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Self-consistent approach of the constitutive law of a two-phase visco-elastic material described by fractional derivative models

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The constitutive law of a two-phase isotropic polymer blending described by fractional derivative models is obtained through a classical self-consistent scheme. A parametric analysis is driven to describe the influence of the four parameters associated with the constitutive law description and to comprise the conditions of application of the model. An identification of the set of parameters is performed by mechanical spectroscopy for two amorphous polymers: the polymethyl methacrylate (PMMA) and the styrene acrylonytrile copolymer (SAN) and their mixture, to evaluate the ability of the model to reproduce the experimental results obtained from the Dynamic Mechanical Thermal Analysis.

Key words: homogenisation, self-consistent theory, visco-elastic properties, fractional derivative, glass transition.

1. Introduction

Blending of polymeric materials is an efficient way of improving the mechanical and/or the physicochemical properties of existing polymers. The problem is significant both from the academic and practical points of view. An adequate description of the visco-elastic constitutive law of polymers is prescribed by hierarchical elements often called 'spring dashpots' (Koeller, [1]). These elements are particularly efficient to describe the polymer constitutive law in the glass transition range, in great accordance with experimental results (see Oldham and Spanier, [2]). The corresponding memory kernel is formulated in function of a characteristic relaxation time which may be related to the effective disentanglement vibration frequency. The creep and stress relaxation phenomena are decaying non-exponentially unlike the classical Maxwell or Kelvin–Voigt descriptions.

Several attempts have already been conducted to describe the equivalent constitutive law of visco-elastic heterogeneous media. If the employed methods are often concentrated on dealing with the difficulties induced by the visco-elastic coupling in the constitutive equations, the material constitutive law is proposed as Maxwellian. However, there is experimental evidence that the equivalent constitutive law of a multiphase material made of Maxwellian constituents is not Maxwellian either. This results from complex long-range memory effects described by an additional effective contribution which takes the form of an interaction kernel (Suquet, [3]). This particular feature was subjected to different treatments intended to get through the difference of derivative orders of stress and strain, encountered in the constitutive equations. Some resolution schemes were based on the tangent linearisation of the local material constitutive law (Molinari *et al.*, [4]). An alternative procedure proposed the description of the visco-elastic effects by adequate internal variables, leading to a step-by-step estimate of the effective behavior by means of variational methods (Lahellec and Suquet, [5]). Paquin *et al.* [6] applied the internal variables procedure with translated fields to give a new instantaneous formulation of the strain rate and its derivations. More recently, Coulibaly [7] included the viscoelastic effects via a second independent integral equation written for the stress rate field.

The difficulty of the simultaneous occurrence of different derivative orders may be bypassed with the help of the Laplace–Carson technique and the associated correspondence principle formulated by Mandel [8]. After a direct Laplace–Carson transform, the visco-elastic problem is written as a symbolical elastic one which may have a closed-form solution known from the reference work. Using this elegant scheme, Laws and McLaughlin [9] proposed the equivalent compliance of composites, they emphasized however the complex and computer time-consuming character of the Laplace inversion. Rougier *et al.* [10] proposed a representation of the equivalent two-phases Maxwellian media in relaxation spectra; this spectral analysis was further extended by Beurthey and Zaoui [11] for a multiphase model, under a self-consistent scheme method first historically presented by Hershey [12]. In order to improve the inverse Laplace transform usually conducted by a collocation method, Brenner *et al.* [13] gave an approximate estimate of the time-response by considering a quasi-linear development of the frequency response in the vicinity of a 'well-chosen' frequency in a logarithmic scale, in combination with the direct inversion method advocated by Schapery [14].

The occurrence of a particular frequency in this work corresponds to the characteristic time relaxation associated to the 'spring dashpots' or 'fractional order viscous elements', which is one of the material parameters of the fourth-order fractional derivative model. As presented in the second section, this model describes worthily the material constitutive law throughout the several frequency decades covering the glass transition. The visco-elastic constitutive law is described in the Fourier space by complex modulus supplied by a Dynamic Mechanical Thermal Analysis device (DMTA). The evolutions of the loss factor defined as the ratio of the dissipative and conservative moduli, are translated according to the frequency to allow their treatment in the homogenisation model. The inherent mathematical properties of the fractional order derivation are particularly powerful in the Laplace and Fourier domains, when the correspondence principle is used to transform the visco-elastic problem. The equivalent constitutive law of the two-phase isotropic visco-elastic materials described by fractional derivative model is developed in the third section by means of a classical self-consistent scheme. A parametric study gives the numerical equivalent response in the Fourier domain when the phases present alternatively close and separated glass transitions. The fourth section is devoted to an experimental validation of the proposed model for a blending, consisting of two amorphous polymers whose glass transition are relatively close: the polymethyl methacrylate (PMMA) and the styrene acrylonytrile copolymer (SAN). The model developed in this work supplies the estimation of the blend constitutive law according to the set of four parameters identified for every pure polymer and of the volume fraction. The loss factor calculated by the homogenisation technique is compared to the results following from the spectroscopic experimental analysis. The last, concluding section proposes further developments that may be conducted.

2. Constitutive modelling of visco-elastic materials using fractional differential operators

2.1. Statement of reasons

Among the specific properties of amorphous polymers and elastomers, the substantial modifications of physical properties in the glass transition is subject of great interest as it concerns a wide variety of engineering applications – such as tire conception and vibration isolation. The glass transition, indeed, is commonly observed through the behaviour change from glassy state to rubbery state (and *vice versa*) when frequency and/or temperature are modified. The material behaviour follows a variable combination of pure elastic and viscous contributions depending on the frequency and the temperature. As a consequence, the visco-elastic constitutive behaviour of amorphous polymers in glass transition is affected by this mixed dependence, which reveals to be linked by the corresponding effects commonly called time-dependence superposition. This equivalence principle allows to present the experimental data recorded at various frequencies and temperatures in a single curve, called by FERRY [15] a master curve. The spectroscopic experiments, usually called Dynamic Mechanic Thermal Analyses (DMTA), are conducted by imposing elementary cyclic loading spectra (traction or shearing) to the polymeric sample during a temperature increase cycle, at various frequencies. DMTA can exhibit both elastic and viscous behaviours which are respectively correlated to stored and dissipated energies.

In the Fourier domain, constitutive equations of the visco-elastic material can be expressed as:

$$\bar{\sigma}(i\omega) = \bar{E}(i\omega)\bar{\varepsilon}(i\omega). \tag{2.1}$$

The complex modulus $\bar{E}(i\omega)$ is decomposed into real and imaginary parts $E'(\omega)$ and $E''(\omega)$, defined respectively as conservative and dissipative moduli:

$$\bar{E}(i\omega) = E'(\omega) + iE''(\omega). \tag{2.2}$$

The quantity of primary industrial interest is the ratio E''/E' which is a measure of the damping efficiency. It represents the tangent of the phase angle between stress and strain and is called the loss factor $\eta(\omega)$:

$$\eta(\omega) = \frac{E''(\omega)}{E'(\omega)}. \tag{2.3}$$

The loss factor appears to be the most significant function to consider when identification of relaxation parameters is conducted. Moreover, it allows an accurate description of the damping properties in the glass transition.

