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CHARACTERIZATION OF POLYMERS BY MEANS OF A STANDARD VISCOELASTIC MODEL AND FRACTIONAL DERIVATE CALCULUS

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Polymeric materials are known to be more or less dispersive and absorptive. Dispersion has a consequence that the dynamic modulus is frequency dependent, and absorption is exhibited by the fact that these materials have the ability to absorb energy under vibratory motion. The phenomenon of dispersion in conjunction with the powerful notion of complex Modulus of Elasticity (MOE), permits to establish the relation between the real and the imaginary components of the MOE, that is, respectively the Storage and loss moduli. The loss factor is simply determined through taking the Ratio of these two MOE components. The theoretical background for the interrelations between the Storage modulus and the loss modulus is found in the Kramers-Kronig relations. However, due to the mathematical difficulties encountered in using the exact expressions of these relations, approximations are necessary for applications in practical situations. On the other hand, several simple models have been proposed to explain the viscoelastic behavior of materials, but all fail in giving a full account of the phenomenon. Among these models, the standard viscoelastic model, better known as the Zener model, is perhaps the most attractive. To improve the performance of this model, the concept of fractional derivatives has been incorporated into it, which results in a four-parameter model. Applications have also shown the superiority of this model when theoretical predictions are compared to experimental data of different polymeric materials. The aim of this article is to present the results of applying this model to rubber, both natural and filled, and to some other selected more general polymer.

Keywords: polymers, dispersion, fractional derivatives, Kramers-Kronig relations, dynamical MOE, loss factor, rubber, polyisobutylene

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INTRODUCTION

Polymers constitute the raw material of several industries, and plastic and rubber products are used in various applications. In order to ensure an optimal use of these materials, a knowledge of their properties is of primary concern. Considering a simple example, rubber-like materials are often used in structural mechanics and in building technology to reduce the vibrations and sound radiation from structural members [1]. This may be achieved either through coating extended vibrating areas by rubber-like materials to dampen their vibration amplitude, or through interposing discrete rubber components between connecting elements to reduce the vibration transmission path between them [2].

From a scientific point of view, the two major material properties characterizing polymeric materials, or more generally any solid material, are the strength as formulated by the Modulus of Elasticity (MOE) and the damping capability of the material as quantified by the loss factor. However, these two properties are not completely independent of one another. For solid materials, like steel and concrete, it is often, erroneously, made mention of their “constant” MOE and loss factor, η , but in reality this is, to some extent, true only within a certain frequency range. There is always some variation of these quantities with the frequency, although the variation is too slow in the case of most building materials to have a crucial effect in practical applications. Things are noticeably different for polymeric materials. The dependence on the frequency of the two material properties of concern is usually so strong that it can no longer be neglected when dealing with these materials. Furthermore, the range of frequency where the dependence is strongest may sometimes extend over several decades. On the other hand, some engineering applications require, for instance, to process damping materials that are tuned to operate with maximum efficiency at well-defined frequencies or frequency ranges. Thus, to ensure an optimal use of these materials for such applications a knowledge of the mechanisms behind such frequency dependency may help to establish simple predictive models.

THEORETICAL BACKGROUND

Definition of the Modulus of Elasticity and its Analogy in Linear Systems Theory

An important parameter for characterizing a solid material is its Modulus of Elasticity. If $\sigma(t)$ is the time history of the stress applied to a sample of the material, and $\varepsilon(t)$ the resulting strain time history, the

relation between these two functions may be expressed in terms of the memory function $m(t)$, [3–4]

$$\sigma(t) = \int_{-\infty}^t m(t - \tau)\varepsilon(\tau)d\tau \tag{1}$$

In the frequency domain, the Fourier transform of $m(t)$ is defined by:

$$M(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} m(t)e^{-j\omega t} dt \tag{2}$$

and transforming Equation (1) gives:

$$\sigma(\omega) = M(\omega) \cdot \varepsilon(\omega) \tag{3}$$

where $\sigma(\omega)$ and $\varepsilon(\omega)$ are respectively the frequency forms of $\sigma(t)$ and $\varepsilon(t)$ (use of the symbol M is made here for the MOE simply for the reason that the following results may in a broad sense be generalized to any modulus, be it shear or bulk). This last equation is nothing more than Hooke’s law, where $M(\omega)$ may be recognized as the MOE.

