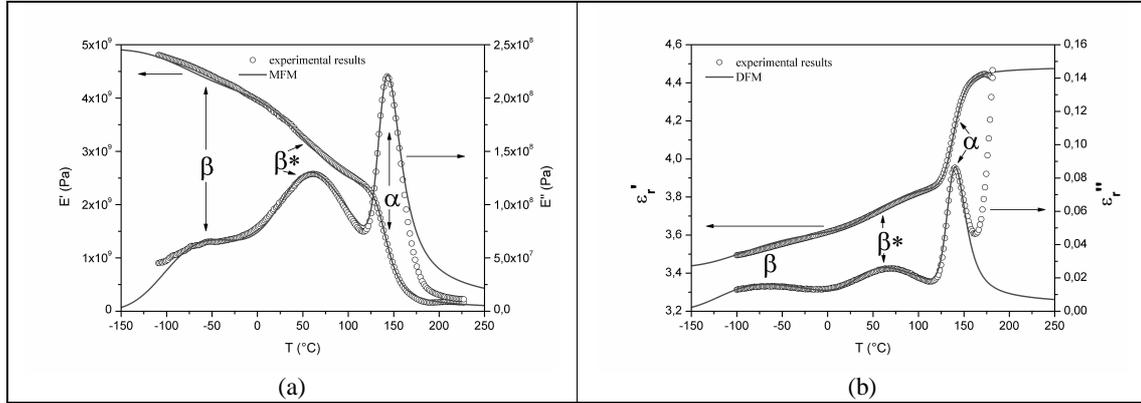


Fig. 4. Comparison of the model predictions and experimental results. a) The real and imaginary parts of E^* , b) The real and imaginary parts of ϵ_r^* .

Table 2 shows the values of fractional orders of “spring-pots” and “cap-resistors” and activation parameters used to obtain the predictions of the MFM and DFM in Fig. 4a and Fig. 4b. For the MFM, we obtain $b > a > c > d$ and for the DFM, $f > e > g > h$.

Table 2. The parameters of the MFM and DFM.

Relaxation	MFM	DFM
α Cooperative movements	$a=0.17$	$e=0.24$
	$b=0.27$	$f=0.41$
	$E1_U-E1_0=1.96 \times 10^9 \text{ Pa}$	$\epsilon1_{rs}-\epsilon1_{r\infty}=0.58$
	$\tau_0=1 \times 10^{-18} \text{ s}$	$\tau_0=1 \times 10^{-14} \text{ s}$
	$E_{a \text{ single-movement}}=0.66 \text{ eV}$	$E_{a \text{ single-movement}}=0.47 \text{ eV}$
	$T^*=267^\circ \text{ C}$	$T^*=267^\circ \text{ C}$
	$T_0=77^\circ \text{ C}$	$T_0=76^\circ \text{ C}$
β^* Partially cooperative movements	$c=0.142$	$g=0.19$
	$E2_U-E2_0=1.64 \times 10^9 \text{ Pa}$	$\epsilon2_{rs}-\epsilon2_{r\infty}=0.25$
	$\tau_0=1 \times 10^{-34} \text{ s}$	$\tau_0=1 \times 10^{-14} \text{ s}$
	$E_{a \text{ single-movement}}=2.04 \text{ eV}$	$E_{a \text{ single-movement}}=0.56 \text{ eV}$
	$T^*=267^\circ \text{ C}$	$T^*=267^\circ \text{ C}$
β Non-cooperative movements	$T_0=-238^\circ \text{ C}$	$T_0=-83^\circ \text{ C}$
	$d=0.13$	$h=0.17$
	$E3_U-E3_0=1.35 \times 10^9 \text{ Pa}$	$\epsilon3_{rs}-\epsilon3_{r\infty}=0.24$
	$\tau_0=1 \times 10^{-18} \text{ s}$	$\tau_0=1 \times 10^{-14} \text{ s}$
	$E_{a \text{ apparent}}=0.715 \text{ eV}$	$E_{a \text{ apparent}}=0.5 \text{ eV}$

