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Application of a fractional model for simulation of the viscoelastic functions of polymers

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ABSTRACT: In the present work the dynamic behavior of two representative polymeric materials, experimentally studied in previous works, has been analyzed by a fractional derivative model. It is shown that the well-known fractional derivative Zener model, in its simplest form as a four-parameter model is capable of capturing the main features of the dynamic moduli of the polymeric structures examined. Furthermore, the time dependent viscoelastic functions, namely the compliance and the relaxation modulus could be simulated with the same model parameter values, indicating this way that the fractional model can provide a method of interconversion between viscoelastic material functions. The model's inadequacy of describing the loss modulus peak asymmetry, exhibited by the materials, has been encountered by the five-parameter version of the fractional Zener model. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43505.

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INTRODUCTION

Modeling the viscoelastic behavior of polymeric materials over a wide time–frequency and temperature range is always an interesting topic.[1,2] This analysis can be carried out within the frame of various viscoelastic models, such as standard linear solid, generalized Maxwelll or generalized Kelvin–Voigt model.[2] As an alternative approach, fractional calculus has been an empirical method of analyzing the linear viscoelastic response of polymeric materials, in an increasing number of research papers,[3–9] while an analytical appearance of this method is contained in Ref. 10. Parallel to the description of the time-dependent properties, the implementation of fractional calculus was proved to be a useful tool for the modeling of the dynamic response of polymeric materials as well.[3,11–13]

By this approach, the capacity of conventional viscoelastic models can be enhanced, and their well known limitations can be overcome, while a satisfactory description of viscoelastic response can be obtained by a reduced number of model parameters.

The alternative approach, introduced by fractional viscoelastic models compared to the classical viscoelastic models, is the replacement of the Newtonian dashpot with the so-called spring-pot or the so-called Scott–Blair element, as the dissipative rheological parameter. However, it has been shown that the spring-pot can be derived from hierarchical and self-similar models comprising springs and dashpots.[8,14] On the other hand, as it is mentioned in Ref. 14, recent works have shown that fractional order models arise from the classical generalized Maxwell model and generalized Kelvin model when the number of elements in these models tend to infinity.[15] Several efforts have been made to develop an efficient method for the numerical evaluation of the fractional operator.

The increasing use of fractional differential equations in mathematical models requires the development of convergent and accurate methods for evaluating fractional integrals and for solving fractional differential equations.[16] To this trend, a novel approach based on the approximation of fractional order models with integer order models has been proposed.[15] This allows fractional models to have the computational efficiency of the generalized Maxwell model and generalized Kelvin model, with a reduced number of parameters.

The scope of the present work is to explore the fractional derivative Zener model's capacity[17] to describe the time and frequency dependent response of two polymeric materials with different structures, namely a thermosetting epoxy resin, and a biodegradable polymer and its nanocomposite. Storage and loss moduli of the materials, experimentally studied in previous works[18,19] were analyzed, while it was shown that the compliance and the relaxation function could be obtained by almost

the same model parameters. It was therefore proved that the fractional derivative model could be a powerful tool for the interconversion of viscoelastic functions. The loss modulus peak asymmetry, exhibited by the materials, was hereafter successfully described by the five-parameter version of the employed model.

MODEL PRESENTATION

The Fractional Zener Model

Considering the conventional model, constituted by a spring in series with a Kelvin model (its mechanical representation in Figure 1), the so-called Zener model, introduced by Zener,[17] the following differential constitutive equation is derived:

$$\sigma(t)+a_1\frac{d\sigma(t)}{dt}=m\ \varepsilon(t)+b_1\frac{d\varepsilon(t)}{dt} \tag{1}$$

Where

$$a_1=\frac{\eta_2}{m_1+m_2},\quad m=\frac{m_1\ m_2}{m_1+m_2},\quad b_1=\frac{\eta_2 m_1}{m_1+m_2} \tag{2}$$

And $\sigma(t),\varepsilon(t)$ are the stress and strain time dependent functions.