First attempts to describe visco-elastic behaviour implied a combination of ideal elementary elements: spring and dashpot. The simplest combinations in series and in parallel give respectively the Maxwell and Kelvin–Voigt models. In the Maxwell model, the strain rate is taken as the sum of parts proportional to the stress and the rate of stress as:

$$\dot{\varepsilon} = (1/E_\infty)\dot{\sigma} + (1/\tau E_\infty)\sigma \tag{2.4}$$

and the Kelvin–Voigt model corresponds to a stress equal to the sum of parts proportional to the strain and the strain rate

$$\sigma = \tau E_\infty \dot{\varepsilon} + E_0 \varepsilon. \tag{2.5}$$

E_0 and E_∞ denote respectively the long time (or relaxed) and the instantaneous (or un-relaxed) moduli. The index in moduli notation has to be interpreted as frequency limit as described in [19]. The viscosity η_e associated to the dashpot has been expressed as a function of the relaxation time: $\tau = \eta_e/E_\infty$ for the sake of comparison between the different formulations. Unfortunately, these simplified models do not describe the real behaviour of a wide class of polymers in the glass transition: the Maxwell model does not describe any strain recovery and the Kelvin–Voigt model does not describe any instantaneous response after sudden change in stress. The simplest improvement is a three-element association called Zener or a single relaxation time model whose constitutive equation is

$$\sigma + \tau\dot{\sigma} = E_0\varepsilon + E_\infty \tau \dot{\varepsilon}. \tag{2.6}$$

It is found that this model is not coherent with certain experimental observations: the width dependence of the loss tangent $\eta = E''/E'$ versus the material is insufficiently described by the set of the parameters (E_0, E_∞, τ).

These limitations conducted first to add more elementary associations of Maxwell or Kelvin–Voigt type, to end up at the Generalized Maxwell or Kelvin–Voigt models. However, the multiple combination and the number of involved parameters led to consider alternative formulations.

2.2. Fractional derivative model

Polymeric materials exhibit fading memory, i.e. the stress generates a strain state which not only depends on the current strain history but also on the previous strain states. A particular class of material constitutive laws has been formulated through integral, hereditary or convolution forms, following the superposition principle introduced by BOLTZMANN [16]. The classical hereditary models correspond to exponentially decaying memory resulting from a continuous distribution of relaxation times of the Generalized Maxwell model. ENELUND and OLSSON [17] gave an alternative formulation of this spectral description by means of a fractional derivative operator. They proposed a mathematical frame to previous empirical descriptions of constitutive laws, based on similarities observed between the mechanical and dielectric relaxations.

The generic fractional-order constitutive law equation is retained in the following form:

$$\begin{aligned}\sigma(t) + b_1\frac{d^{\beta_1}\sigma(t)}{dt^{\beta_1}} + b_2\frac{d^{\beta_2}\sigma(t)}{dt^{\beta_2}} + \cdots + b_m\frac{d^{\beta_m}\sigma(t)}{dt^{\beta_m}} \\ = a_0\varepsilon(t) + a_1\frac{d^{\alpha_1}\varepsilon(t)}{dt^{\alpha_1}} + a_2\frac{d^{\alpha_2}\varepsilon(t)}{dt^{\alpha_2}} + \cdots + a_n\frac{d^{\alpha_n}\varepsilon(t)}{dt^{\alpha_n}},\end{aligned} \tag{2.7}$$

where σ and ε can be referred equally to deviatoric or hydrostatic parts with appropriate set of a parameters, as demonstated by ENELUND and LESIEUTRE [18] for a high damping polymer. The operator d^α of the fractional derivative of the αth order is defined for $0 < \alpha < 1$ as:

$$d^\alpha[x(t)] = \frac{1}{\Gamma(1-\alpha)}\frac{d}{dt}\int_0^t \frac{x(u)}{(t-u)^\alpha}du \tag{2.8}$$

where Γ denotes the Gamma function. It is important that the number of time derivatives of strain and stress in (2.7) can not be arbitrary to ensure the description of an effective material constitutive law and to satisfy the causality condition formulated as $\beta_m \le \alpha_n$.

2.2.1. Four-parameter fractional derivative model. As previous attempts of identifications of visco-elastic constitutive law have already proved (HARTMANN *et al.* [19]), fractional order derivative models of visco-elasticity are efficient to describe polymer relaxation in glass transition with fewer parameters. Typically, a four-parameter model allows an accurate description of the polymers exhibiting the symmetrical evolution of the loss factor versus the normalized frequency $\omega\tau$ (Fig. 1). The so-called fractional Zener formulation – corresponding to the Cole-Cole empirical identification – relies on the strain and the stress histories in the time domain as:

$$\sigma(t) + \tau^{\alpha} \frac{d^{\alpha}\sigma(t)}{dt^{\alpha}} = E_0 \varepsilon(t) + E_{\infty} \tau^{\alpha} \frac{d^{\alpha}\varepsilon(t)}{dt^{\alpha}}. \tag{2.9}$$

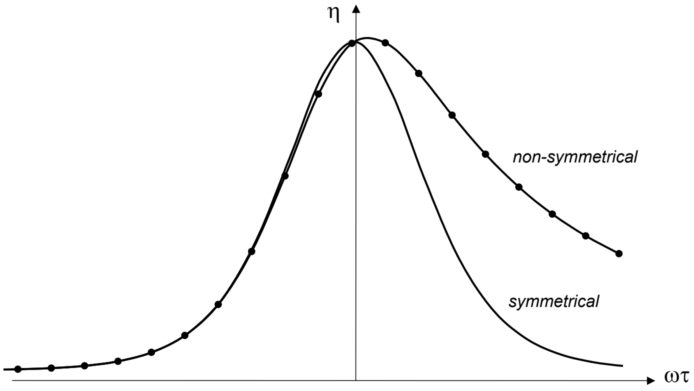

Fig. 1. Symmetrical and non-symmetrical loss factor.

The dispersion modulus defined as $d = E_{\infty}/E_0$ ranges between 100 and 1000 for a large class of polymers. A qualitative interpretation of the fractional order α given by Davies and Lamb [20] suggests that the limit value ($\alpha = 1$) corresponds to relaxation of pairs of molecules typically in liquid. The parameter α may be interpreted as a measure of the strength of coupling between the molecular chains within the polymer entanglements. The characteristic time τ describes a particular oscillation time of the polymeric chains during relaxation; it is considered as the only temperature-dependent parameter. The most commonly used functional form relating the time relaxation to the temperature in the glass transition, is the WLF (Williams–Landel–Ferry) equation.

The complex modulus $\bar{E}(i\omega)$ is expressed as:

$$\bar{E}(i\omega) = \frac{E_0 + E_{\infty}(i\omega\tau)^{\alpha}}{1 + (i\omega\tau)^{\alpha}}. \tag{2.10}$$

The loss factor modulus $\eta(\omega)$ is written:

$$\eta(\omega) = \frac{(d-1)\sin(\alpha\pi/2)(\omega\tau)^{\alpha}}{1 + (1+d)\cos(\alpha\pi/2)(\omega\tau)^{\alpha} + d(\omega\tau)^{2\alpha}}. \tag{2.11}$$

2.2.2. Five parameter fractional derivative model. When the loss factor appears clearly to be non-symmetrical as a function of the logarithm of the frequency, an additional parameter has to be introduced in order to produce different slopes for each side surrounding the loss factor peak (see Fig. 1). A generalization of the fractional Zener model was proposed by HAVRILIAK and NEGAMI in [21] to describe the α-dispersions in polymer system: the complex modulus $\bar{G}(i\omega)$ was empirically written as:

$$\frac{\bar{G}(i\omega) - G_\infty}{G_0 - G_\infty} = \frac{1}{(1 + (i\omega\tau)^\alpha)^\beta} \tag{2.12}$$

where the parameter β controls the asymmetry of the loss factor.