A close analogy between the MOE and the frequency response of a linear system may then be drawn, and this is schematically represented in the illustration of Figure 1.

The Loss Factor

The frequency-dependent quantities entering in Eq. 3 are usually complex. It follows then that the complex MOE may be written as the sum of a real part, denoted as the Storage modulus, and an imaginary part, denoted as the loss modulus, i.e.

$$M(\omega) = \frac{\sigma(\omega)}{\varepsilon(\omega)} = M_d(\omega) + jM_l(\omega) = M_d(\omega)(1 + j\eta(\omega)) \tag{4}$$

with

$$\eta(\omega) = \frac{M_l(\omega)}{M_d(\omega)} \tag{5}$$

a coefficient used for assessing the amount of loss in the material, called the loss factor. The notion of complex MOE is a powerful means for studying the viscoelastic properties of materials. If under the regime of harmonic vibrations, the available, reversible, vibratory energy per period of vibration is W_R , and the amount of energy lost

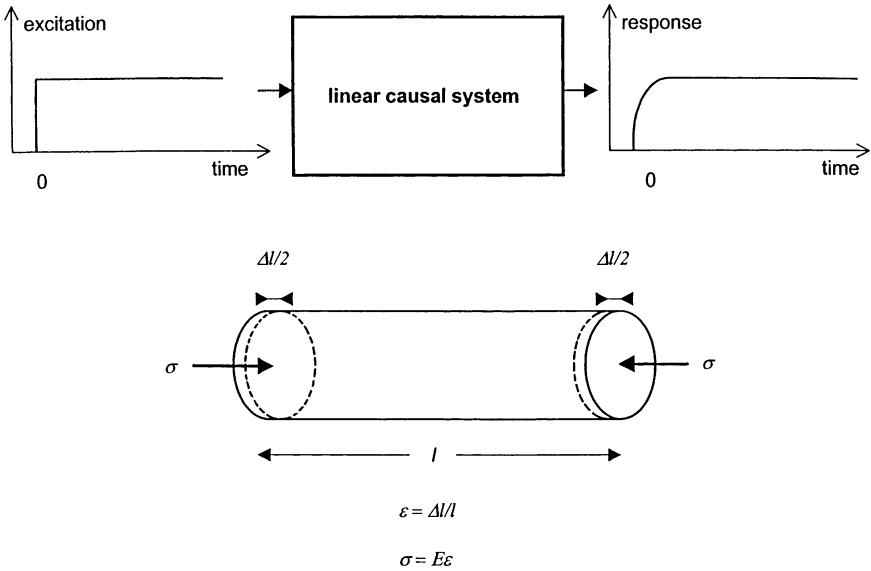


FIGURE 1 Analogy between the Modulus of Elasticity of a sample of solid material and the frequency response of a linear system.

during the same period is W_l , then the loss factor may alternatively be defined by:

$$\eta(\omega) = \frac{1}{2\pi} \frac{W_l}{W_r} \quad (6)$$

For solid materials, and in the audio frequency range, typical values observed for η lie in the range between approximately 0.001 and 0.01, whereas for polymers they may be up to three orders of magnitude larger.

Dispersion of Materials and Response of Linear Systems

The notion of dispersion is brought from optics to refer to the phenomenon by which waves with different frequencies propagate with different speeds within a medium. The speed of wave propagation in solids is a dynamic property that is formulated in terms of the MOE, and as this latter is dependent on the frequency of operation, dispersion then follows.

The concept of dispersion relations is attributed to Kronig [5] and Kramers [6] who were the first to introduce it in the field of material

sciences. However, a generalization of this label lies in the consideration of any pair of equations that express the real part of a function as an integral of its imaginary part, and vice versa. A real solid material, or more generally any physically realizable system satisfies the principle of causality by which it is meant that no response is expected from the system prior to the application of an excitation. The principle of causality has as a main consequence that the real and imaginary parts of the frequency response function are interrelated (see for instance Reference 7, p. 286 or Reference 8, p. 198).

