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NONLINEAR VISCOELASTIC CHARACTERIZATION OF POLYMER MATERIALS USING A DYNAMIC-MECHANICAL METHODOLOGY*

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ABSTRACT

Polymer materials retrieved from LDEF exhibit nonlinear constitutive behavior, thus the authors present a method to characterize nonlinear viscoelastic behavior using measurements from dynamic (oscillatory) mechanical tests. Frequency-derived measurements are transformed into time-domain properties providing the capability to predict long term material performance without a lengthy experimentation program. Results are presented for thin-film high-performance polymer materials used in the fabrication of high-altitude scientific balloons. Predictions based upon a linear test and analysis approach are shown to deteriorate for moderate to high stress levels expected for extended applications. Tests verify that nonlinear viscoelastic response is induced by large stresses. Hence, an approach is developed in which the stress-dependent behavior is examined in a manner analogous to modeling temperature-dependent behavior with time-temperature correspondence and superposition principles. The development leads to time-stress correspondence and superposition of measurements obtained through dynamic mechanical tests. Predictions of material behavior using measurements based upon linear and nonlinear approaches are compared with experimental results obtained from traditional creep tests. Excellent agreement is shown for the nonlinear model.

INTRODUCTION

The authors present a method to describe the nonlinear viscoelastic behavior of polymer materials used in the fabrication of high-altitude scientific balloons. The primary objectives of this research include the experimental measurement of nonlinear viscoelastic properties using dynamic (oscillatory) mechanical methods and the development of nonlinear constitutive laws which employ these measurements. Three primary issues are examined: (1) the superposition of

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630

material properties measured at different conditions, such that measurements at one condition (for example, temperature or load) are equivalent to measurements at another condition but on a compressed or expanded time scale; (2) the transformation of measurements obtained in the frequency domain into material properties in the time domain, thus characterization is performed on a much shorter time scale; and, (3) the nonlinear characterization of material behavior examined in a manner analogous to modeling temperature-dependent behavior using time-temperature correspondence and linear superposition principles.

Many investigators characterize thin-film materials using linear viscoelastic techniques. Wilbeck[1] has developed a constitutive relationship for thin polyethylene films such as those used in high-altitude scientific balloons. Wilbeck predicts the state of stress in the film given strain and temperature histories; however, he shows that the properties of these materials exhibit nonlinear behavior due to the dependence of the behavior on the load history. In several studies, the efforts of Schapery[2-5] form the basis for the characterization of nonlinear behavior of viscoelastic materials. Smart and Williams[6] compare Schapery's theory to the modified superposition principle (MSP) in which the creep behavior is separated into time-dependent and stress-dependent components. Predictions using the MSP are poor; however, Schapery's theory is shown to accurately model the constitutive behavior. In another investigation, Dillard, et. al[7] compares Schapery's theory to several nonlinear viscoelastic models, including the MSP. Dillard's findings also suggest that Schapery's theory produces the most accurate results. Additionally, Dillard shows that Schapery's theory is appropriate for complex load histories.

A comparison of experimental results and predictions using Schapery's theory is presented by Crook[8]. Crook's research utilizes the experimental results from traditional creep tests as parameters for Schapery's theory. Crook accurately predicts the strain response of polycarbonate materials to a three-step stress input. In another study, Popelar, et. al[9] analyzes a comprehensive set of experimental data obtained from stress relaxation and constant strain-rate tests. Again, the relaxation data are utilized to develop the nonlinear constitutive model, and the nonlinear response is accurately characterized by Schapery's theory.

These earlier studies have shown that Schapery's theory is the most general and the most adaptable of the examined techniques. Herein, we describe a technique to predict nonlinear viscoelastic response based on Schapery's theory but extended to incorporate results derived from dynamic oscillatory tests. Strganac, et. al[10,11] and Letton, et. al[12] examine materials retrieved from NASA's Long Duration Exposure Facility (LDEF). The linear viscoelastic characteristics of these materials are determined using dynamic mechanical methods. Payne, et. al[13] describe the initial efforts to examine nonlinear behavior of materials using superposition of measurements obtained from dynamic mechanical methods.

THEORETICAL APPROACH

The constitutive properties of viscoelastic materials are dependent upon the rate at which the load or deformation occurs. Additionally, nonlinear viscoelastic behavior exists if the material properties are dependent upon the magnitude of stress or strain as well as the rate at which the load or deformation occurs. The theory developed by Schapery allows the material properties to be expressed in terms of either stress- or strain-dependent behavior. This theory is a modification of the single integral solution for linear viscoelasticity at a constant temperature.