Given the efficiency of the fractional derivative models in capturing the time- and frequency-dependent properties of viscoelastic materials, the replacement of the integer order derivatives of eq. (1) with fractional ones results to the fractional version of Zener model as:

$$\sigma(t)+a_1\frac{d^{\alpha}{}_1\sigma(t)}{dt^{\alpha_1}}=m\ \varepsilon(t)+b_1\frac{d^{\beta_1}\varepsilon(t)}{dt^{\beta_1}} \tag{3}$$

where α, β is the order of the fractional derivative with $0<\alpha_1<1$ and $0<\beta_1<1$. For a first approximation and in order to reduce the number of parameters, it is assumed that $\alpha=\beta$, and therefore, the fractional Zener model takes the form:

$$\sigma(t)+\tau^{\alpha}\frac{d^{\alpha}}{dt^{\alpha}}\sigma(t)=G_0\ \varepsilon(t)+G_{\infty}\tau^{\alpha}\frac{d^{\alpha}}{dt^{\alpha}}\varepsilon(t) \tag{4}$$

Where α is the order of the fractional derivative, with $\alpha<1$ and $\tau^{\alpha}=a_1$, given that a_1 has time dimensions, according to eq. (2). In addition, constant m has been replaced with G_0, which expresses the low frequency (high time) modulus of the model's elasticity. Constant b_1 is replaced, following eq. (2), by the quantity $G_{\infty}\tau^{\alpha}$, where $G_{\infty}$is the high frequency (low time) modulus m_1 of the conventional Zener model. Therefore, the fractional model parameters are $G_0, G_{\infty}, \tau, \alpha$.

To obtain the dynamic moduli, expressed in the frequency domain, we perform the Fourier transform of eq. (4) and taking into account that:

$$F\ \frac{d^{\alpha}}{dt^{\alpha}}\sigma(t)=(j\omega)^{\alpha}F\sigma(t) \tag{5}$$

We obtain:

$$F\ \sigma(t)\ (1+\tau^{\alpha}(j\omega)^{\alpha})=F\ \varepsilon(t)\ (G_0+G_{\infty}\tau^{\alpha}(j\omega)^{\alpha}) \tag{6}$$

And therefore the dynamic complex modulus E^* is given by:

$$E^*=\frac{(G_0+G_{\infty}\tau^{\alpha}(j\omega)^{\alpha})}{(1+\tau^{\alpha}(j\omega)^{\alpha})}=G_0\frac{1+d\ (j\omega\tau)^{\alpha}}{1+(j\omega)^{\alpha}} \tag{7}$$

Where ω is the frequency, and $d=G_{\infty}/G_0$.

Following eq. (7) and after making some algebra, given that $E^*=E'+jE''$, the storage E' and loss modulus E'' are expressed by the equations:

$$E'(\omega)=G_0\frac{1+(d+1)\ \cos(\alpha\pi/2)\omega_n^{\alpha}+d\omega_n^{2\alpha}}{1+2\ \cos(\alpha\pi/2)\ \omega_n^{\alpha}+\omega_n^{2\alpha}} \tag{8}$$

$$E''(\omega)=G_0\frac{(d-1)\ \sin(\alpha\pi/2)\omega_n^{\alpha}}{1+2\ \cos(\alpha\pi/2)\ \omega_n^{\alpha}+\omega_n^{2\alpha}} \tag{9}$$

Where

$$\omega_n=\omega\tau \tag{10}$$

is a normalized frequency.

To obtain the material functions in the time domain of the fractional Zener model, complicated calculations need to be done, and following the analysis performed by Mainardi and Spada,[5] the compliance modulus $J(t)$ and the relaxation function $Y(t)$ are given by:

$$J(t)=\frac{1}{G_{\infty}}+\frac{1}{G_0}(1-E_{\alpha}(-(t/\tau)^{\alpha})) \tag{11}$$

$$Y(t)=\frac{G_0G_{\infty}}{G_0+G_{\infty}}\left[1+\frac{G_{\infty}}{G_0}\ E_{\alpha}(-(t/\tau_2)^{\alpha})\right] \tag{12}$$

Where

$$\tau_2=\frac{G_0}{G_{\infty}+G_0}\tau^{\alpha} \tag{13}$$

and E_{α} is the Mittag–Leffler function of two parameters, given by the expression:

$$E_{\alpha}(t)=\sum_{n=0}^{\infty}(-1)^n\frac{(t/\tau)^{\alpha n}}{\Gamma(\alpha n+1)} \tag{14}$$

with Γ the gamma function.