Mathematically speaking, the dispersion relations are formulated with the help of Hilbert transforms, and are of general nature, finding applications in several branches of physics, including acoustics, electromagnetism, and optics. Several forms of such pairs of relations have been formulated for viscoelastic materials, and for instance a simplified form of such a set which includes the static Modulus M_0 is [4]:

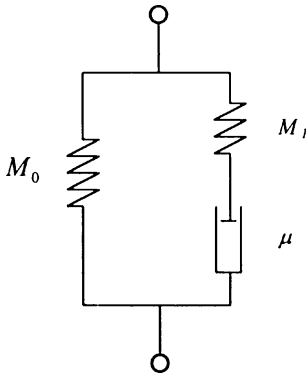
$$M_d(\omega) = M_0 + \frac{2\omega^2}{\pi} P \int_0^\infty \frac{M_l(x)/x}{\omega^2 - x^2} dx; \quad M_l(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{M_d(x)}{\omega^2 - x^2} dx \quad (7)$$

where x is an integration variable and P stands for the principal value of the integrals. These last formulas express the fact that the knowledge of the frequency behavior of one of the moduli permits the determination of the other modulus at any frequency. It may be shown that the value of the dynamic modulus at zero frequency is equal to that of the static modulus.

Usually, the study of a material sample requires, in the ideal situation, the knowledge of its response to a Dirac impulse-like excitation. However, the response to a step excitation is also a good alternative (actually, the step excitation is more easily realizable in practical experimental situations, and the two types of excitation are related to each other through Fourier transforms [9]).

The Zener Model and its New Improvement

A simple model, namely the one developed by Zener [10], has quite often been referred to in dealing with modeling the viscoelastic behavior of materials. The model is built on the parallel coupling of a linear spring and a Maxwell element (a serial coupling of a linear spring and a viscous damper; see Figure 2) Knowing that this model fails to describe adequately the problem of viscoelastic behavior, Pritz [11] proposed a slight modification of it through making appeal to the concept of fractional derivates [12–13].



$$\tau_r = \frac{\mu}{M_1}$$

$$M_\infty = M_0 + M_1$$

$$M(\omega) = \frac{M_0 + M_\infty j\omega\tau_r}{1 + j\omega\tau_r}$$

FIGURE 2 The Zener model, also known as the standard viscoelastic body.

Thus, let the fractional derivative of order α of a function $f(t)$ of time t be defined by:

$$\frac{d^\alpha}{dt^\alpha} f(t) = \frac{1}{\Gamma(1-\alpha)} \frac{d}{dt} \int_0^t \frac{f(\tau)}{(t-\tau)^\alpha} d\tau \tag{8}$$

Γ being the Gamma function, and τ a dummy variable. Referring to Figure 2, the complex elastic modulus becomes then:

$$M(\omega) = \frac{M_0 + M_\infty (j\omega\tau_r)^\alpha}{1 + (j\omega\tau_r)^\alpha} \tag{9}$$

and an identification of the real and imaginary parts as respectively the storage and loss moduli gives, after normalizing:

$$\begin{aligned} \frac{M_d(\omega)}{M_0} &= \frac{1 + (c+1) \cos(\alpha\pi/2) \omega_n^\alpha + c\omega_n^{2\alpha}}{1 + 2 \cos(\alpha\pi/2) \omega_n^\alpha + \omega_n^{2\alpha}}; \\ \frac{M_l(\omega)}{M_0} &= \frac{(c-1) \sin(\alpha\pi/2) \omega_n^\alpha}{1 + 2 \cos(\alpha\pi/2) \omega_n^\alpha + \omega_n^{2\alpha}} \end{aligned} \tag{10a, b}$$

The loss factor is simply taken as the ratio of these two expressions, and is therefore given by:

$$\eta(\omega) = \frac{(c-1) \sin(\alpha\pi/2) \omega_n^\alpha}{1 + (c+1) \cos(\alpha\pi/2) \omega_n^\alpha + c\omega_n^{2\alpha}} \tag{11}$$

where $c = M_\infty/M_0$, M_∞ being the value taken by the MOE in the limit of infinite frequency. The quantity $\omega_n = \omega\tau_r$ is the normalized frequency

with τ_r being the relaxation time. It may be noted that the application of fractional calculus to viscoelasticity is not a novelty in itself, but dates back to about a century ago with early contributions due to Volterra. The fractional calculus models are used to describe the viscoelastic properties of materials for the reasons that they are in harmony with the molecular theories describing these materials, that their predictions fit reasonably well with the experimental data and further that they permit a material modeling using fewer parameters than those based on classical differential calculus [14–15].