For linear theory, the stress and strain are related by the Boltzmann superposition integral,

$$\varepsilon(t) = \int_0^t D(t-\tau)\frac{\partial\sigma}{\partial\tau}\,d\tau \tag{1}$$

where ε is strain, σ is stress, D(t) is the compliance, and *t* is time. A similar relation defines stress in terms of strain, but is not presented for brevity. By assuming a form of the compliance, such that $D(t) = D_O + \Delta D(t)$, Eq. (1) may be expressed as

$$\varepsilon(t) = D_o\,\sigma(t) + \int_0^t \Delta D(t-\tau)\frac{\partial\sigma}{\partial\tau}\,d\tau \tag{2}$$

where D_O is the initial component and ΔD is the transient component of the compliance.

Time-temperature correspondence principles[14] are typically employed to characterize the viscoelastic behavior of materials. The strength of the method is the superposition of data measured on different time scales - properties measured at one temperature are equivalent to those at a second temperature on a compressed or expanded time scale. Furthermore, transformations between measurements in the frequency domain and response in the time domain exist allowing for measurement of properties in the frequency domain and prediction of properties in the time domain. Thus, the properties measured at one temperature and frequency correspond to the properties at another temperature and frequency through a temperature-dependent shift factor

$$E^{\ddagger}(\omega, T_1) = E^{\ddagger}\left(\frac{\omega}{a_T}, T_2\right) \tag{3}$$

where $E^{\ddagger}$ represents either the dynamic modulus or a component of the dynamic modulus for the material, T is the temperature, and a_T is the temperature-dependent shift factor. This approach is similar to time-temperature correspondence principles in the time domain.

This shift factor is a measure of the temperature dependence of the relaxation process[12] for the material and is determined by the superposition of measurements at two distinct temperatures. The effect of a change in temperature is equivalent to measurements on a different frequency scale. This strategy allows the superposition of measurements taken over a range of temperatures at a specific frequency interval. A master curve of the dynamic modulus as a function of frequency is formed for a reference temperature.

Traditional creep measurements require significant test time to adequately characterize the material response for a large time interval. However, the transformation of the modulus measured in the frequency domain to the modulus in the time domain provides rapid characterization and, consequently, long experimentation is eliminated. A numerical transformation from the frequency domain to the time domain is described by Ninomiya and Ferry[14] for determining the relaxation modulus

$$E(t) = E'(\omega) - 0.40\, E''(.4\,\omega) + .014\, E''(10\,\omega)\Big|_{t=\frac{1}{\omega}} \tag{4}$$

where E' is the storage modulus, E" is the loss modulus, t is the relaxation time, and ω is the frequency.

We extend the approach of time-temperature superposition to time-stress superposition based upon the work of Schapery. Schapery modifies the constitutive equation to describe nonlinear viscoelastic responses by introducing a reduced time variable which is dependent upon the magnitude of the stress. If stress is the independent state variable, Schapery suggests the constitutive behavior may be described by

$$\varepsilon(t) = g_o D_o\, \sigma(t) + g_1 \int_0^t \Delta D(\Psi - \Psi') \frac{\partial g_2 \sigma}{\partial \tau} d\tau \tag{5}$$

where g_O, g_1, and g_2 are stress-dependent material properties, Ψ and Ψ' are reduced time variables defined by

$$\Psi = \Psi(t) = \int_0^t \frac{dt}{a_\sigma} \tag{6}$$

$$\Psi' = \Psi'(\tau) = \int_0^\tau \frac{dt}{a_\sigma} \tag{7}$$

and a_σ is the stress-dependent shift factor.

The parameters g_o, g_1, and g_2 are unique for each material. These parameters are determined experimentally if traditional creep tests are used; but, with our approach, these parameters are integrated within the experimental measurements. The creep compliance (or relaxation modulus) developed from the experimental measurements will contain the effects of these parameters.

As will be fully described in the subsequent section, the dynamic modulus is measured as a function of preload and frequency, and these measurements are used to describe nonlinear behavior resulting from the preload. Using a method analogous to time-temperature correspondence based on temperature-dependent shift factors, time-stress correspondence[13] is employed to identify stress-dependent shift factors. Thus, the properties measured at one preload and frequency correspond to the properties at another preload and frequency

$$E^{\ddagger}(\omega, \sigma_o) = E^{\ddagger}\left(\frac{\omega}{a_\sigma}, \sigma_{o_2}\right) \tag{8}$$

where $E^{\ddagger}$ represents either the dynamic modulus or a component of the dynamic modulus for the material, σ_o is the preload, and a_σ is the stress-dependent shift factor.