EXPERIMENTAL

Materials-Experiments

To check the fractional Zener model's capability of describing the time and frequency behavior of polymeric materials, two different types of polymer were selected.

The first material type is a diglycidyl-ether of bisphenol A epoxy resin, with a molecular weight between 370 and 384 and a viscosity of 15×10^3 cp at 25 °C. It was cured with triethylenetetramine at 8% by wt of epoxy, and post cured at 100 °C for 48 h. The dynamic mechanical measurements were performed for a frequency range from 0.1 to 100 Hz, at temperatures 80 to 145 °C. The experimental procedure is described in detail in Ref. 18.

The second material studied, is a biodegradable polymer, under the commercial name Ecovio®, supplied by BASF SE (Ludwigshafen, Germany). The selected grade Ecovio® L BX 8145 (EC), is basically a blend of poly(butylene adipate-terephthalate) copolyester (Ecoflex® F BX 7011), which is based on non-renewable resources, and PLA (NatureWorks). Because of the PLA content, Ecovio® L BX 8145 consists of 45% of renewable resources. This polymer has been studied as a matrix reinforced with silica nanoparticles, namely Silica Aerosil® R972 (supplied by Degussa Chemicals, Marl, Germany) and described in detail

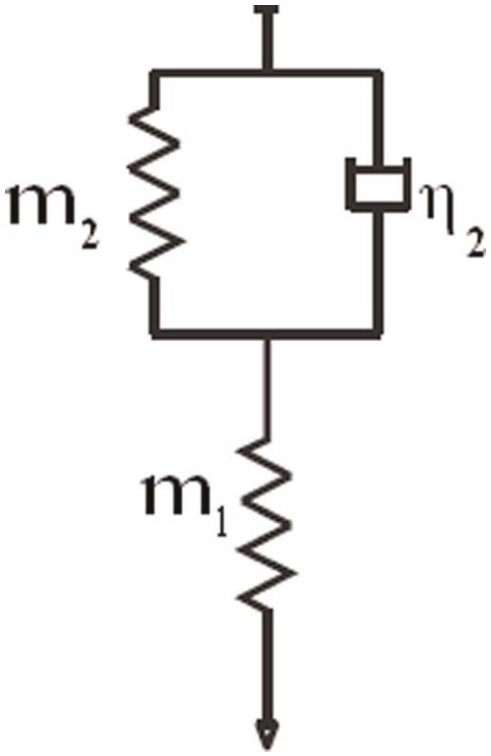

Figure 1. Schematic presentation of Zener's model.

in Ref. 19. In the present work the experimental data of Ecovio and its nanocomposite with 5% wt silica nanoparticles performed in Ref. 19 will be analyzed on the basis of the fractional Zener model.

The temperature range varied from 20 up to 150 °C, and the experiments were performed at five frequency values of 1, 5, 10, 20, and 40 Hz, while the heating rate was 3 °C min^{-1}. The storage and loss modulus curves versus temperature were then evaluated. Creep experiments have also been performed, for a specific time period equal to 15 min, at various temperatures varying from 25 up 85 °C, with an interval of 5 °C. A constant stress level of 2 MPa has been applied for all material types. The isothermal creep compliance curves were evaluated, for all materials examined.

Modeling of Experimental Data

The master curves of storage and loss modulus for the epoxy resin were successfully constructed at a reference temperature of 110 °C, and presented in Figures 2 and 3. Because of the chemical crosslinks, introduced into the material, apart from the transition region, a great part of the glassy and rubbery state, expressed by a plateau, are shown in the storage modulus master curve (Figure 2).