VERIFICATION OF THE MODEL ON AVAILABLE DATA ON RUBBER

As a direct application, comparison is made between experimental data on the viscoelastic properties of rubber and theory as predicted by use of the fractional Zener model proposed here. The results are

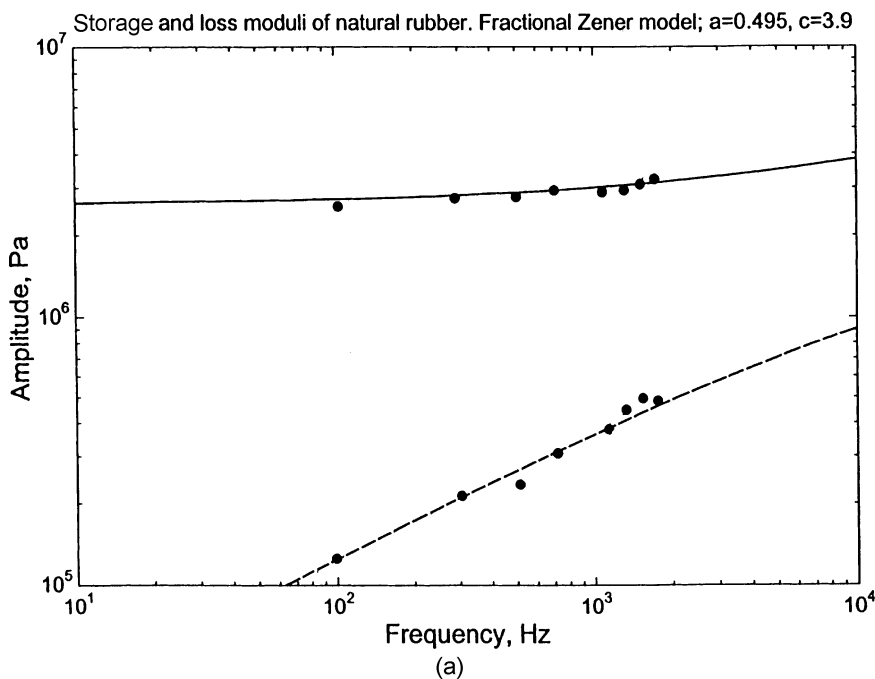


FIGURE 3 Comparison between model prediction and experimental data of natural rubber. a) Storage modulus: —, and loss modulus: - - -. b) loss factor. •: experimental data.

