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Nonlinear viscoelastic modeling of soft polymers

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ABSTRACT: A one-dimensional phenomenological constitutive model, representing the nonlinear viscoelastic behavior of polymers is developed in this study. The proposed model is based on a modification of the well-known three element standard solid model. The linear dashpot is replaced by an Eyring type one, while the nonlinearity is enhanced by a nonlinear, strain dependent spring constant. The new constitutive model was proved to be capable of capturing the main aspects of nonlinear viscoelastic response, namely, monotonic and cyclic loading, creep and stress relaxation, with the same parameter values. Model validation was tested on the experimental results at various modes of deformation for two elastomeric type materials, performed elsewhere. A very good agreement between model simulations and experimental data was obtained in all cases. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42141.

KEYWORDS: elastomers; properties and characterization; viscosity and viscoelasticity

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INTRODUCTION

Because of the extended use of polymeric materials in a variety of applications over the last decades, a thorough understanding of their mechanical properties is a crucial matter in order to design the appropriate materials. The mechanical behavior of polymeric structure is mainly governed by rheological (time dependent) effects, and therefore the prediction of their inelastic mechanical behavior, in terms of monotonic and cycling loading, as well as creep and relaxation, is of great importance. The classical linear theory of viscoelasticity[1,2] has adequately described the creep, relaxation and loading-rate dependence of polymers. This theory can be presented by two major forms: hereditary integrals or differential forms. This well-known theory, however, is limited to narrow loading rate and temperature regimes, while polymeric materials demonstrate a nonlinear response at relatively small strains.

The most general multiple integral constitutive relation for a nonlinear viscoelastic material is given by Green-Rivlin theory.[3] The complexity of this model and the large amount of experimental data, required to determine the material parameters, resulted in a very limited use. Significant works related to more applicable models for nonlinear viscoelasticity have been developed.[4,5] The modified superposition principle was first introduced by Leaderman in 1940,[6] and hereafter, a number of physical and semiempirical single integral constitutive relations have also been proposed by Caruthers *et al.*[7] Progress has been made in developing mathematical models for the small strain regime under a specific narrow spectrum of strain rates,[8] while much less progress has been made for multi-axial finite deformation response under a wide range of strain rates and temperatures, from a continuum point of view. [9] A thermodynamically consistent theory of nonlinear viscoelastic and viscoplastic materials was developed by Schapery.[10] This model considers the nonlinear viscoplastic response of materials as a particular case of nonlinear viscoelasticity corresponding to infinite retardation times. Experimental methodology for complete material characterization in the framework of this model was presented by Megnis and Varna.[11]

Numerous investigations have been focused on the nonlinear viscoelasticity[12–15] and viscoplastic response of polymers.[16–19] This response is strongly rate and temperature dependent and thermomechanically prehistory of the material dependent. An interesting paper dealing with the long-term material performance in short-term stress relaxation tests on polycarbonate has been published. [20] However, until now, all these aspects of deformation behavior have been treated separately. A number of interesting approaches deal with nonlinear viscoelastic behavior, using integral representation with multiple relaxation times, stress dependent, or using state variables related to the free volume.[21] In a previous work,[22] a theoretical treatment is presented, which takes into account the viscoelastic path at small strains and the viscoplastic one at higher stresses, proved to be capable of describing the main aspects of mechanical response of glassy polymers, i.e. nonlinear viscoelasticity during creep

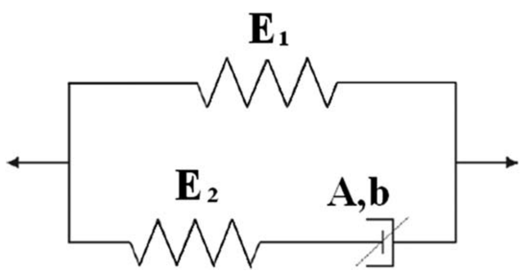

Figure 1. Schematic presentation of the modified standard solid model.

procedure, and monotonic loading. In recent works[23,24] the nonlinear viscoelastic/viscoplastic response of polymeric materials, in terms of monotonic loading and creep is described by a new model within the concept of transient network, introducing the nonlinearity by a stress dependent term of the activation energy, while the viscoplastic response is successfully analyzed by a proper kinematic formulation.