EXPERIMENTAL APPROACH

Dynamic oscillatory tests[10] are used to measure the viscoelastic response. Experimental measurements are conducted with the Rheometrics Solids Analyzer II. Measurements are obtained through a sweep of frequencies ($0.1 \leq \omega \leq 100$ rad / sec) at a constant temperature and preload. Depending upon the nature of the analysis, either the temperature or preload is changed and new measurements are obtained through a sweep of frequencies. Temperatures range from -150°C (-238°F) to the melt temperatures. Preloads may approach the yield of the material. This test strategy is illustrated in Figure 1.

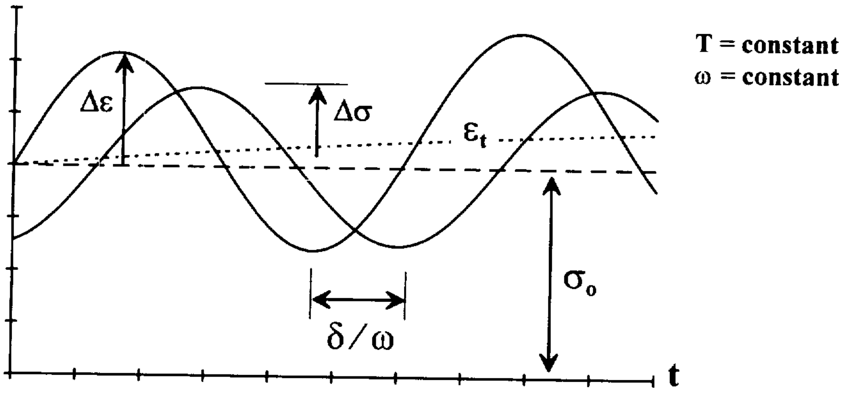

Figure 1. Force ($\Delta\sigma$) and damping (δ) is measured from an oscillatory deformation ($\Delta\varepsilon$) input. A constant preload (σ_o) is applied.

Two parameters are measured directly - the force due to an oscillatory deformation input and the phase lag between input and output. Material damping is measured as the phase lag , δ, between the measured force (stress) response output,

$$\sigma(t) = \sigma_o + \Delta\sigma\, e^{(i\omega t + \delta)} \tag{9}$$

and the oscillatory deformation (strain) input,

$$\varepsilon(t) = \varepsilon_t + \Delta\varepsilon\, e^{i\omega t} \tag{10}$$

In Eqs. (9) and (10), σ_o is the stress resulting from the preload which is held constant during the experiment, $\Delta\sigma$ is the measured stress response, ε_t is the strain (creep) which occurs during the dynamic oscillatory test, and $\Delta\varepsilon$ is the magnitude of the oscillatory strain input.

Typically, dynamic oscillatory tests are used to measure the linear viscoelastic properties of the test specimen. A dynamic modulus, E*, is derived from these measurements as

$$E^*(\omega,T) = \frac{\Delta\sigma\, e^{(i\omega t+\delta)}}{\Delta\varepsilon\, e^{i\omega t}} = |E|\, e^{\delta} = |E|\cos\delta + i\,|E|\sin\delta \qquad (11)$$

where $|E|\cos\delta$ is defined as the storage modulus, *E'*, and $|E|\sin\delta$ is defined as the loss modulus, *E''*.[14, 15]

However, in our studies, two sources of nonlinear behavior are identified with the dynamic oscillatory tests.[10,13] The first source is associated with the magnitude of the oscillatory strain, $\Delta\varepsilon$. The second source is associated with the magnitude of the preload, σ_o. Thus, the dynamic modulus should appear as

$$E^*(\omega,T,\sigma_o) = \frac{\sigma_o + \Delta\sigma\, e^{(i\omega t+\delta)}}{\varepsilon_t + \Delta\varepsilon\, e^{i\omega t}} \qquad (12)$$

A preload is used to maintain a tensile load on the specimen throughout the test; however, our results indicate a strong dependence of the measured response due to this preload. Typical measurements of the dynamic modulus are illustrated in Figure 2.