An alternative way to describe non-symmetrical loss factor has been developed by DINZART and LIPIŃSKI [22], which allows a faithful description of this particularity. The constitutive differential equation is simplified to:

$$\sigma(t) + \tau^\alpha \frac{d^\alpha \sigma(t)}{dt^\alpha} + \tau^\beta \frac{d^\beta \sigma(t)}{dt^\beta} = E_0 \varepsilon(t) + E_0 \tau^\beta \frac{d^\beta \varepsilon(t)}{dt^\beta} + E_\infty \tau^\alpha \frac{d^\alpha \varepsilon(t)}{dt^\alpha}.$$

The complex modulus $\bar{E}(\omega)$ is written as:

$$\bar{E}(\omega) = \frac{E_0 + E_0(i\omega\tau)^\beta + E_\infty(i\omega\tau)^\alpha}{1 + (i\omega\tau)^\alpha + (i\omega\tau)^\beta} \tag{2.13}$$

where the parameter β controls the loss peak non-symmetry. It appears also to be close to α when the loss factor is quasi-symmetrical. The loss factor modulus calculated by Dinzart and Lipinski is expressed as:

$$\eta(\omega) = \frac{(d-1)(\sin(\alpha\pi/2)(\omega\tau)^\alpha + \sin((\alpha-\beta)\pi/2)(\omega\tau)^{(\alpha+\beta)})}{[1+(d+1)\cos(\alpha\pi/2)(\omega\tau)^\alpha + 2\cos(\beta\pi/2)(\omega\tau)^\beta + d(\omega\tau)^{2\alpha} + (\omega\tau)^{2\beta} + (d+1)\cos((\alpha-\beta)\pi/2)(\omega\tau)^{(\alpha+\beta)}]}.$$

2.3. Laplace–Carson transform of the fractional derivative equation

The Laplace transforms of fractional derivative functions present similar properties as those well-known for transforms of integer derivatives. These characteristic properties favour an easier treatment of the constitutive equations. The Laplace–Carson transform of a fractional derivative of order αth of the function $x(t)$ is defined by

$$\mathcal{L}[D^\alpha[x(t)]] = p^\alpha \mathcal{L}[x(t)] + \sum_{k=0}^{n-1} p^k D^{\alpha-1-k} x(0^+) \tag{2.14}$$

where n is an integer such that $n - 1 < \alpha \leq n$.

The transform of the general constitutive equation may be written as $\bar{\sigma}(p) = \bar{E}(p)\bar{\varepsilon}(p)$ where the modulus $\bar{E}$ has the form:

$$\bar{E}(p) = \frac{E_0 + E_\infty(\tau p)^\alpha}{1 + (\tau p)^\alpha}. \tag{2.15}$$

The memory kernel $\bar{F}(p)$ related to the complex modulus by $\bar{E}(p) = E_0(1 - \bar{F}(p))$ presents a simplified expression in the case of a fourth-order fractional derivative model:

$$\bar{F}(p) = 1/(1 + (\tau p)^\alpha). \tag{2.16}$$

2.4. Inverse Laplace–Carson transform of the fractional derivative equation

As demonstrated by ENELUND and OLSSON [17], the inverse Laplace transform of the memory kernel (2.16) can be expressed as below:

$$F(t) = -d[E_\alpha(-t/\tau)^\alpha]/dt \tag{2.17}$$

where E_α is the α-order Mittag–Leffler function defined by

$$E_\alpha(t) = \sum_{k=0}^{\infty} t^k / \mathit{\Gamma}(1 + \alpha k).$$

As a consequence, the estimation of the set of parameters α and τ gives a first closed-form expression of the memory kernel in the time space. This direct inversion method is easier and less time-consuming than the classical collocation method described by SCHAPERY [14], which requires the first Dirichlet approximation of the complex function $\bar{F}(p)$ as:

$$\overline{x}(p) = a + b/p + \sum_{k=1}^{N} f_k[1/(1 + p\tau_k)]. \tag{2.18}$$

The order N is selected and the distribution of the retardation times τ_k allows to determine the weights f_k. The response in the time domain is estimated as:

$$x(t) = a + bt + \sum_{k=1}^{N} f_k(1 - \exp(-t/\tau_k)). \tag{2.19}$$

BRENNER *et al.* [13] suggested the direct inversion method based on a variable change $\omega = \log_{10}(pt)$ in the vicinity of a frequency ω_0, where the material creep compliance presents a quasi-linear constitutive law. The response in the time domain is estimated as:

$$x(t) = a + b10^{-\omega_0 t} + \sum_{k=1}^{N} f_k(1 - 1/(1 + 10^{-\omega_0 t/\tau_k})). \tag{2.20}$$

The choice of a particular frequency ω_0 for which a linear development is driven, may be assimilated to the use of a relaxation time associated to the phenomenon of relaxation governing the glass transition.

3. Self-consistent modelling of a biphasic visco-elastic material

3.1. Constitutive law for inhomogeneous visco-elastic materials

The equivalent resolution of an inhomogeneous visco-elastic problem in the form of a symbolic elastic one was first dedicated as a 'correspondence principle' by Mandel [8]. Laws and MacLaughlin [9] gave the mathematical frame with the use of Stieltjes convolution for the determination of equivalent creep compliance. The self-consistent estimate of the overall visco-elastic moduli was expressed after the Laplace–Carson transform.

A two-phase isotropic blend is considered where each phase denoted by i (with $i = 1, 2$) is described by a fractional derivative model characterised by the following set of parameters $(\alpha_i, \tau_i, E_{0i}, E_{\infty i})$. The constitutive law of each phase given by the fractional derivative Eq. (2.9) is then formulated in the Laplace-Carson domain according to equations:

$$\bar{\sigma}(p) = \bar{E}_i(p)\bar{\varepsilon}(p), \qquad i = 1, 2, \tag{3.1}$$

where the modulus $\bar{E}_i$ has the generic form:

$$\bar{E}_i(p) = \frac{E_{0i} + E_{\infty i}(\tau_i p)^{\alpha_i}}{1 + (\tau_i p)^{\alpha_i}}. \tag{3.2}$$

The two phases of the blend are considered to be separated at a mesoscopic scale, which means that no particular requirements are imposed on interaction parameters, miscibility or phase separation. The phases are only considered to be rather disordered, allowing to consider that they play a similar morphological role, i.e. no phase plays a matrix or inclusion role. The blends refer only to basically different chain compositions and cannot be described by identical models. The self-consistent scheme first presented by Hersley [12] was extended by Hill [23] to a two-phase isotropic composite, inducing a simplification of the set of equations to a single quartic one. Owing to the correspondence principle, this single equation may be rewritten in the Laplace domain to express the effective modulus of the two materials blending:

$$X^2 + 2\left(\frac{2-5c}{6}X_2 + \frac{5c-3}{6}X_1\right)X - \frac{2}{3}X_1X_2 = 0 \tag{3.3}$$

where X, X_1 and X_2 represent respectively the modulus of the equivalent material and both constituents. The volume fraction of the phase 2 is denoted c.

