Strain Sensitive Response of Filled Elastomers

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The strain dependence of the elastic and the anelastic behavior of filled elastomers is discussed in the light of recent experiments on carbon-black filled rubber as well as on sodium chloride filled polyurethane. The latter experiments suggest that the apparent creep of filled elastomers is the manifestation of the gradual change of the elastic moduli resulting from the loss with strain of effective filler matrix interaction, rather than a truly viscoelastic phenomenon.

I. Introduction

In recent years linear viscoelastic analysis of an assumedly homogeneous, isotropic and thermorheologically simple medium has been accepted as a standard procedure for evaluating the structural integrity of solid-propellant rocket motors.[1] Although it is generally recognized that, on the microscale, the solid propellant is neither continuous nor homogeneous, the previously mentioned idealization is assumed to be "permissible with important exceptions, such as stress induced anisotropy and fracture origins," on the basis of the purported similarity of the effect of microstructure in such materials with those in "concrete, asphalt or for that matter metals" (Ref. 1, p. 785). Coupling this assumption with the desire to introduce the "least amount of analytical complexity," the way is opened for the application of the classical methods of linear viscoelastic analysis using the various well established procedures of material characterization and the "correspondence principle" between elastic and linear viscoelastic solutions of boundary value problems, the implicit assumption being that the relevant range of structural performance coincides, for all practical purposes, with the range of infinitesimal or, at least, of very small strains. Once these premises of the structural integrity analysis have been accepted, the further development is exclusively concerned with increasingly sophisticated analytical methods within the given framework, with their computerization and with increasingly elaborate generalizations.

Unfortunately, the assumptions which have produced an accessible analytical theory have, at the same time, dissociated the analytical results from reality, simply because they have become irrelevant to the principal engineering purpose of the analysis, which is a realistic evaluation of structural integrity. The main reason for this dissociation is the fact that the highly filled elastomeric propellant can be represented by the linear viscoelastic medium only within the range of infinitesimal strains, which is not the range that is of particular relevance in structural integrity evaluation. The structurally relevant strain ranges are those of *a*) short-time straining with strain rates of the order of up to 10 in./in./sec during firing and flight, with maximum strains at the inner bore of the order of 10 to 60% reached in tens of milliseconds, *b*) of thermal strain cycling at rates of the order of 10^{-3} to 10^{-5} in./in./sec and maximum strains in the one to several percent range, and *c*) of long-time storage strains of a similar order of magnitude but considerably lower strain rates and material degradation.

Although in materials other than solid propellants, the structural integrity analysis of which requires the consideration of small or moderate strains, this analysis is usually based on the approximation of the deformed by the undeformed configuration and thus on the assumption of infinitesimal strains, this assumption cannot be justified for the highly filled elastomeric solid-propellant grains because of the very pronounced strain dependence of their mechanical response. However, it is less the geometric effect of the deformation of the configuration itself (finite strain) which has to be considered in the integrity analysis, than the change of material response as a function of the strain.

This strain effect is rather well known in carbon-black filled natural and synthetic rubbers. When a specimen has been strained in tension, the subsequent stress strain diagram is substantially below that of initial straining ("Mullins effect").[2] In forced vibrations in tension-compression as well as in shear, the dynamic modulus, which is a function of the filler content, decreases with increasing strain amplitude similarly to the way it decreases with decreasing frequency. The specific damping which also increases with increasing filler content, first increases with increasing strain amplitude until it reaches a peak at about the location of the inflection point of the modulus curve, from which it then decreases[3] (Fig. 1 and Fig. 2). The strain amplitude at which this strain effect becomes significant is consistently low and located at about 0.1%. At amplitudes of between 1% and 2% strain the elastic moduli of the highly filled compounds are reduced to about one-half of their initial values, while the specific damping attains its peak. The phenomenon has been attributed either to vacuole formation in the matrix or to the destruction with strain of the rubber filler adhesion, or to the existence of some molecular stress relaxation mechanism at the interface between filler and matrix to accommodate the relative motion of the rubber with respect to the filler surface,[4] since vacuole formation in rubber can usually not be observed optically at strain amplitudes lower than about 10%.

If the pronounced strain dependence of the viscoelastic parameters is observed when the filler is chemically interacting with the matrix and therefore "active," such as carbon black, it must obviously be expected to arise in a material with an inert ("nonactive") filler because of the dependence, in this case, of the filler matrix interaction on interface forces alone. However, observation of this effect requires rheological tests of specimens in which filler content and filler particle size and, possibly, particle shape are systematically varied. It is the series of creep tests performed by TNO Delft[5] as well as the high strain rate tensile tests performed at Columbia University on specimens provided by TNO, Delft,[6] which provide experimental confirmation of the strain dependence of the rheological parameters of the sodium chloride filled polyurethane rubbers used as a model substance of a solid propellant.