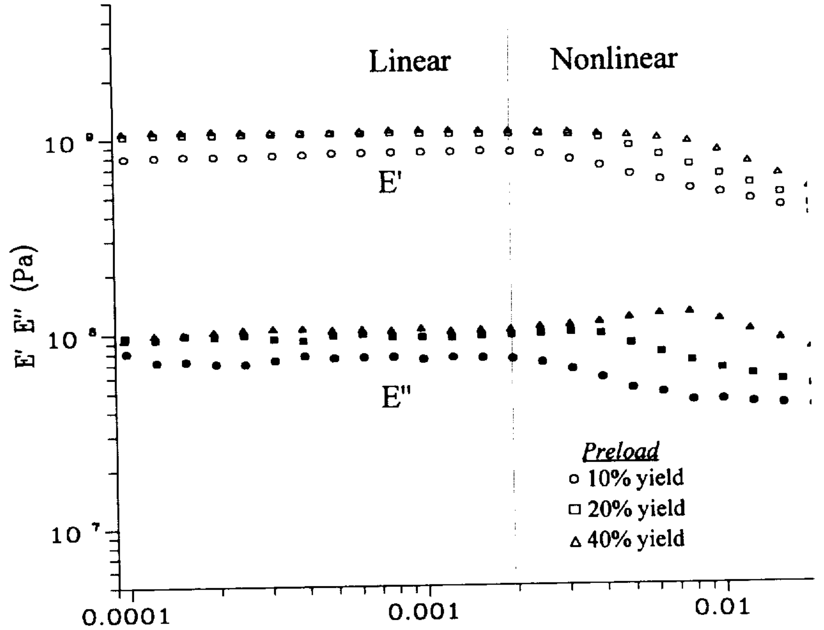

Figure 2. Measurements of the dynamic modulus are dependent upon the magnitude of the oscillatory deformation ($\Delta\varepsilon$) and preload (σ_o).

In our measurements of the linear viscoelastic behavior for the material we require that the measured properties are independent of the magnitude of both the oscillatory strain and the preload. In our measurements of the nonlinear viscoelastic behavior for the material we require that the measurements are dependent of only the magnitude of the preload. Thus, in either case, the magnitude of the oscillatory strain is selected such that measurements of the dynamic modulus are independent of the magnitude of oscillatory strain. Nonlinearities are due only to preload.

In the linear analysis we measure the dynamic modulus at different temperatures.12 In the nonlinear analysis we measure the dynamic modulus at different preloads (stresses).13 In both the linear analysis and nonlinear analysis the process of forming the master curve is identical. The experimental data consist of a collection of measurements obtained for the full range of test frequencies at a constant temperature (or preload for the nonlinear tests). This data establishes a family of curves relating the dynamic modulus to frequency. This family of temperature-dependent (or stress-dependent) curves are used to form a master curve which provides the dynamic modulus over a larger range of frequencies for a reference temperature (or reference preload). The temperature-dependent (or stress-dependent) shift factors are produced as a result of shifting and 'superposing' the measured data.12 The properties measured at one temperature (or preload) and frequency correspond to the properties at another temperature (or preload) and frequency through the shift factor. The effect of a change in temperature (or preload) is equivalent to measurements on a different frequency scale. We note that the master curve provides the dynamic modulus over a larger range of time when the results are appropriately transformed from the frequency domain to the time domain.

RESULTS

We examine results for two thin-film polyethylenes - Stratofilmr and Astrofilmr - which are used in the fabrication of high-altitude scientific balloons. Stratofilmr (SF-372) is a linear-low density polyethylene manufactured by Winzen International, Inc. Astrofilmr (AF-E2) is a low density polyethylene manufactured by Raven Industries. These films are produced through a blown-film extrusion process which induces a directionality in the properties of the material. Thus, tests are conducted in the 'machine' direction and the 'transverse' direction; tests are not conducted through the thickness. The nominal length of each test specimen is 2.54 cm (1.0 in), the nominal width of is .635 cm (0.25 in), and the nominal film thickness is .0201 mm (0.0008 in).

Linear viscoelastic characteristics are measured for SF-372 and AF-E2 at temperatures ranging from -150°C (-238°F) to the melt temperature of the specimen. For the linear analysis, the dynamic modulus is dependent upon the frequency and temperature. Although a preload is used to maintain a tensile load on the specimen, in our measurements of the linear behavior we require that the measurements are independent of the preload.

The dynamic modulus for SF-372 and associated temperature-dependent shift factors are presented in Figure 3. The dynamic modulus for AF-E2 and associated temperature-dependent shift factors are presented in Figure 4.