So, the Laplace transform of the effective modulus $\bar{E}^{\mathrm{eff}}$ satisfies the following equation:

$$\bar{E}^{\mathrm{eff}^2} + 2\left(\frac{2-5c}{6}\bar{E}_2 + \frac{5c-3}{6}\bar{E}_1\right)\bar{E}^{\mathrm{eff}} - \frac{2}{3}\bar{E}_1\bar{E}_2 = 0 \tag{3.4}$$

which may be rewritten into (3.6) by the following variable changes:

$$\begin{aligned} \bar{E}^{\mathrm{eff}}(p) &= E_0\bar{Y}^{\mathrm{eff}}(p), \\ \bar{E}_1(p) &= E_{01}\bar{Y}_1(p) = E_{01}\frac{1+d_1(\tau_1 p)^{\alpha_1}}{1+(\tau_1 p)^{\alpha_1}}, \\ \bar{E}_2(p) &= E_{02}\bar{Y}_2(p) = E_{02}\frac{1+d_2(\tau_2 p)^{\alpha_2}}{1+(\tau_2 p)^{\alpha_2}}, \end{aligned} \tag{3.5}$$

$$E_0^2\bar{Y}^{\mathrm{eff}^2} + 2\left(\frac{2-5c}{6}E_{02}\bar{Y}_2 + \frac{5c-3}{6}E_{01}\bar{Y}_1\right)E_0\bar{Y}^{\mathrm{eff}} - \frac{2}{3}E_{01}E_{02}\bar{Y}_1\bar{Y}_2 = 0. \tag{3.6}$$

The dispersion moduli $d_1$and d_2, are defined as the ratios of the instantaneous and relaxed moduli relative to the two phases and their blending.

As the blending properties have to be retrieved for instantaneous or long-time conditions, the relaxed and un-relaxed moduli are assumed to satisfy also the relationship given by (3.3):

$$\begin{aligned} E_0^2 + 2\left(\frac{2-5c}{6}E_{02} + \frac{5c-3}{6}E_{01}\right)E_0 - \frac{2}{3}E_{01}E_{02} &= 0, \\ E_\infty^2 + 2\left(\frac{2-5c}{6}E_{\infty 2} + \frac{5c-3}{6}E_{\infty 1}\right)E_\infty - \frac{2}{3}E_{\infty 1}E_{\infty 2} &= 0. \end{aligned} \tag{3.7}$$

The modified effective modulus $\bar{Y}^{\mathrm{eff}}$ satisfies the equation:

$$\left(\frac{\bar{Y}^{\mathrm{eff}^2}}{\bar{Y}_1\bar{Y}_2} - 1\right) + 2\left(a_2\left(\frac{\bar{Y}^{\mathrm{eff}}}{\bar{Y}_1} - 1\right) + a_1\left(\frac{\bar{Y}^{\mathrm{eff}}}{\bar{Y}_2} - 1\right)\right) = 0 \tag{3.8}$$

where the constants $a_1 = \dfrac{5c-3}{6}\dfrac{E_{01}}{E_0}$ and $a_2 = \dfrac{2-5c}{6}\dfrac{E_{02}}{E_0}$ are determined as functions of the positive root E_0 of the first Eq. 3.7).

The effective relaxation modulus $\bar{Y}^{\mathrm{eff}}$ is the positive root of the equation:

$$\bar{Y}^{\mathrm{eff}} = -(a_1\bar{Y}_1 + a_2\bar{Y}_2) + \sqrt{(a_1\bar{Y}_1 + a_2\bar{Y}_2)^2 + (2(a_1+a_2)+1)\bar{Y}_1\bar{Y}_2}. \tag{3.9}$$

3.2. Numerical estimation of the blend constitutive law

In order to further compare the response of the two phases and of their blending via the Dynamic Mechanical Analysis, we have to express the storage and dissipative moduli and the loss factor in the Fourier domain. The estimation of the blend constitutive law consists of the numerical extraction of the real and imaginary parts of the complex effective relaxation modulus $\bar{Y}^{\text{eff}}$. The equivalent storage and loss moduli $E^{\text{eff}\prime}$ and $E^{\text{eff}\prime\prime}$ are obtained after multiplication of $Y^{\text{eff}\prime}$ and $Y^{\text{eff}\prime\prime}$ by E_0. The equivalent loss factor $\eta^{\text{eff}}(\omega)$ is defined as the ratio of $Y^{\text{eff}\prime\prime}$ and $Y^{\text{eff}\prime}$.

A numerical parametric study is conducted in order to describe the influence of the phases' characteristics and their fraction ratio. The effect of the volume fraction c is analysed throughout two particular cases of blending: (1) for two materials whose glass transitions are close and (2) – for two materials whose glass transition is decayed in temperature (equivalent to frequency decay). The characteristics of each phases (Tables 1 and 2) are chosen as to have a simplified mathematical correlation between couples of values (α_1, α_2), (τ_1, τ_2), $(E_{01,}, E_{02,})$ and $(E_{\infty 1}, E_{\infty 2})$ and do not describe any real material behaviour. Coherent material description will be conducted in the last section illustrated by PMMA-SAN blending.

Table 1. Fourth-order parametric description – case of identical relaxation times.

	α	E_0	E_∞	τ	d
1	0.4	1	10	1	10
2	0.4	2	15	1	7.5

Table 2. Fourth-order parametric description – case of different relaxation times.

	α	E_0	E_∞	τ	d
1	0.4	1	10	100	10
2	0.4	2	15	0.1	7.5

3.2.1. Case of close glass transition. The equivalent relaxed and unrelaxed moduli E_0 and E_∞ are calculated by using the formulas (3.7), allowing the first approximation in a generalized simple linear regression Maple internal package [24] used to determine the complete set of parameters (α, d, τ). The trial run of (α, τ) is equal to one of the phase. The asymmetry factor β is taken close to α at the first iteration.

The numerical fitting of the equivalent loss factor conducts to the following sets of parameters for a classical fourth-order fractional derivative model and for the Havriliak–Negami description respectively summarized in Tables 3 and 5.

Table 3. Fourth-order approximation of the equivalent loss factor – case of close glass transition.

	α	d	τ
$c = 0.3$	0.3992	9.1311	1.001
$c = 0.5$	0.3992	8.5969	1.0006
$c = 0.7$	0.3994	8.1082	1.0007

Table 4. Fifth-order approximation of the equivalent loss factor – case of close glass transition.