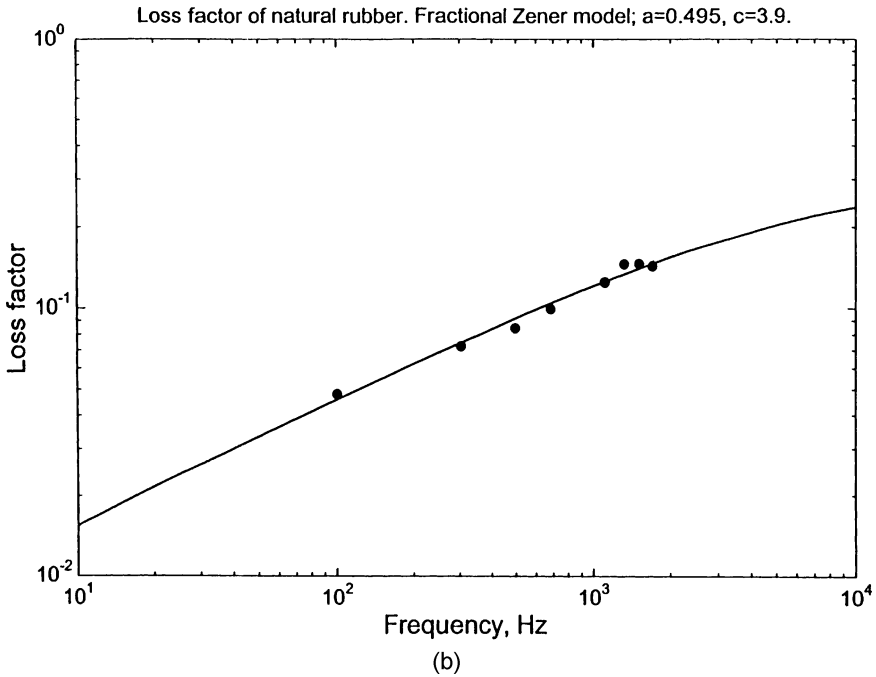


FIGURE 3 (Continued).

presented in Figures 3 and 4, respectively, for natural and filled rubber in the audio frequency range.

With reference to Equations 10 and 11, the corresponding relaxation times were of about 9.10^{-7} s and 6.10^{-8} s for the respective materials, values that are not totally unexpected for polymeric materials (a crude estimate of the relaxation time is $\tau_r = \eta/M_d$). One may see that the curves of frequency variation as predicted by the present model are in a quite satisfactory agreement with the experimentally determined values.

Some discrepancies are, however, to be noticed at higher frequencies that may be attributed to limitations of the proposed model. Indeed, the best fits of the fractional Zener model with the exact K–K theory are expected for materials with $\alpha < 0.3$, to be compared with the value $\alpha \approx 0.5$, found for rubber in this study, and which is the over limit for acceptable performance of the approximate model. The parameter α is an indicator of the rate of frequency dependence of the dynamic properties, and the choice of its value is crucial for the accuracy of the approximate model. Smaller values of

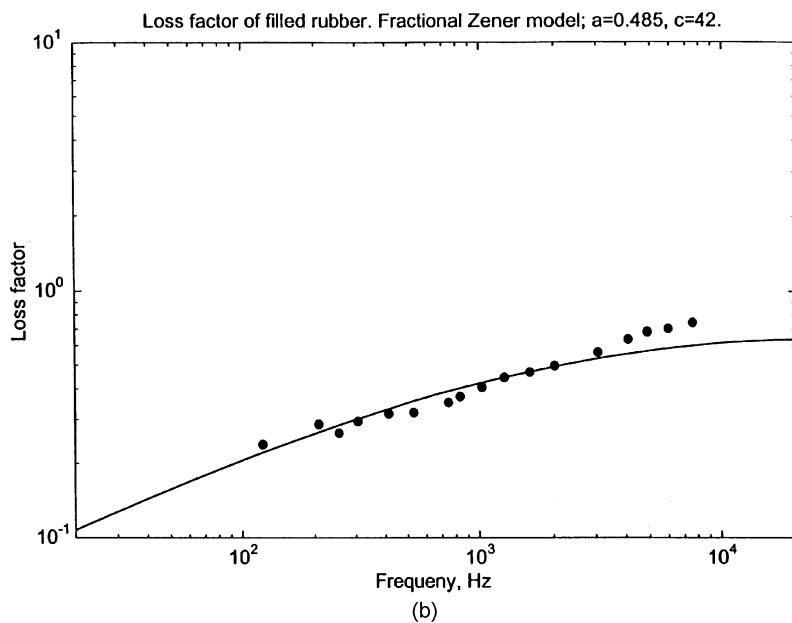
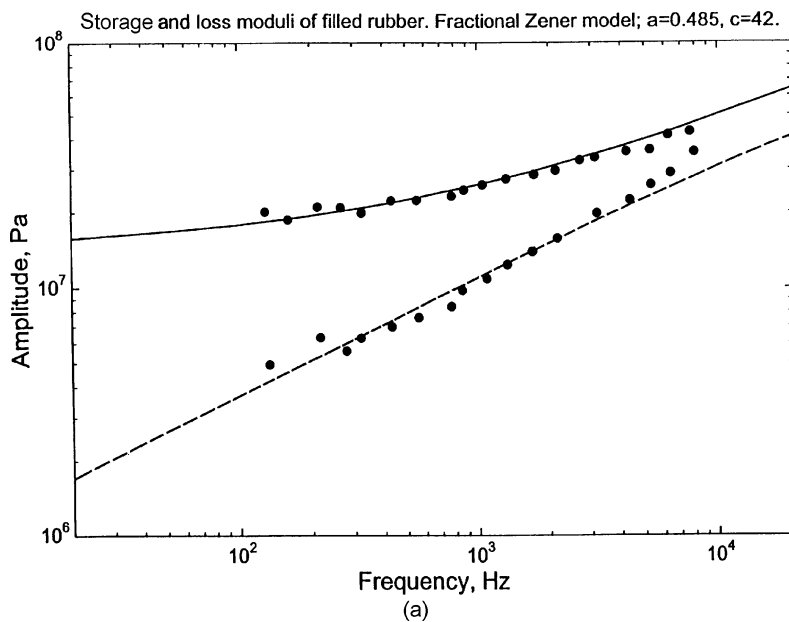