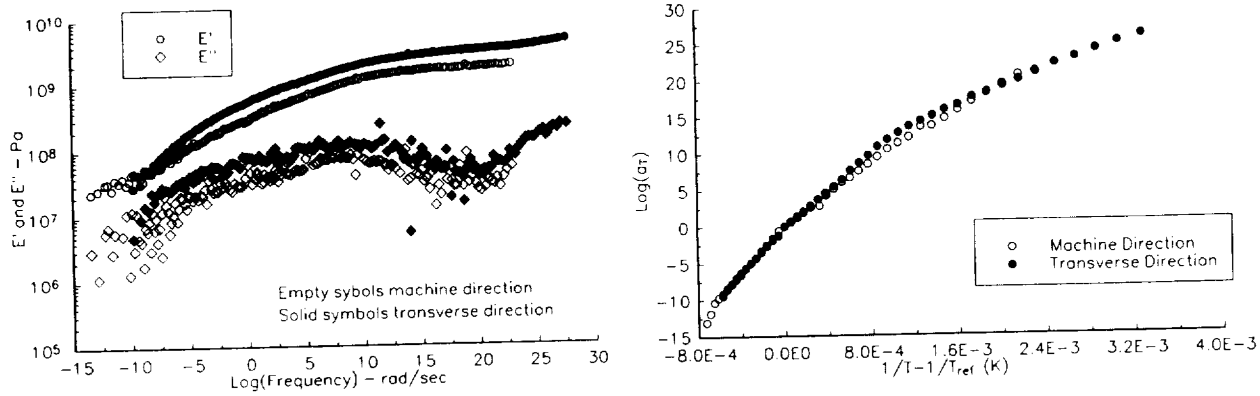

Figure 3. The master curve for SF-372, derived from temperature-frequency measurements of the dynamic modulus, is shown in the left view. The temperature dependent shift factors are presented in the right view (T_{ref} = 20°C (68°F)).

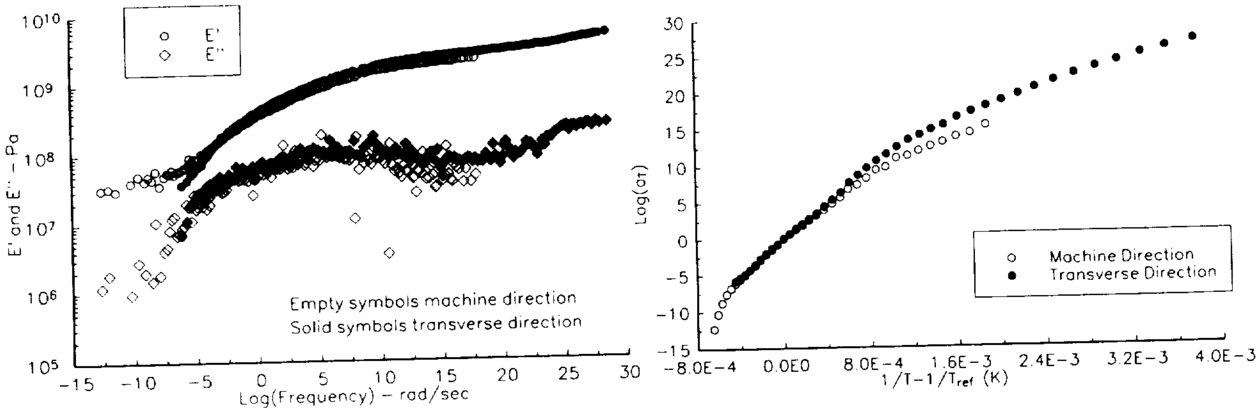

Figure 4. The master curve for AF-E2, derived from temperature-frequency measurements of the dynamic modulus, is shown in the left view. The temperature dependent shift factors are presented in the right view (T_{ref} = 20°C (68°F)).

Although the viscoelastic properties for both materials are measured under identical conditions (frequency and temperature range), the results presented in the above figures suggest otherwise. Two reasons for this aberration exist: first, the measured data does not behave in a linear manner (thus, the data cannot be superposed) at the extremely low temperatures (which relates to behavior at high frequency or short time scales); and, second, the melt temperature is not uniform for all specimens.

The relaxation modulus measured for SF-372 and AF-E2 is presented in Figure 5. These measured values of the dynamic modulus and the method of Ninomiya and Ferry are used to derive the relaxation modulus. Since measurements of the dynamic modulus are used in the derivation, differences in the range of time for the presented data exist for the same reasons as described in the preceding paragraph.