	α	β	d	τ
$c = 0.3$	0.3991	0.3993	17.276	0.1755
$c = 0.5$	0.3990	0.3993	16.208	0.1753
$c = 0.7$	0.3993	0.3995	15.225	0.1784

Figures 2 to 4 describe the equivalent constitutive law in comparison with the respective constitutive laws of both phases in the case (1) of close glass transitions. When the two phases mixed together present quite similar relaxation times, the equivalent constitutive response of the blend appears as a combination

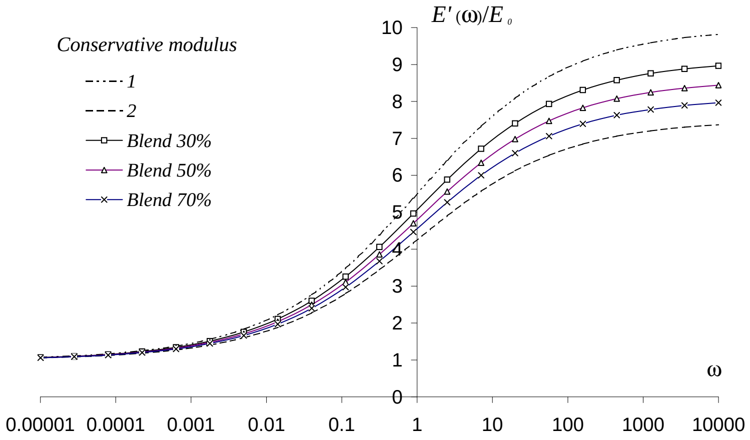

Fig. 2. Influence of the volume fraction c on the storage modulus E' – case of close glass transitions.

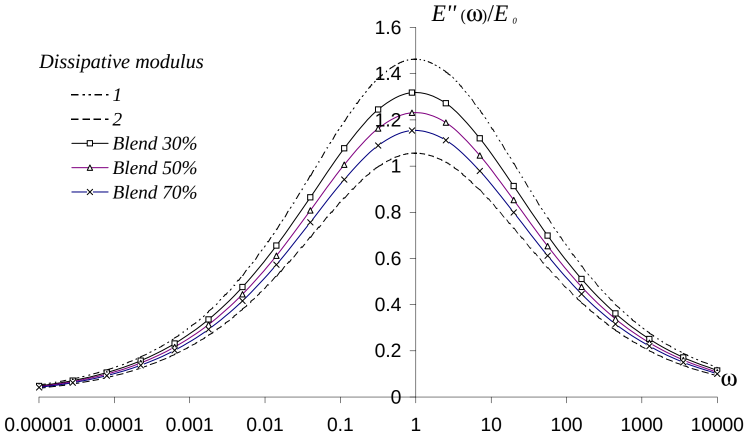

Fig. 3. Influence of the volume fraction c on the dissipative modulus E'' – case of close glass transitions.

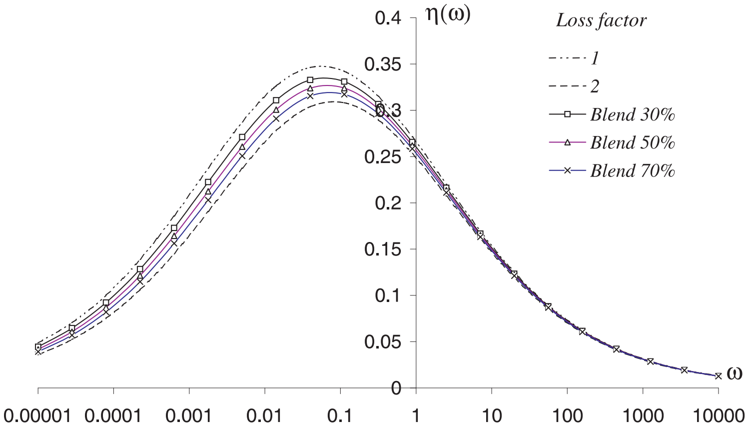

Fig. 4. Influence of the volume fraction c on the loss factor η – case of close glass transitions.

between the two phases constitutive law: the slope of the loss factor is between the values of the parameter α_1 and α_2 relative to each phases. No surprisingly, the curves corresponding to the fraction $c = 0.3$ are close to that of the phase 1 (and similarly, the curves relative to the fraction $c = 0.7$ are close to the phase 2). Under the hypothesis of presenting a symmetrical shape, the equivalent loss factor may be approached by the similar description as the one used for the two mixed phases. Because the loss factor is symmetric with respect to the frequency, the parameter β is close to α. As a consequence, when the phases present glass transition in the same range of temperature or frequency, it appears that the material constitutive description of the blending may be achieved by a fourth-order fractional derivative model. The relaxation time τ appears close to the common value of the two phases, the slight difference (0.1%) may be attributed to the interpolation procedure that is conducted on curves described by 20 points.

3.2.2. Case of separated glass transition. The set of Fig. 5 to 7 illustrates the equivalent storage dissipative moduli and the equivalent loss factor for two materials of separated glass transition. As seen previously, the dominant phase (typically $c = 0.3$ and $c = 0.7$) imposes widely their characteristics. The loss factor peak of the resulting blend is less pronounced and the slopes are different from either side, leading to a non-symmetrical loss factor plots. For equal

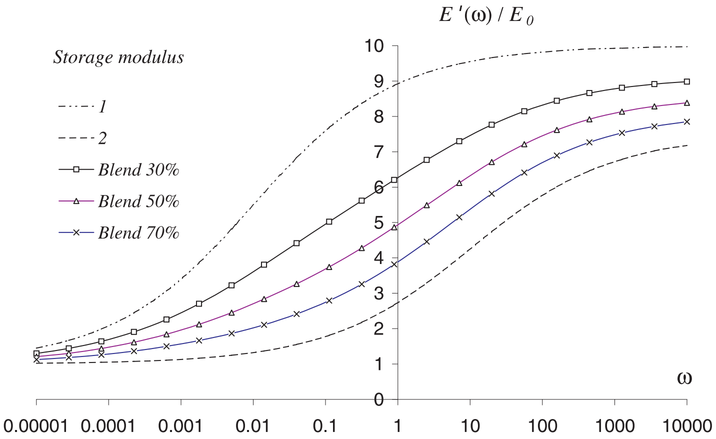

Fig. 5. Influence of the volume fraction c on the storage modulus E' – case of separated glass transitions.

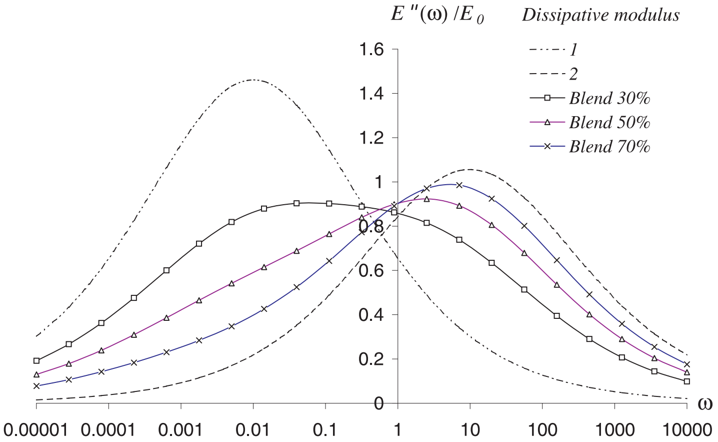

Fig. 6. Influence of the volume fraction c on the dissipative modulus E'' – case of separated glass transitions.