The evaluation of model parameters, $G_0, G_\infty, \tau, \alpha$ has been performed considering the physical meaning of these parameters. Parameter G_0 is related to the low frequency modulus, (equivalent to the high time modulus), while parameter G_∞, taking the physical meaning of the high frequency modulus, it should be close to the value of the glassy plateau of Figure 2. Analyzing eq. (9), it is extracted that parameter τ is actually the inverse

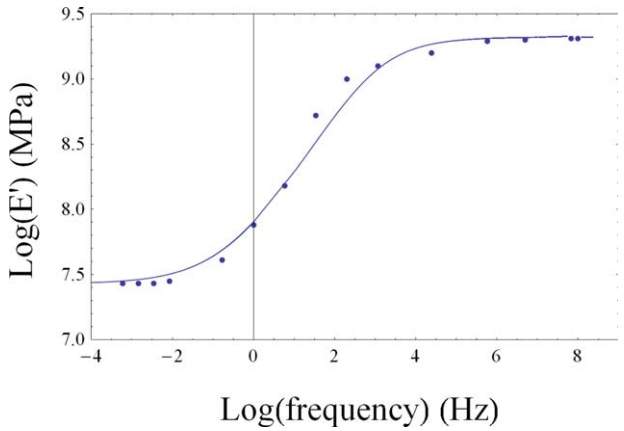

Figure 2. Master curve of storage modulus E' versus frequency for the epoxy resin. Points: experimental data, Line: Model simulation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

frequency of maximum in the loss modulus peak. Regarding parameter α, it is a fitting parameter, which affects the slope of the transition region. Therefore, parameters G_0, G_∞, τ are estimated from the experimental data of Figures 2 and 3 and taken equal to 2.5 × 10^7 Pa, 2.0 × 10^9 Pa and 0.0013 s correspondingly. Parameter α hereafter was fitted to be equal to 0.5.

The quality of simulation for storage [eq. (8)] and loss modulus [eq. (9)] of the epoxy resin examined are depicted in Figures 2 and 3, where a quite good agreement is obtained for the storage modulus, while the model is not capable of describing the asymmetry of the loss modulus peak.

Regarding the second material type, namely Ecovio (EC) and its nanocomposite (ECSi5), a different frequency response is obtained than that of the epoxy resin. Based on dynamic mechanical analysis data as described in Ref. 19 and applying the time-temperature superposition principle (TTS), the corresponding master curves at a reference temperature of 65 °C of storage modulus (Figure 4) and loss modulus (Figure 5) have been constructed for EC and ECSi5. Because of the fact that

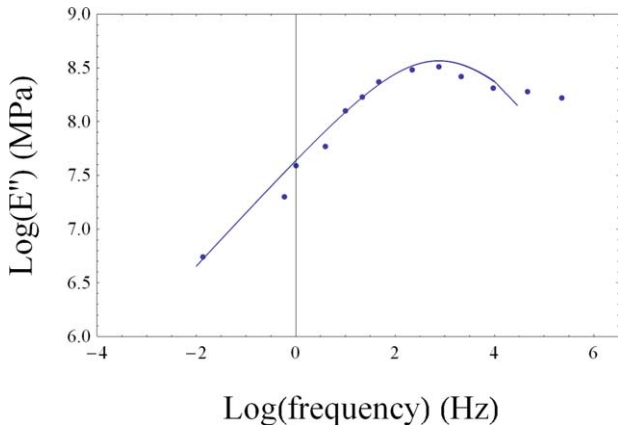

Figure 3. Master curve of loss modulus E'' versus frequency for the epoxy resin. Points: experimental data, Line: Model simulation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