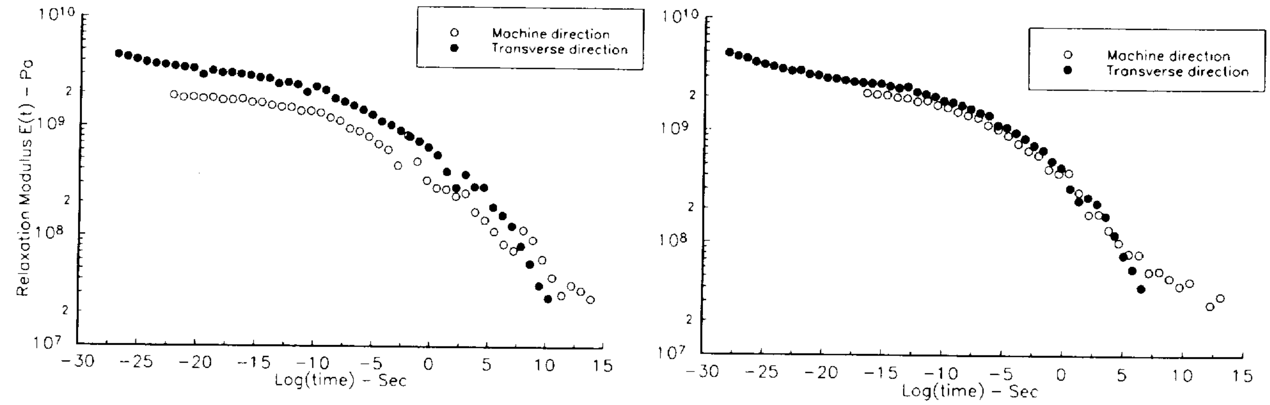

Figure 5. The relaxation modulus for SF-372 is shown in the left view. The relaxation modulus for AF-E2 is shown in the right view. The modulus is derived from measurements of the dynamic modulus (refer to Figures 3 and 4). T_{ref} = 20°C (68°F).

Creep response is predicted using the creep compliance derived from the dynamic oscillatory measurements. These predictions are compared with the creep response measured in traditional creep tests. Figure 6 provides a comparison of predictions and measurements for SF-372 and AF-E2.

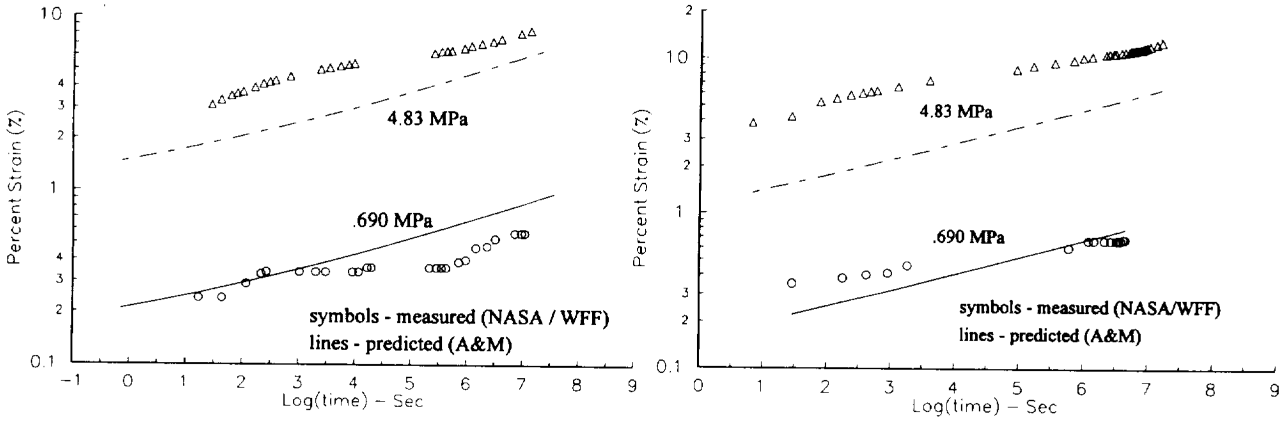

Figure 6. Creep is predicted using the compliance derived from measurements of the dynamic modulus. Comparisons are made with traditional creep measurements for SF-372 (left view) and AF-E2 (right view). The specimens are oriented in the machine direction. Measured creep data provided by NASA-GSFC/WFF.

Predictions for two preloads are shown in each figure. As expected due to the nonlinear effects induced by the large stresses due to preload, the predictions clearly deteriorate for both SF-372 and AF-E2 as the preload increases. Consequently, stress-dependent contributions must be included in the characterization of viscoelastic properties for materials exposed to higher stresses.

The yield stress for these materials is highly dependent upon the temperature.[13] The yield stress for these materials is approximately 40 MPa (5800 psi) at T = -100° C (-148° F) and 9 MPa (1300 psi) at T = 23° C (73.4° F) (data courtesy of Winzen International, Inc., these measurements are determined from a 0.2% strain offset on the stress-strain curve). Thus, a preload which is 25% of the yield stress at T= -100° C (-148°F) exceeds the yield stress at room temperature. We introduce a convention in which we refer to the preload as a percentage of the yield stress; and, therefore, tests performed at different temperatures will be compared with preloads at identical percents of yield stress. Stress-dependent shift factors are also developed using this convention.