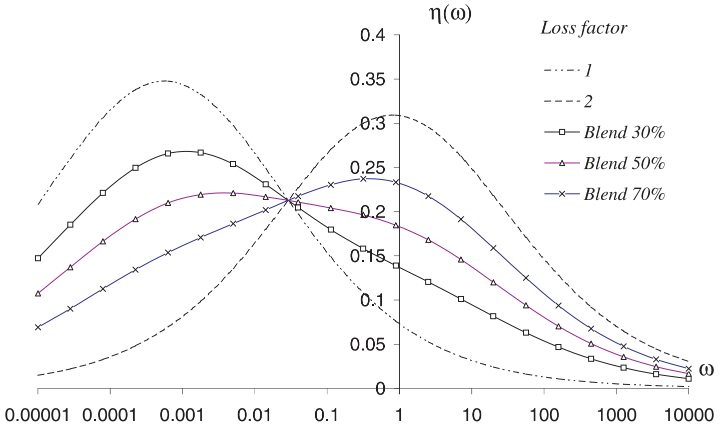

FIG. 7. Influence of the volume fraction c on the loss factor η – case of separated glass transitions.

contribution of each phase, the equivalent loss factor seems to average the loss factors of both phases and consecutively, presents a single extremum associated to a unique glass transition. However, the real blending material of far separated glass transitions gives frequently a non-miscibility of two phases, experimentally described by two distinct extrema of the loss factor. It is important that the miscibility criterion considered here corresponds to the glass transition valuation by differential scanning calorimetry or differential mechanical analysis (DMTA). As miscibility in polymer blends may be studied by various techniques (IR absorption, light scattering ...), many definitions may be proposed implying up to the molecular structure. Similar fitting approximations are conducted for the case of separated loss factor peaks. A first attempt of identification was conducted under the hypothesis of quasi-symmetrical loss factor leading to a fourth-order fractional derivative description (Table 5). A fifth-order fractional derivative model appears more appropriate to describe the asymmetrical loss factor (Table 6, see also Fig. 8). However, the real blending material of far separated glass transition exhibits frequently a non-miscibility, experimentally identified by two distinct extrema of the loss factor. Similar fitting approximations are conducted for the case of separated loss factor peaks in the case of the volume fraction $c = 0.5$ in Fig. 9.

Table 5. Fourth-order approximation of the equivalent loss factor – case of separated glass transition.

	α	d	τ
$c = 0.3$	0.31287	9.5177	11.3466
$c = 0.5$	0.27934	9.5025	1.20784
$c = 0.7$	0.2973	8.6142	0.23410

Table 6. Fifth-order approximation of the equivalent loss factor – case of separated glass transition.

	α	β	d	τ
$c = 0.3$	0.33155	0.3099	16.21	2.634
$c = 0.5$	0.27097	0.2834	19.05	0.0623
$c = 0.7$	0.27610	0.3128	18.53	0.0075

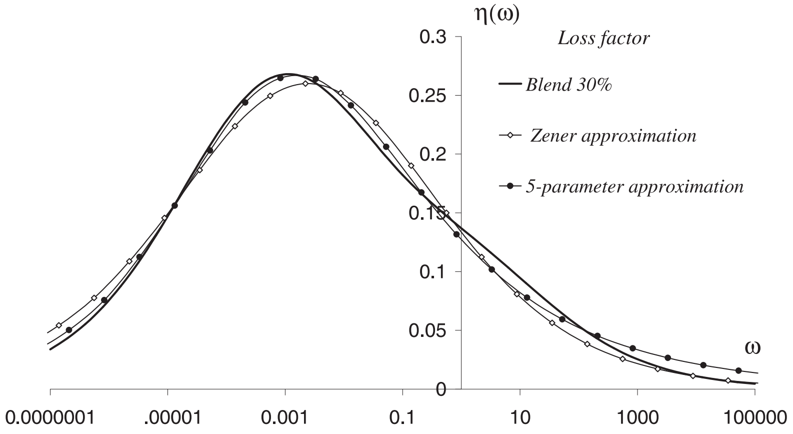

FIG. 8. Approximation of the loss factor – $c = 0.3$.

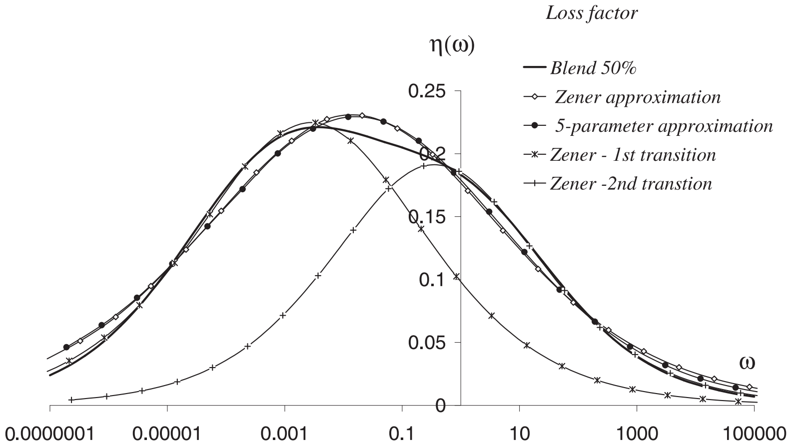

FIG. 9. Approximation of the loss factor – $c = 0.5$.

4. Experiments

4.1. Experimental device

The polymers tested within the framework of the validation of the homogenisation model are the poly(methyl-methacrymate) (PMMA) , the poly(styrene-co-acrylonitrile) (SAN) and blend of these two grades at a 50% volume percentage. The blend was obtained by a conventional solution casting method. They were purchased from SORECO and injected so as to obtain a classical bending sample of rectangular section of 4 mm width and 10 mm long. The level of interaction of SAN with PMMA has not been investigated as it corresponds to a lower level of description, required by the self-consistent scheme which only specifies randomly distributed phases.

The experiments were conducted on a Dynamic Mechanical Analyser from Netzsch. Dynamic three-points cyclic bending tests were performed under a temperature range from room temperature (300 K) to 413 K and under the temperature rate 3 K/min. The frequency may be singly imposed or under a multiplexing way.

4.2. Results and discussion

The experimental results reported are the storage and dissipative moduli and the loss factor ratio as functions of the time and temperature.

As the loss factor modulus $\eta(\omega)$ is the most sensitive property to small changes in behaviour, the parameters identification was brought onto its plots. The experimental results are reported as functions of the time and temperature and have consequently to be treated to describe the material evolution in function of the frequency or the normalized frequency $(\omega\tau)$ instead of the temperature. The first identification is conducted via the Cole–Cole plot giving the dissipative modulus as a function of the storage modulus. The slope at the origin of the Cole–Cole plot may be approximated by $\alpha\pi/2$ which allows the estimation of this fractional derivative order (see Fig. 10). For a material constitutive law described by (2.9), the extremum of the loss factor $\eta(\omega)$ which occurs at the normalized frequency

$$(\omega\tau)_{\max} = (1/d)^{(1/2\alpha)} \tag{4.1}$$

takes the value:

$$\eta_{\max} = \frac{\frac{d-1}{\sqrt{d}}\sin(\alpha\pi/2)}{2+\frac{d+1}{\sqrt{d}}\cos(\alpha\pi/2)}. \tag{4.2}$$

Providing that the parameter α has already been approached, the loss factor extremum allows the estimation of the ratio $d = E_\infty/E_0$ and consecutively,