On the other hand, modeling large deformations in polymers was made by Haupt *et al.*[25] and Ehlers and Markert.[26] In addition, micromechanics models were proposed and analyzed,[27–29] being, however, difficult in use.[9]

Therefore, studying the polymer's inelastic behavior in terms of creep, stress–relaxation and monotonic loading, and its further implementation in polymeric composites is still a very interesting topic.

A matter of considerable interest is the nonlinear viscoelastic response exhibited by elastomers. Elastomeric materials, are generally used as shock absorbers because of their low modulus and high damping characteristics.[30,31] Especially elastomers of type Hydrogenated Nitrile Butadiene Rubbers (HNBR) are characterized by enhanced mechanical properties and retain these properties after long-term exposure to heat, oil, and fuel.[30,31] Therefore, they are widely used in the automotive industry for a variety of applications. They are also used as sealing materials in oil exploration and its processing. Because of their high damping characteristics, elastomers are increasingly used in applications that are subjected to shock, impact, and vibrations. Measurements of tensile creep and stress relaxation response of a dielectric elastomer, which is a widely researched electro-active material for actuator applications, are presented in.[32] Power law-based models were proved to satisfactory predict of creep and stress relaxation behavior. For all the above reasons, insight of the mechanical behavior of elastomers over a wide range of strain-rates and modes of deformation may be a useful tool for material design.

In the work by Khan *et al.*,[9] a simple phenomelogical viscoelastic model is introduced to describe the time and temperature dependent mechanical properties of elastomeric type soft polymers under finite deformations. Uniaxial experimental data of stress–relaxation and monotonic loading at various strain rates were successfully analyzed,[9] considering that the material under investigation exhibits mainly viscoelastic behavior, with the viscoplastic one being negligible. To this trend, the aim of the present work, is to develop and analyze a nonlinear viscoelastic model, for the characterization of the rheological response of polymers. It has been shown that the proposed model is capable of describing the main aspects of viscoelastic behavior of polymers, namely creep, stress–relaxation, monotonic loading, as well as cyclic loading and step-relaxation testing. Experimental data of the aforementioned modes of deformation, performed in previous studies for elastomeric materials at moderate and large deformations were employed to test the model's capability.

MODIFIED STANDARD SOLID MODEL

Development and Constitutive Analysis of the Nonlinear Viscoelastic Model

A very popular viscoelastic model, composed of a Maxwell element (linear spring and dashpot in series) in parallel with a linear spring[33] is the so-called standard linear solid. In the present work a modified standard solid model is adapted and shown in Figure 1. It is composed by a nonlinear spring, designated by E_1, in parallel with a nonlinear Maxwell element, consisted by a linear spring (constant E_2) in series with an Eyring type dashpot. The nonlinear spring E_1 is assumed to be dependent on strain $\varepsilon(t)$, according to the formula:

$$E_1(t)=\eta_1\varepsilon(t)^{-\eta_2} \tag{1}$$

where η_1, η_2 are constants that need to be calculated. Given that E_1 depends on strain, which evolves with time, the physical meaning of eq. (1) is that spring's constant E_1 is a strain hardening parameter. On the other hand, the strain rate for the Eyring dashpot is given by the following equation:[33]

$$\dot{\varepsilon}=A\ \sinh[b\ (\sigma\text{-}\varepsilon\ E_1)] \tag{2}$$

where A, b are constants, ε is the total strain, and σ is the total stress imposed. Constant A is a pre-exponential factor and b is equal to β/RT, where β is the activation volume for the molecular event,[33] R the gas constant and T is the temperature.

The one-dimensional constitutive equation for the viscoelastic model of Figure 1 is thus given by

$$\dot{\sigma}=\varepsilon\ \dot{E}_1+\dot{\varepsilon}\ (E_1+E_2)-A\ E_2\sinh\left[b\ (\sigma\text{-}\varepsilon\ E_1)\right] \tag{3}$$

Moreover, for a stress relaxation experiment, by substituting in the constitutive equation (3), the strain rate $\dot{\varepsilon}$ equal to zero, we obtain the stress evolution with time as follows:

$$\dot{\sigma}=-A\ E_2\ \sinh[b\ (\sigma\text{-}\varepsilon\ E_1)] \tag{4}$$

RESULTS AND DISCUSSION

Monotonic Loading, Stress–Relaxation, Cyclic Loading Experiments in Adiprene L100