As a first approximation, the molecular motions associated with β -relaxation can be represented by parameter d in the case of the mechanical spectra, and h in the case of dielectric spectra. The partially cooperative motions associated with β^* -relaxation can be represented by parameter c for mechanical spectra and g in the case of dielectric spectra. Finally parameters a and b could be used to represent mechanical motions associated with α -relaxation, and parameters e and f to represent dipolar movements associated with dielectric manifestation of α -relaxation.

The molecular mobility associated with the mechanical and dielectric manifestation of α -relaxation are cooperative processes in the temperature range from $T_0 \approx T_g - 50^\circ \text{ C}$ to $T^* \approx 267^\circ \text{ C}$, in

this case, T^* is equal to the fusion temperature of PEN. For β^* -relaxation, the molecular movements are less cooperative than α -movements in the temperature range from $T_0 < T_g - 50$ °C to $T^* \approx 267$ °C. For β -relaxation, the apparent activation energies for both the MFM and DFM are of low value corresponding to non-cooperative processes.

4. Conclusions

The fractional models proposed: MFM and DFM give predictions of the mechanical and dielectric behaviour of semi-crystalline polymers having three important relaxation phenomena. The comparison between experimental results and theoretical predictions show good agreement and consequently a success for our MFM and DFM. We noted that the fractional orders of the “spring-pots” and “cap-resistors” of the MFM and DFM are related to molecular motions associated with α , β^* , and β relaxations.

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References

- [1] T. Higashioji, T. Tsunekawa, B. Bhushan; *Tribology International* **36**, 437 (2003).
- [2] W. Duk Lee, E. Sang Yoo, S. Soon Im, *Polymer* **44**, 6617 (2003).
- [3] M. Moshrefi-Torbati, J.K. Hammond, *Journal Franklin Institute* **335B**, 6, 1077 (1998).
- [4] P. L. Butzer, U. Westphal; “An introduction to fractional calculus”, *Applications of fractional calculus in physics*, Editor R. Hilfer, World Scientific, (2000).
- [5] M. Alcoutlabi, J. J. Martinez-Vega, *Polymer* **44**, 7199(2003).
- [6] N. Heymans, *Signal Processing* **83**, 2345 (2003).
- [7] E. Reyes-Melo, J. J. Martinez-Vega, C. Guerrero-Salazar, U. Ortiz-Mendez, *Revue des composites et de matériaux avancés* **12**, 2, 337 (2002).
- [8] M. E. Reyes-Melo, J. J. Martinez-Vega, C. Guerrero-Salazar, U. Ortiz-Mendez; “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 Avril 2003.
- [9] E. Reyes-Melo, J. J. Martinez-Vega, C. Guerrero-Salazar, U. Ortiz-Mendez; “On the modeling of the dynamic-elastic modulus for polymer materials under isochronal conditions”, impress for publication JAPS.
- [10] M. E. Reyes-Melo, J. J. Martinez-Vega, M. Salvia; “Modélisation du module dynamique sur conditions isochrones des isolants organiques à l’état solide. Application du calcul fractionnaire”, *Colloque Electrotechnique du Futur, Supélec, Gif-sur-Yvette, Paris France 9-10 Décembre 2003*.
- [11] J. J. Martinez-Vega, N. Zouzou, L. Boudou, J. Guastavino, *IEEE Transactions on Dielectrics and Electrical Insulation* **8**, 5, 776 (2001).
- [12] K. L. Ngai, *Journal of Chemical Physics* **109**, 16, 6982 (1998).
- [13] S. Matsuoka, *Journal of Research of the National Institute of Standards and Technology* **102**, 2, 213 (1997).
- [14] J. Rault, *Journal of Non-Crystalline Solids* **271**, 177 (2000).