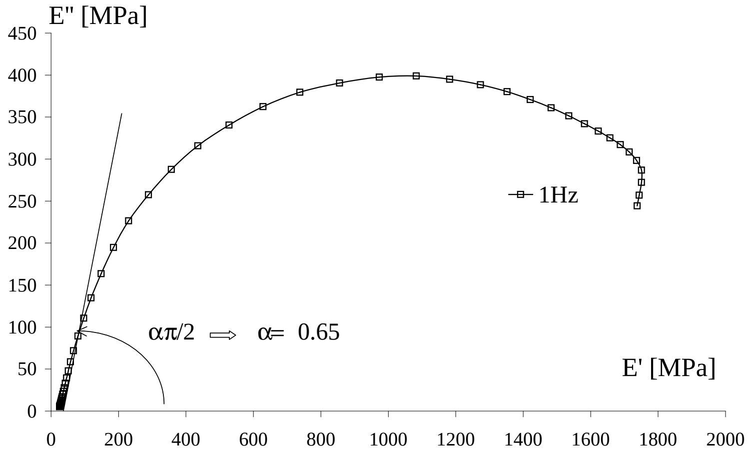

Fig. 10. Determination of the fractional derivative order – case of the PMMA.

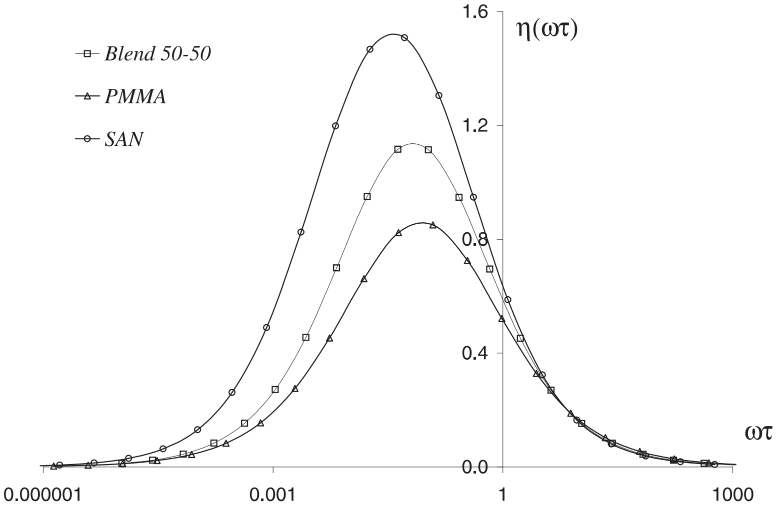

Fig. 11. Experimental results for the loss factor versus the normalized frequency $\omega\tau$.

the normalized frequency associated to the peak by formula (4.1). Knowing the couple (α, d), the normalized frequency $(\omega\tau)$ appears as a solution of the equation resulting from expression (2.9), where the loss factor $\eta(\omega\tau)$ is successively replaced by the experimental values. This leads to the set of curves shown in Fig. 11 where the loss factor $\eta(\omega\tau)$ is plotted versus the normalized frequency $\omega\tau$. The figure shows that the loss factor of every pure polymer presents a symmetrical shape versus the normalized frequency in logarithmic scale. It should be noted that the glass transition and the correlated extrema of the loss factor are close together. The blending of the two polymers presents a loss factor which fits perfectly between those of the two pure phases. It appears also symmetrical according to the normalized frequency and can be described consequently by the same fourth-order fractional derivative model.

In order to compare it with the loss factor predicted by the model, a relaxation time τ is chosen for each phase to change the previous plot of the loss factor in order to consider the frequency dependence ω. The chosen values for the variable change are optimised in view to have close peaks. These values corresponds, for each phase, to the relaxation time at the loss factor for a frequency equal to $f = 1$ Hz. The following table [7] summarizes the identified parameters according to the fourth-order fractional derivative model on which is based the homogenisation scheme for the two considered phases (pure PMMA and SAN) and for a 50-50 blend. The estimation of the relaxation time τ is also given for the experimental frequency $f = 1$ Hz.

As shown in Fig. 9, the fourth-order parameter fractional derivative allows a complete description of the loss factor master curve as a function of the normalized frequency in logarithmic scale. The symmetrical shape reinforces the choice of this constitutive law description also for the resulting 50-50 blend of the two phases. Different experimental loss factor curves were studied at various frequencies (5 Hz and 10 Hz) and the dispersion did not exceed 5% of the plotted master curves given in Fig. 12.

The blend constitutive law is predicted by the model by considering the estimated sets of parameters (α_i, τ_i, d_i) for the PMMA and the SAN given in Table 7. The numerical equivalent loss factor provided by the model is compared in Fig. 12 with the loss factor curve obtained from the experiences. The equivalent constitutive law predicted is in a quite good agreement with the experimental results when a 5% dispersion percentage of the experimental results is considered.

Table 7. Identification of the characteristic parameters of the tested polymers and blend.

	α	d	τ
PMMA	0.65	24.18	0.137
SAN	0.73	125	0.00583
PMMA-SAN 50-50	0.70	50.9	0.01068

The numerical equivalent constitutive law may be approached also be a fourth-order fractional derivative model and the estimation of this numerical set appears in great accordance with the estimation obtained from the experimental results (see Table 8).

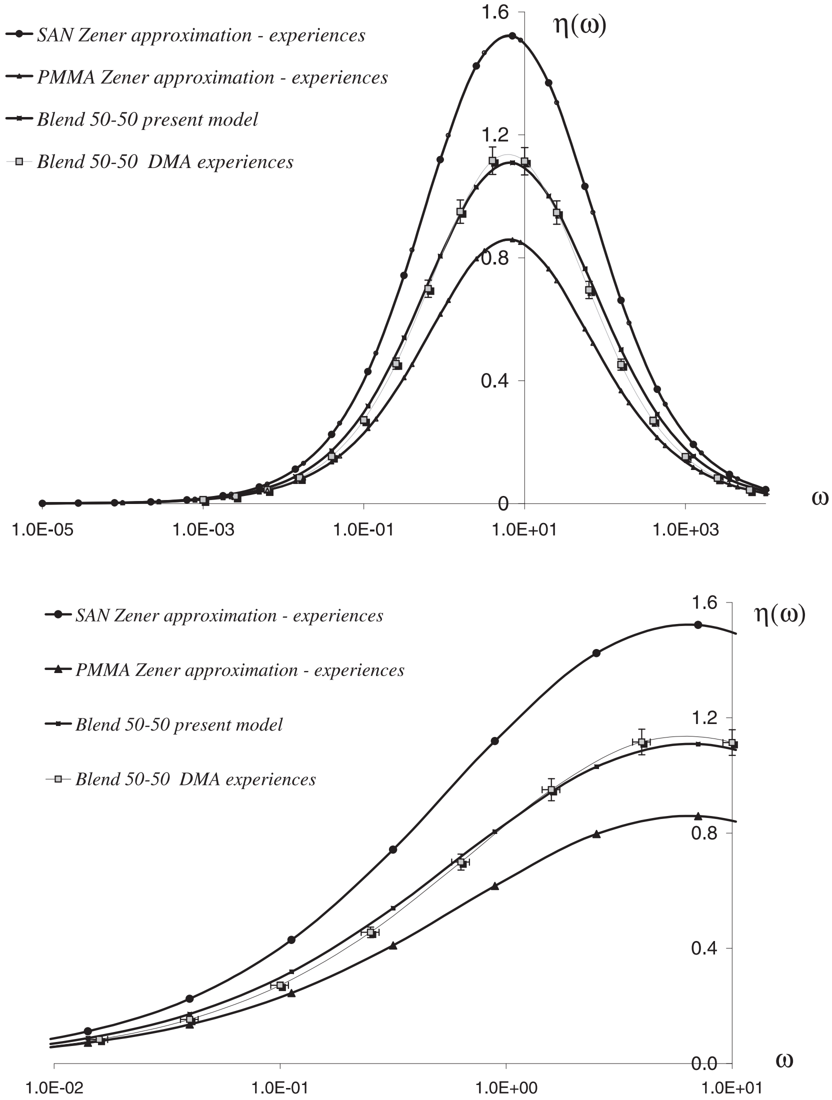

Fig. 12. Comparison between model predictions and experimental results conducted on PMMA-SAN blend.