FIGURE 4 Same as Figure 3, but for filled rubber.

this parameter have been found to correspond to foam-like polymers and PVC with low mass density [11], but a generalization of this claim requires further in-depth investigations.

VERIFICATION OF THE MODEL ON AVAILABLE DATA ON OTHER POLYMERS

Figure 5 summarizes the results of comparison between experimental data and theoretical predictions on a polymer, namely polyisobutylene, PIB². The experimental curves taken for this comparison were those corresponding to a temperature of 50°F. The theoretical curves were obtained for a relaxation time $\tau_r = 10^{-6}$ s and a constant $c = 420$. The order of the fractional derivate was $\alpha = 0.7$, and the static value of the MOE was taken as $M_0 = 1.9 \cdot 10^2$ psi.

The agreement between experimental data and theoretical predictions is also found here to be satisfactory, and the determined values

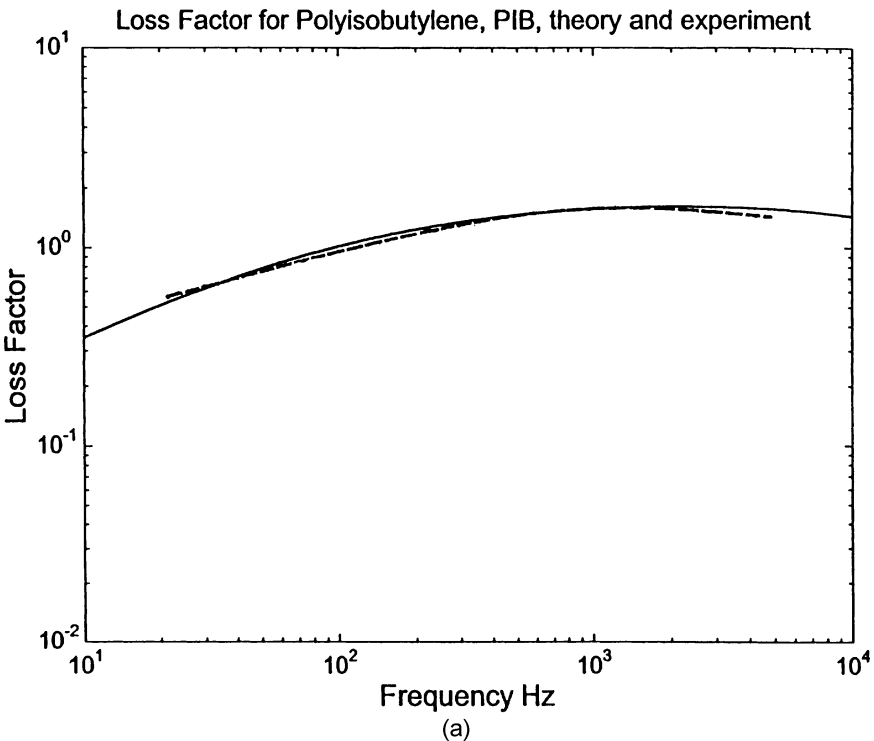


FIGURE 5 Comparison between model prediction and experimental data of PIB. a) Storage modulus. b) loss factor. — —: experimental curves and —: theory.