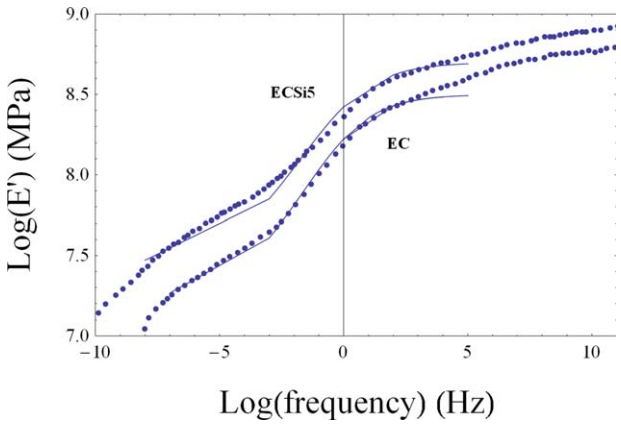

Figure 4. Master curve of storage modulus E' versus frequency for the EC and ECSi5. Points: experimental data, Line: Model simulation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Ecovio is a semicrystalline polymer, and therefore TTS can be considered inapplicable, a quite sensitive method to check qualitatively the thermorheological behavior of a material, is the shift of the storage modulus in the master curves. Because the curves overlap in the frequency range examined, a thermorheologically simple behavior can be assumed.[2] Another indication that the implementation of TTS is valid is the fact that the loss modulus master curves were constructed with the same shift factor values used for the storage modulus master curves.[2] By performing a similar simulation procedure, it is extracted from Figure 4 that the fractional Zener model can adequately describe the storage modulus of EC and ECSi5, but in a more limited frequency range than that obtained by the TTS application. This is mainly due to the upper limit of storage modulus at high frequencies, which is determined by the value of parameter G_∞. Therefore, the constantly increasing slope of the experimental storage modulus in Figure 4, is not possible to be captured by the model. Regarding the loss modulus curves of Figure 5, an adequate description of loss modulus is obtained, but the asymmetry of the loss modulus peak beyond a frequency value equal

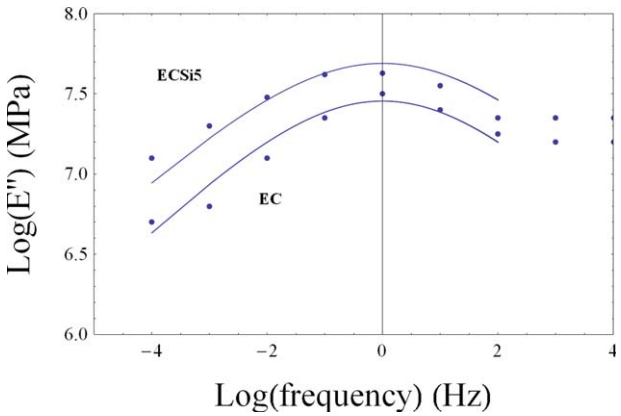

Figure 5. Master curve of loss modulus E'' versus frequency for the EC and ECSi5. Points: experimental data, Line: Model simulation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Parameter Values of the Fractional Zener Model

	Four-parameter model			
Material	G_0 (Pa)	G_∞ (Pa)	τ (sec)	α
Resin	$2.5\ 10^7$	$2\ 10^9$	0.0013	0.5
EC	$2.0\ 10^7$	$3.0\ 10^8$	1.5	0.34
ECSi5	$4.0\ 10^7$	$4.0\ 10^8$	3.0	0.32

	Five-parameter model				
	G_0 (Pa)	G_∞ (Pa)	τ (sec)	α	β
Resin	$2.5\ 10^7$	$2\ 10^9$	0.0015	0.5	0.45
EC	$2.0\ 10^7$	$3.0\ 10^8$	1.5	0.37	0.335
ECSi5	$3.8\ 10^7$	$3.8\ 10^8$	3.0	0.38	0.36

to 100 Hz could not be simulated. The model parameter values for all materials examined are presented in Table I.

Regarding the time dependent material functions of the above mentioned materials, the master curves of the compliance functions of EC and ECSi5, were constructed from the creep data at various temperatures,[19] and are analyzed here. Moreover, it has been checked that the strain values are within the limits of linear viscoelasticity. In order for the simulation procedure to be comparable with the one of the above paragraph, the master curves of the compliance were constructed at the same reference temperature of 65 °C, and are depicted in Figure 6 for EC and ECSi5. For a more integrated analysis, stress relaxation experiments for EC, at a strain level 0.7%, at various temperatures were performed as well and the relaxation function master curve was hereafter constructed at the same reference temperature 65 °C and plotted together with the simulated one in