The tensile creep tests have demonstrated[5] that creep is closely related to filler content and does not exist or is in-

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Received March 3, 1969; revision received September 17, 1969.

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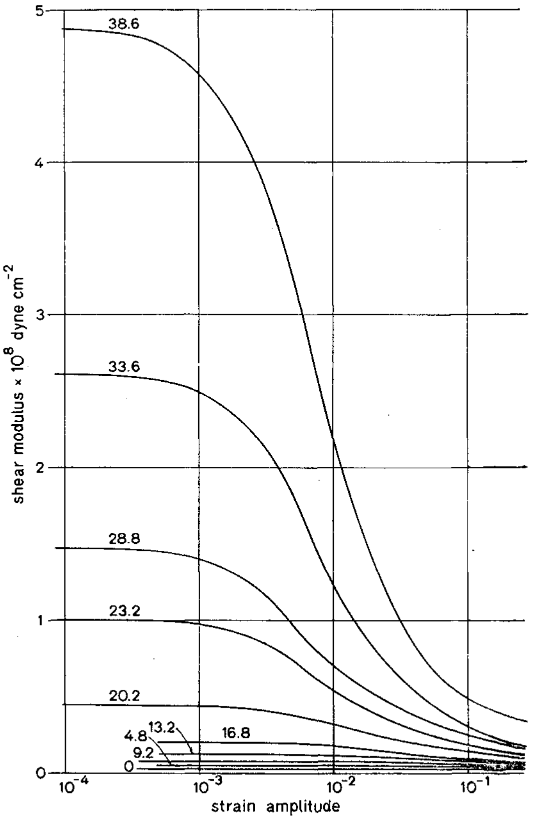

Fig. 1 Strain amplitude dependence of in phase shear modulus G_1 of carbon-black filled butyl rubber at 0.1 cps and different filler content.[3]

significant in the unfilled polyurethane matrix (Fig. 3). It is the more pronounced the higher the filler content; it also is affected significantly by filler size: a decrease in particle size from 200 to 300μm to 30 to 40μm produces a delay of the creep by a factor of 10^3 in time (Fig. 4). Thus the shape of the creep curve at a given stress level depends on filler concentration, its location on the time-scale on particle size as well as on particle shape. The effect of the stress level on creep reflects its effect on the process of gradual dewetting of which creep is the phenomenological manifestation. The creep rate increases, therefore, rapidly with increasing stress (Fig. 5).

The results of high strain rate tension tests[6] support the conclusion that the apparent viscoelasticity of the filled polyurethane is the reflection of the time dependence of the dewetting process. The strain rate effect is much more significant with respect to the peak stress (Fig. 6), the location and height of which is related to filler content and dewetting process, than with respect to the stress-strain diagram before the peak, which would be significantly affected by a truly viscoelastic response of the medium.

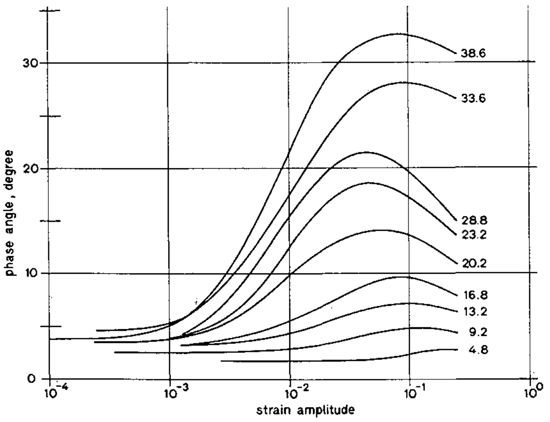

Fig. 2 Strain amplitude dependence of phase angle of carbon-black filled butyl rubber at 0.1 cps and different filler content.[3]

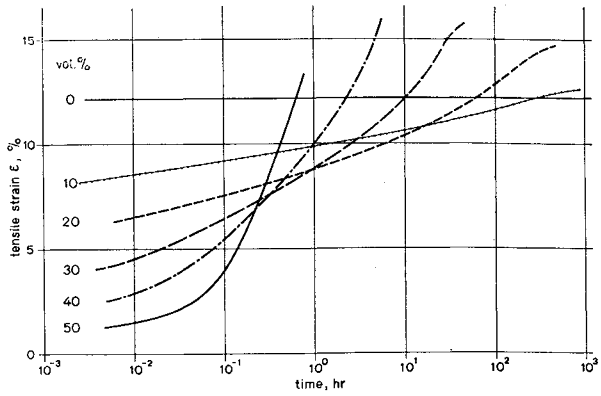

Fig. 3 Tensile creep under a tensile stress of 3 kg/cm² of polyurethane rubber filled with various percentages of sodium chloride.[5]

Although the strain dependence of the true viscoelastic response of elastomers has been discussed in the literature, and a nonlinear constitutive equation for uniaxial tension was proposed by Guth[7] in the form of the relaxation equation,

$$\sigma(\epsilon,t) = H(\epsilon) \int_0^t E(t-\theta) \frac{d\epsilon}{d\theta} d\theta \qquad (1.1)$$

the function $H(\epsilon)$ of strain was assumed to express the *geometric nonlinearity* arising from finite strains, under the expedient assumption that the effects of strain and time are separable. Although this assumption has been shown by experiments to provide a fair approximation of the real behavior, recent experiments have shown[8] that the strain effects on the relaxation modulus considerably exceed those due to finite strain alone.