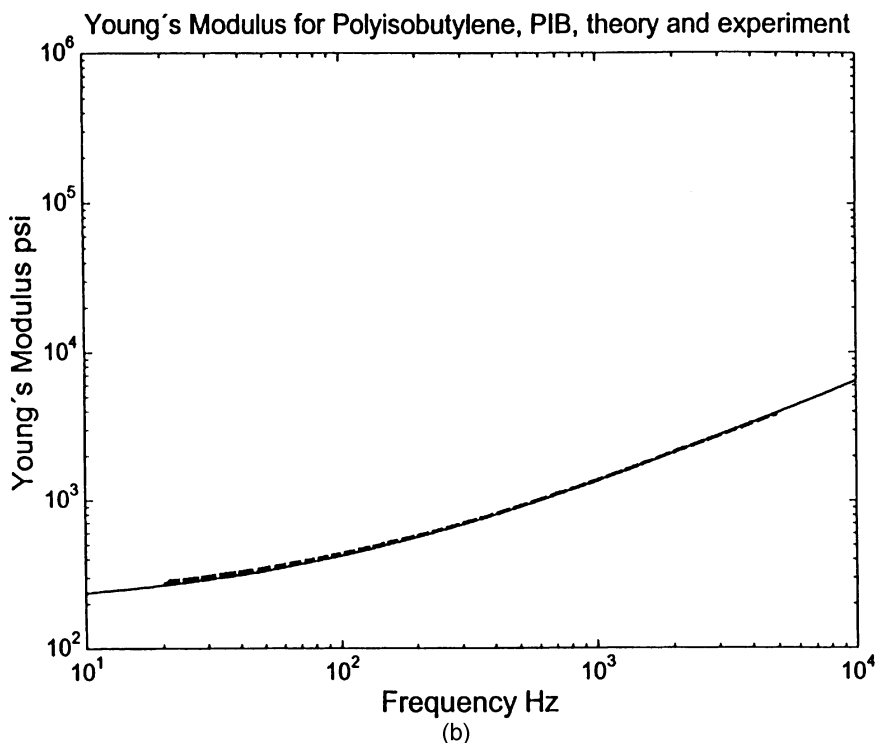


FIGURE 5 (Continued).

of the parameters adequately describing the Zener fractional derivate model may be used as specific to characterize this polymer.

CONCLUSIONS

In this article a novel model has been presented for characterizing the dynamic mechanical properties of polymeric materials. The model is based on the classical model as proposed by Zener, in which slight modifications have been incorporated through introducing the concept of fractional derivates. The model is sometimes also known as the four-parameter fractional derivative model, after the number of parameters involved in it (M_0 , M_∞ , τ_r and α), and was baptized by its author [11] as the *fractional Zener model*.

Under some assumptions, namely for the order of the fractional derivative $\alpha \leq 0.3$, the model gives excellent agreement with the exact theory as formulated by the Kramers–Kronig relations. For many polymers, this condition is fulfilled, as demonstrated in the

examples where the approximate model has originally been-presented [11]. The present study extends the validity of this model at even higher values of α exceeding 0.6.

Applications made to rubber show an overall satisfactory performance. Moreover, considering the specific engineering purpose of using rubber elements as vibration dampers, it may be concluded that the present model achieves excellent performance in the important low audio frequency range, and up to around 2 KHz. Furthermore, the model gives better correlation with experimental data when applied to carbon black filled rubber, the manufacture of which has more interesting engineering implications than natural rubber. For the less interesting range of higher frequencies, the fractional derivate Zener model seems to suffer some shortcomings, which may be attributed to the fact that other kinds of damping than viscous damping, like friction, take place.

For more general applications on polymers, the fractional Zener model shows reasonably acceptable achievements when applied to PIB. It is however not a limitation that application was specifically made to this polymer, because other polymers may as well have been considered. Although the model proposed in this study is expected to have its best achievements for materials with α -values not exceeding 0.3, good agreement has been found for the present polymer whose α -value has been found to be more than twice as high.

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