The proposed nonlinear viscoelastic model has been implemented to a polymer, namely Adiprene L100, studied in a previous work by Khan *et al.*[9] The model's flexibility has been tested for stress–relaxation at various strain levels, monotonic loading in a variety of strain rates, and cyclic loading at room temperature. The cyclic loading tests involve a monotonic loading, a stress–relaxation for a specific time period of 2 hours and a monotonic unloading. The afore-mentioned experiments were performed and adequately analyzed by Khan *et al.*[9]

In Figure 2 the stress–relaxation experimental curves of Adiprene-L100 at different levels of strain at the engineering

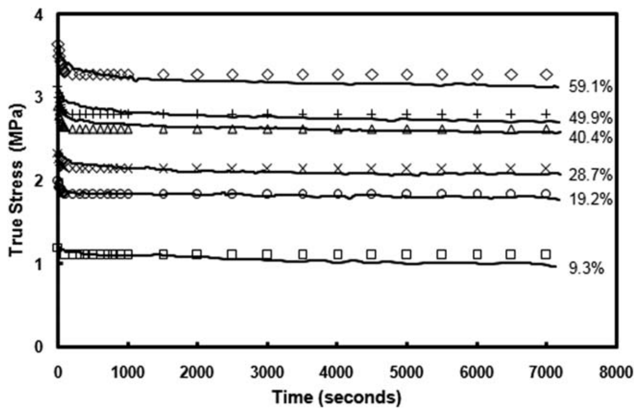

Figure 2. True stress–relaxation curves of Adiprene-L100 at various strain levels (compressive stress and strain are assumed positive). Points: Model simulations. Solid lines: Experimental data after Khan *et al.* 2006.

strain rate of 1 s^{-1} are illustrated. In this Figure the compressive stress and strains are assumed positive. In the same Figure the model simulated results, obtained by numerically solving eq. (4), are also depicted, exhibiting a good correlation between model simulation and experiment. Proceeding further with the compressive stress–strain experimental results of the same polymer, at various strain rates, namely 10^{-5}, 10^{-4}, 10^{-2}, and 1 s^{-1}, the comparison between model simulation and experimental data are presented in Figure 3. The model simulation was performed following the constitutive eq. (3), while a satisfactory agreement with experiments is observed.

To further check the model's capability in describing the viscoelastic response of the materials, simulations were performed for a more complex experimental procedure[9] as follows. A constant compressive strain rate of 1 s^{-1}, followed by a 2 h stress–relaxation process around 0.15, 0.30, 0.45, and 0.60 strain levels. The corresponding experimental curves are depicted in Figure 4, along with the model simulations, indicating again a good approximation between theory and experiments. Moreover, The true stress–strain for relaxation experiments at different strain levels at a strain rate equal to 1 s^{-1},[9] are shown in Figure 5.

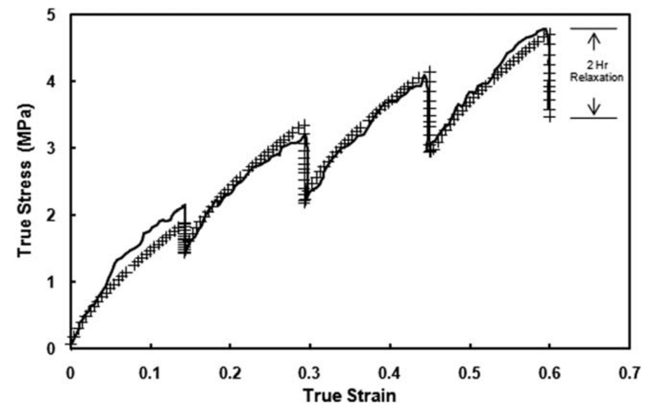

Figure 4. Multiple step relaxation experiment at 1 s^{-1} strain rate, with 2 h relaxation period of Adiprene-L100. Compressive stress and strain are assumed positive. Points: Model simulations. Solid lines: Experimental data after Khan *et al.* 2006.

These curves, which actually represent cyclic testing, are shown in comparison with the model simulations.

Because of the nonlinearity of the involved equations, it was not possible to have a closed from solution for all the deformation procedures applied. Therefore, the model calculations were performed numerically, the using the software Mathematica, and the differential equations were solved by applying small time steps, while the convergence of the solutions was monitored in all cases. It should be emphasized that the experimental data of all types of deformation were simulated by the same values of model parameters.