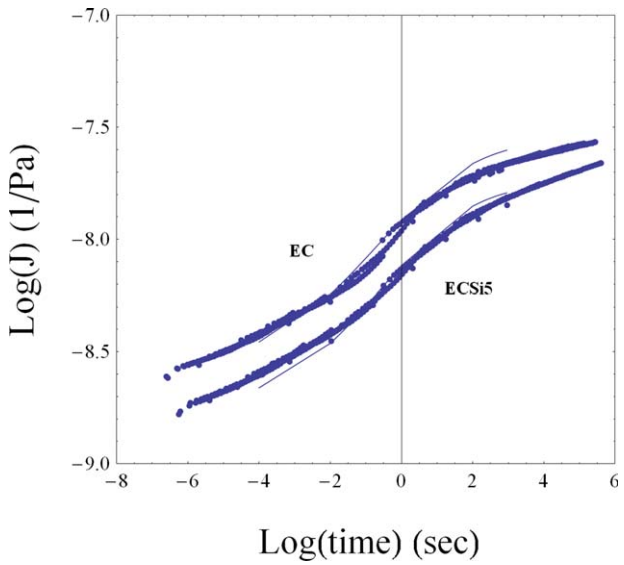

Figure 6. Compliance master curve of EC and ECSi5. Points: experimental data, Line: Model simulation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

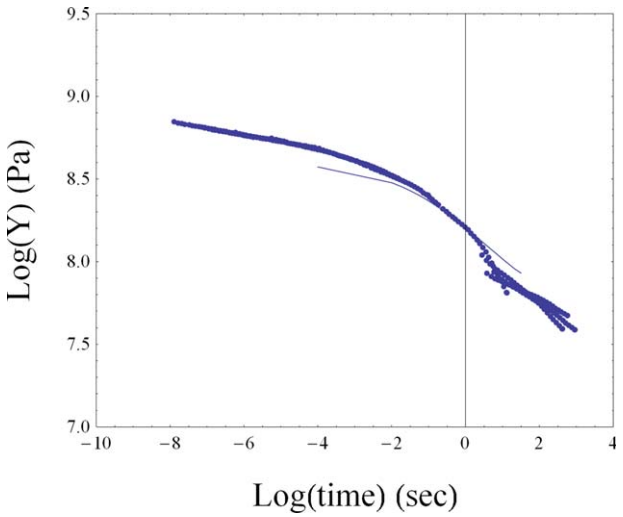

Figure 7. Relaxation modulus master curve of EC. Points: experimental data, Line: Model simulation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7. The simulation has been performed with the software Mathematica, and it has been postulated that a good agreement with the experimental data is achieved, with the same parameter values as the ones evaluated in the dynamic moduli simulation, as it is shown in Table I. It must be mentioned however, that the limits of the time domain where a good approximation between model simulation and experiments is achieved is much narrower than that of the complete master curve. From the above analysis, it can be postulated that this procedure may be employed as an alternative method for the interconversion of viscoelastic functions.

From the above treatment, it is revealed that the four parameter fractional Zener model is capable of describing the dynamic moduli versus frequency and the compliance-relaxation functions versus time with the same model parameter values. It is also however extracted that this model is not possible to capture

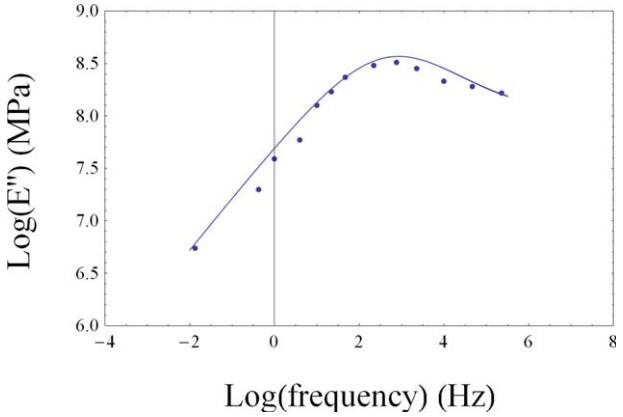

Figure 8. Master curve of loss modulus E'' versus frequency for the epoxy resin. Points: experimental data, Line: Five-parameter model simulation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