Table 8. Comparison between the experimental and the model estimations of the set of characteristic parameters.

	α	d	τ
PMMA-SAN 50-50 – experimental estimation	0.70	50.9	0.01068
PMMA-SAN 50-50 – model approximation	0.678	51.566	0.00834

5. Conclusion

This work combines an already well-known formalism articulated around the classical self-consistent scheme to a sophisticated description of the polymer constitutive law in the glass transition. Self-consistent approach of the equivalent constitutive law of a two-phase visco-elastic material was developed by using the mathematical peculiarities of the constitutive equations written with fractional order derivation of strain and stress. The method is based on the Laplace–Carson transform of the visco-elastic problem into a symbolic elastic one, whose solutions are known according to the classical self-consistent procedure. The parametric analysis showed a high flexibility of the constitutive law in description of blending of the given volume fraction for two visco-elastic materials, described each by a set of four parameters (relaxed and un-relaxed moduli, time relaxation and fractional order parameter). However, it seemed that for materials presenting separated glass transition in temperature or in frequency, the constitutive behaviour may not be described accurately by the fourth-order fractional derivative model used to identify each of the phases, the shape of the loss factor becoming in that case asymmetrical enough in logarithmic scale to present eventually two separated extrema. The polymers chosen for the sake of validation of the proposed model (the polymethyl methacrylate -PMMA- and the styrene acrylonytrile copolymer -SAN-) present close glass transitions when expressed as a function of the frequency. The DMTA analysis of the blend shows that the blend constitutive law can also be described by the four parameter model as that used for each of the phases. The loss factor of the blend calculated by the homogenisation technique is in good agreement with the loss factor determined with the DMTA devices. The set of four parameters identified on the calculated curve is close to that obtained experimentally. Finally, a direct inversion of the expression of the memory kernel associated to the fourth-order fractional derivative model gives the material constitutive law in the time space.

References

1. R.C. Koeller, *Applications of fractional calculus to the theory of visco-elasticity*, J. Appl. Mech., **51**, 299–307, 1984.
2. K.B. Oldham, J. Spanier, *The fractional calculer*, Academic Press, San Diego, L.A., 1974.
3. P. Suquet, *Elements of homogenisation for inelastic solid mechanics, homogenisation Techniques for composite media*, E. Sanchez-Palencia, A. Zaoui [Eds.], Berlin Springer Verlag, 193–278, 1985.
4. A. Molinari, G. Canova, S. Ahzi, *A self-consistent approach of the large deformation polycrystals*, Acta Metall., **25**, 2983–2994, 1987.

5. N. Lahellec, P. Suquet, *Effective behavior of linear viscoelastic composites: A time-integration approach*, Int. J. of Solids and Struct., **44**, 507–529, 2007.
6. A. Paquin, H. Sabar, M. Berveiller, *Integral formulation and self-consistent modeling of elastic-plastic constitutive law of polycrystals*, Arch. Appl. Mech., **69**, 14–35, 1999.
7. M. Coulibay, *Modélisation micromécanique et caractérisation expérimentale du comportement des matériaux hétérogčnes élastovicoplastiques. Application à la valorisation des polymčres recyclés*, PhD Thesis, Université Paul Verlaine de Metz, Juillet 2008.
8. J. Mandel, *Mécanique des milieux continus*, Gauthier-Villars, Paris, 1966.
9. N. Laws, R. McLaughlin, *Self-consistent estimates for the visco-elastic creep compliances of composite materials*, Proc. R. Soc. Lond., **359**, 251–273, 1978.
10. Y. Rougier, C. Stolz, A. Zaoui, *Représentation spectrale en viscoélasticité linéaire des matériaux hétérogčnes*, C.R. Acad. Sci. Paris II, **316**, 1517–1522, 1994.
11. S. Beurthey, A. Zaoui, *Structural morphology and relaxation spectra of visco-elastic heterogeneous materials*, Eur. J. Mech. A/Solids, **19**, 1–16, 2001.
12. A.V. Hershey, *The elasticity of an isotropic aggregate of anisotropic cubic crystals*, J. Appl. Mech., **21**, 236–240, 1954.
13. R. Brenner, R. Masson, O. Castelnau, A. Zaoui, *A 'quasi-elastic' affine formulation for the homogenised behaviour of nonlinear visco-elastic polycrystals and composites*, Eur. J. Mech. A/Solids, **21**, 943–960, 2002.
14. R.A. Schapery, *Approximate methods of transform inversion for visco-elastic stress analysis*, Proc. U.S. Nat. Congr. Appl. Mech. ASME 4th, **1**, 1075–1085, 1962.
15. J.D. Ferry, *Visco-elastic properties of polymers*, John Wiley, 1980.
16. L. Boltzmann, *Zur Theorie des elastischen Nachwirkung*, Annalen der Physik und Chemie, **27**, 624–654, 1876.
17. M. Enelund, P. Olsson, *Damping described by fading memory analysis and application to fractional derivative models*, Int. J. of Solids and Struct., **36**, 939–970, 1999.
18. M. Enelund, G. Lesieutre, *Time domain modeling of damping using anelastic displacement fields and fractional calculus*, Int. J. of Solids and Struct., **36**, 4447–4472, 1999.
19. B. Hartmann, G.F. Lee, J.D. Lee, *Loss factor height and width limits for polymer relaxations*, J. Acoust. Soc. Am. 95, **1**, 226–233, 1994.
20. R.O. Davies, J. Lamb, *Ultrasonic analysis of molecular relaxation process in liquids*, Q. Rev., **11**, 134–161, 1957.
21. S. Havriliak, S. Negami, *A complex plane analysis of α-dispersions in some polymer systems*, [in:] Transitions and Relaxations in Polymers, J. Polym. Sci. Part C, **14**, R. F. Boyer [Ed.], Interscience, New-York, 99–117, 1966.
22. F. Dinzart, P. Lipiński, *Improved five-parameter fractional derivative model for elastomers*, Archives of Mechanics, **61**, 459–474, 2009.
23. R. Hill, *A self-consistent mechanics of composite materials*, J. Mech. Phys. Solids, **13**, 213–222, 1965.
24. W.P. Fox, *Generalized nonlinear regression, maple procedure*, www.mapleapps.com.

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