The values of model parameters, namely η_1, η_2, E_2, A, and b are presented in Table I. These values were calculated by back step analysis. Using a code through Mathematica, we tried different values for each parameter to choose the most appropriate values for describing the behavior of the material. Starting with stress–relaxation, the calculation of the parameters has been done for the best fitting of the experimental data, and hereafter with minimal corrections, the monotonic and cyclic loading data were simulated. The simulation of unloading stress–strain curves was possible with a different value of constant η_1

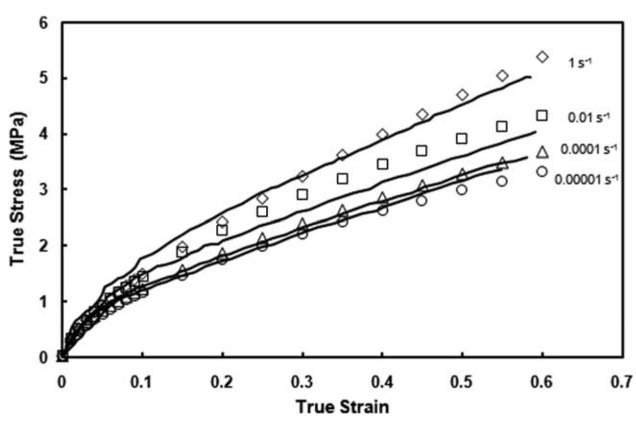

Figure 3. True compressive stress–strain curves of Adiprene-L100 at various strain rates. Points: Model simulations. Solid lines: Experimental data after Khan *et al.* 2006.

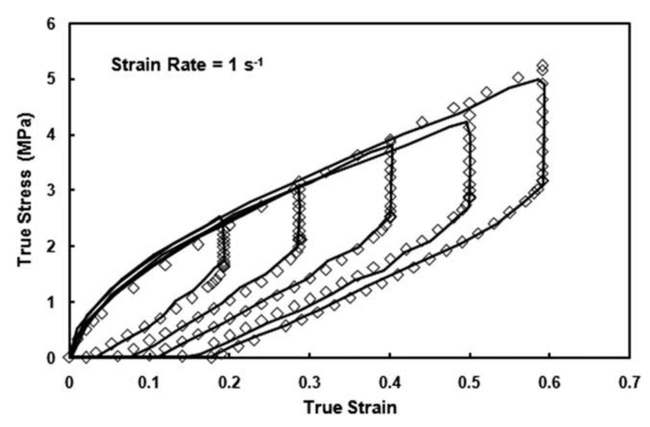

Figure 5. True compressive cyclic stress–strain curves of Adiprene-L100 for relaxation experiments at different strain levels at a strain rate of 1 s^{-1}.

Table I. Model Parameter Values

Material	Model Parameters				
	η_1 (MPa)	η_2	E_2 (MPa)	A (s^{-1})	b (m^3/J)
Adiprene-L100	4.47	0.41	3.5	$10^{-0.8}$	0.05
	2.9*				
HNBR	3.2	0.20	0.5	$10^{-0.01}$	0.03

* the value of η_1 at the unloading

(designated with a star in Table I), which seems reasonable, because of the stress softening of the material, observed in the experimental curves.

It must also be noted that the number of five required parameters, is quite lower than that in previous works,[9] while the model appears to be capable of describing various modes of deformation in unified manner.

Monotonic Loading, Creep, and Stress–Relaxation Experiments of HNBR at Large Deformations

The introduced modified standard solid model was further applied in another material type, namely a HNBR, and a different set of experiments, namely monotonic loading, creep at various stress levels and stress relaxation at various strain levels, all performed at room temperature in Ref. [30].

Quasi-static monotonic compression experiments were performed in Ref. [30] for HNBR at three different strain rates, namely 10^0, 10^{-2}, and 10^{-4} s^{-1}. The experimental procedure is presented in detail in the work by Khan *et al.*[30] A pronounced strain rate sensitivity is of HNBR is observed in the experimental stress–strain results, as shown in Figure 6. In addition, the material's response was proved to be purely viscoelastic, with the viscoplastic strain to be ignored, as it is mentioned in Ref. [30].