A limiting stress is noted in Figure 7, where the storage modulus is presented as a function of preload and frequency. At a preload of approximately 35% yield stress, a drop in E' is observed. This material 'stiffening' is not yet fully understood; consequently, the preload is limited to 30% of the yield stress to avoid complications associated with this region.

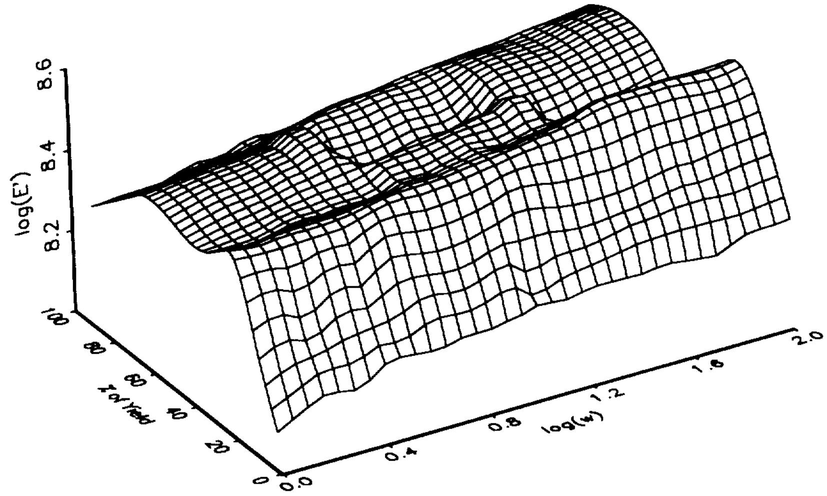

Figure 7. Viscoelastic properties are measured at several preloads and frequencies. The storage modulus is shown as a function of preload (measured as percent yield) and frequency (T_{ref} = 20°C (68°F)).

Nonlinear viscoelastic characteristics are measured for SF-372 for preloads ranging from 2% to 20% of the yield stress. For the nonlinear analysis, the dynamic modulus is dependent upon preload, as well as the frequency and temperature. In these measurements of nonlinear viscoelastic behavior we require that the measurements are dependent upon the magnitude of the preload and measurements are performed at a constant temperature of 23° C (73.4° F).

The results of a series of dynamic oscillatory tests performed at several preloads below 30% of the yield stress are shown in Figure 8. The effect of the stress level on the response of the material is evident. On the basis of time-stress superposition, the data are shifted to obtain the master curve and the corresponding stress-dependent shift factors are derived. The "linear" behavior of the results establishes confidence in the test and analysis procedure.

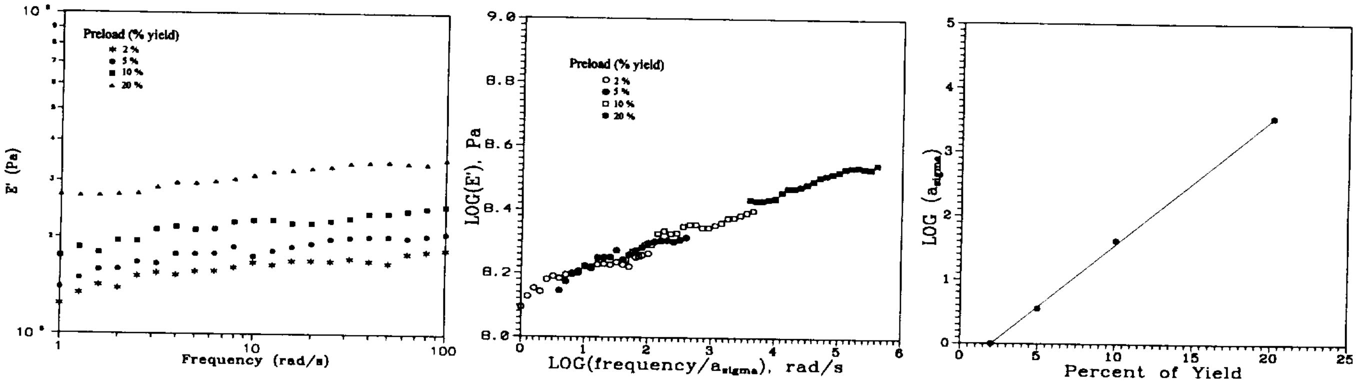

Figure 8. Stress-dependent measurements are obtained for preloads below 30% yield. The master curve of the storage modulus E' is shown (center view) for a reference preload of 2% yield. Stress-dependent shift factors provide correspondence between different stress levels.