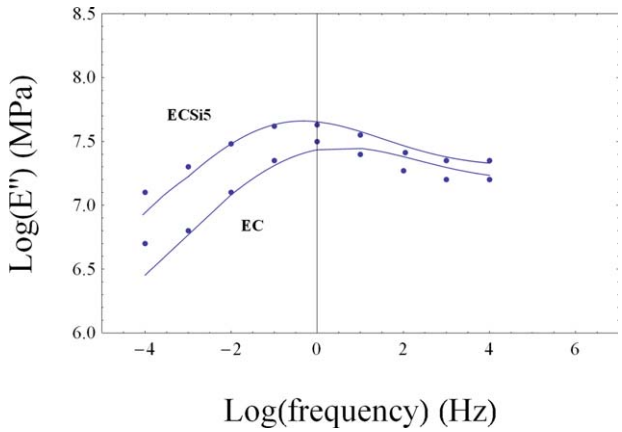

Figure 9. Master curve of loss modulus E'' versus frequency for the EC and ECSi5. Points: experimental data, Line: Five-parameter model simulation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the asymmetrical loss modulus peak, often observed in a variety of polymeric materials.

Therefore, following the analysis by Pritz,[3] the new constitutive equation of the five-parameter Zener model is given as:

$$\sigma(t)+\tau^{\beta}\frac{\mathrm{d}^{\beta}}{\mathrm{dt}^{\beta}}\sigma(t)=G_0\varepsilon(t)+G_0\tau^{\beta}\frac{d^{\beta}}{dt^{\beta}}\varepsilon(t)+(G_{\infty}-G_0)\ \tau^{\alpha}\frac{d^{\alpha}}{dt^{\alpha}}\varepsilon(t) \tag{15}$$

Where the five parameters are $G_0, G_{\infty}, \tau, \alpha, \beta$. Performing the Fourier transform of eq. (15), the complex modulus is derived and hereafter the storage E' and loss modulus E" can be expressed as follows[3]:

$$E'(\omega)=G_0+G_0\ (d-1)\ \frac{\cos(\alpha\pi/2)\ \omega_n^{\alpha}+\cos[(\alpha\text{-}\beta)\pi/2]\ \omega_{\mathrm{n}}^{\alpha+\beta}}{1+2\ \cos(\beta\pi/2)\ \omega_{\mathrm{n}}^{\beta}+\omega_n^{2\beta}} \tag{16}$$

$$E''(\omega)=G_0\ (d-1)\ \frac{\sin(\alpha\pi/2)\ \omega_n^{\alpha}+\sin[(\alpha\text{-}\beta)\pi/2]\ \omega_n^{\alpha+\beta}}{1+2\ \cos(\beta\pi/2)\ \omega_n^{\beta}+\omega_n^{2\beta}} \tag{17}$$

Where the condition $\alpha > \beta$ is necessary for the physical meaning of the five parameter model.

The simulation of the loss modulus of all materials examined is illustrated in Figures 8 and 9 for the epoxy resin and EC/ECSi5 correspondingly. From these plots a good approximation between experimental data and model simulation is obtained, with the asymmetry of the loss peak to be satisfactorily captured. Regarding storage modulus simulation, not presented here, it must be pointed out that no further improvement has been achieved, compared to the one with the four-parameter Zener model.

CONCLUSIONS

In this article, the well known fractional derivative Zener's model is presented and employed for the description of the dynamic behavior of two representative polymeric structures. The first material type, an epoxy resin, due to its chemical network structure, exhibits a storage modulus master curve with the main characteristic regions, i.e. the rubbery and the glassy

plateau, while the loss modulus have an asymmetric loss peak. The other material type examined is a thermoplastic, and semi-crystalline biodegradable polymer under the commercial name Ecovio, as a pure material and its nanocomposite with 5wt % of silica nanoparticles. Unlike to the epoxy resin, the storage modulus of Ecovio exhibits a constantly increasing storage modulus with increasing frequency.

The dynamic moduli of all material types could be successfully simulated with the fractional derivative Zener's model, while the model parameters are of physical significance. Regarding Ecovio/based materials, the compliance and relaxation function could be predicted with the same model parameters, revealing the model's capability for the interconversion of viscoelastic functions.

On the other hand, the loss modulus peak asymmetry has been described by employing the five-parameter version of fractional Zener's model. No further improvement was found for the simulation of the storage modulus with the increased number of parameters.

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