In the same work, the creep response of HNBR was found to be strongly dependent on the strain rate and strain level. In the present work, the creep curves of HNBR,[30] with the applied stress being imposed at a constant strain rate equal to 10^0 s^{-1}

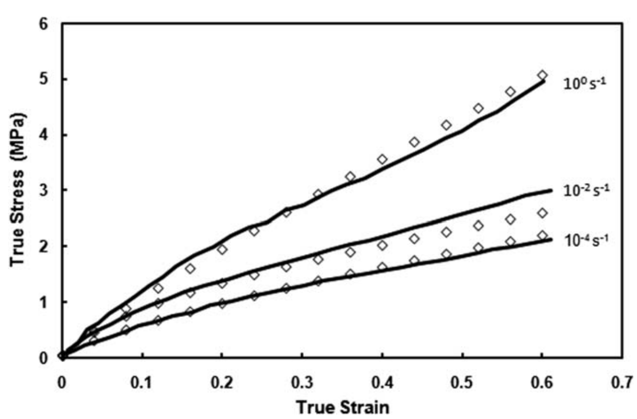

Figure 6. True stress–strain curves of HNBR at various strain rates. Points: Model simulations. Solid lines: Experimental data after Khan *et al.* 2010.

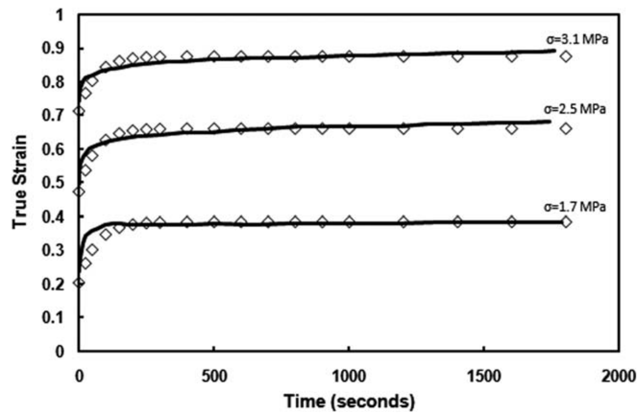

Figure 7. True creep strain–time curves of HNBR at room temperature, with the stress imposed at a strain rate of 10^0 s^{-1}. Points: Model simulations. Solid lines: Experimental data after Khan *et al.* 2010.

were selected and analyzed. The stress level, required for the creep strain evolution, was estimated from the corresponding stress–strain curves. In Figure 7 the creep strain versus time, at various stress levels is illustrated. A fairly good agreement between experiment and modeling is observed.

Moreover, the stress–relaxation experiments performed at room temperature, at strain levels equal to 0.25, 0.50, and 0.75 are presented along with the model predictions in Figure 8, revealing a generally quite good agreement. For all modes of deformation the simulations were made with the same parameter values, which are shown in Table I.

CONCLUSIONS

In the present study a new nonlinear viscoelastic model is developed. The proposed one dimensional model is based on a modification of the three element standard solid, where the dashpot is replaced by an Eyring dashpot, and the elastic spring constant is replaced by a nonlinear one, which is strain dependent.

The model's validity was tested on the experimental data of two polymers, of elastomeric type, namely Adiprene L100 and

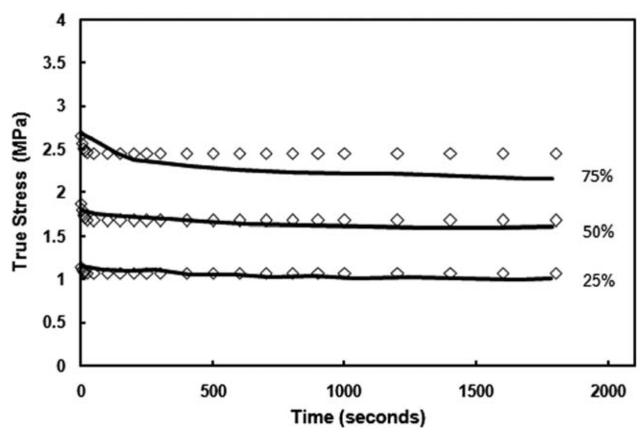

Figure 8. True stress–relaxation curves of HNBR at room temperature, at three different strain levels, with the stress imposed at a strain rate of 10^{-4} s^{-1}. Points: Model simulations. Solid lines: Experimental data after Khan *et al.* 2010.

HNBR. The constitutive model was numerically solved for a variety of complex loadings at moderate and large deformations, such as monotonic and cyclic loading, creep, stress–relaxation, and stress–relaxation step experiments, at various strain rates. A good agreement between model predictions and experimental data was obtained, with the same parameter values. It must be noted that the number of required parameters is lower than that in previous works.

Therefore, the introduced nonlinear viscoelastic model, with the assumption of a strain dependent nonlinear spring, appears to be capable of describing the main aspects of nonlinear viscoelasticity in a unified manner.

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