Measurements obtained from dynamic oscillatory tests are compared to measurements obtained from traditional creep tests. A comparison of the creep compliance is presented in Figure 9. The reference stress (preload) is 20% of the yield stress at room temperature. For the dynamic oscillatory tests, the creep compliance is derived from the stress relaxation modulus found using measurements of the dynamic modulus and the transformation of Ninomiya and Ferry. For the comparison data, the creep compliance is derived from traditional creep measurements provided by Winzen International, Inc.

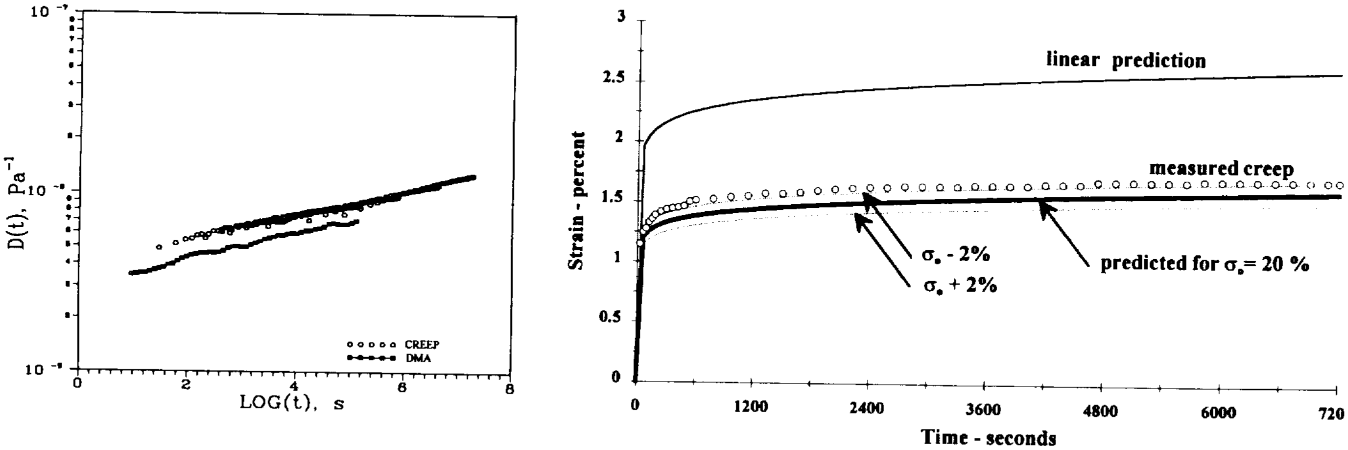

Figure 9. Compliance - derived from dynamic (oscillatory) measurements - is compared to compliance data derived from creep measurements (left view). Creep - predicted using the stress-dependent measurements - is compared with creep measurements (right view). Measured creep data provided by Winzen International, Inc.

The creep compliance is fit to a function of the form $D(t) = D_0 + \Delta D(t)$, and this function is used to predict creep response. The difference between the two sets of data may be attributed to very small differences in the measured thickness of the test specimen and very small differences in the stress-dependent shift factors. Creep response, predicted using the nonlinear stress-dependent behavior due to preload (σ_o), is shown in Figure 9. Comparisons are made with creep measurements provided by Winzen International, Inc. Creep response is predicted for the linear case - the sensitivity to preload is evident. The material is SF-372 (machine direction), the reference stress is 2.07 MPa (300 psi), and the reference temperature is 20°C (68° F). The results from the dynamic oscillatory tests accurately predict the trends of the measured data; however, the predictions are slightly underestimated. The difference between the two sets of data reflects the difference in the creep compliance data. The predictions are sensitive to the stress-dependent shift factors.

CONCLUSIONS

Dynamic (oscillatory) mechanical tests are used as a basis to characterize the linear (temperature-dependent) and nonlinear (stress-dependent) viscoelastic behavior of thin polyethylene materials. Nonlinear stress-dependent behavior is characterized using correspondence and superposition principles. Dynamic oscillatory test measurements produce predictions consistent with the results of traditional creep tests. In addition, the effective transformation of measurements obtained in the frequency domain to response in the time domain allows for the nonlinear characterization of polymer materials without an extended test program. Results show that the response of the materials examined is best characterized by nonlinear viscoelastic methods.

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