II. Characterization of Filled Elastomer

The established methods of linear viscoelastic characterization of solid-propellant materials are of reasonable validity in the range of infinitesimal strains and under the usual assumption of thermorheologically simple behavior without thermomechanical coupling. Only under such conditions are the relaxation moduli in uni-axial tension and in shear $[E(t)$ and $G(t)]$ simply interrelated with the respective storage and loss moduli $E_1(\omega)$, $E_2(\omega)$ and $G_1(\omega)$, $G^2(\omega)$ with the aid of the basic theorems of linear transformations. Because of the validity of the elastic viscoelastic analogy, no particular difficulty arises in correlating one-dimensional with three-dimensional characterization.

Experiments under small but repeated cyclic strain have not only shown the practical significance of thermomechanical coupling which, by producing internal heating interferes with the usually assumed viscoelastic convertibility of relaxation and dynamic moduli; they also disclose that these moduli obtained at infinitesimal strains or strain amplitudes can, at best, be considered as limiting functions at zero strain ($\epsilon \rightarrow 0$) of more general strain dependent moduli $E(t,\epsilon)$, $G(t,\epsilon)$ and $E(\omega,\epsilon)$, $G(\omega,\epsilon)$ which, because of this dependence on strain resulting from the presence of a filler, are obviously no longer interconvertible.

The resulting nonlinearity of the constitutive equations also invalidates the elastic viscoelastic analogy and the simple correlation between one-dimensional and three-dimensional material characterization of elastic and thus also of linear viscoelastic media. The coincidence of the directions of principal shear stress and shear strain or strain

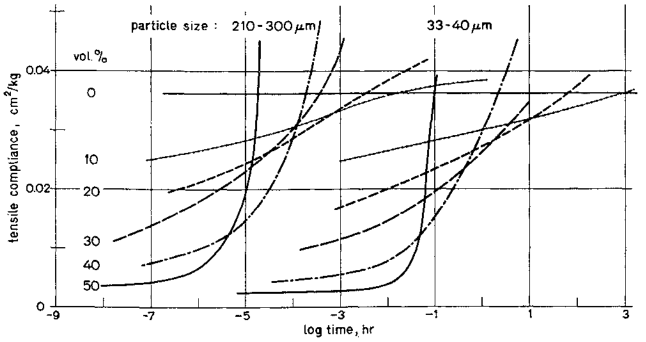

Fig. 4 Tensile creep compliance under a stress of 6 kg/cm² of polyurethane rubber filled with various percentages of sodium chloride of two different particle sizes.[5]

increment (St. Venant's postulate), underlies the theories of plastic and of nonlinear viscous media and leads to three-dimensional characterization expressed in terms of invariant constitutive equations involving only the second invariants of the stress- and strain- or strain-increment tensors. Although it might be reasonable and expedient to base the previously mentioned correlation on this coincidence, no experimental evidence exists to support such an approach.

Existing observations[2-6] of the strain dependence of viscoelastic material parameters are concerned exclusively with one-dimensional (longitudinal) states of stress such as tensile creep of salt filled polyurethane and repeated cyclic strain of carbon-black filled rubbers. Although the filler-matrix bonding is predominantly "mechanical" (whereas strongly dependent on surface effects that cannot be classified as "mechanical") in the first material and predominantly chemical in the second, the results, in both cases, reflect the gradual strain and time-dependent breakdown of filler-matrix interaction. The initial elastic moduli (or compliances) in the unstrained (or infinititesimally strained) condition of the material, created by the full filler-matrix interaction are, therefore, gradually reduced (in the case of compliances increased) with increasing time or strain, or with increasing strain amplitude, towards the moduli or compliances of the unfilled matrix.

As mentioned before, such breakdown at small strains may be the result of molecular force relaxation close to the filler-matrix interface or of bond stress relaxation at the interface or of microvacuole formation in the matrix close to the interface, without observable volume expansion. At moderate strains macrovacuoles form in the matrix close to the filler surface, preferentially near larger particles, a process that is followed by their coalescence and the formation of voids surrounding the particles, producing "dewetting."

It has been shown in tensile tests that the start of observable dewetting coincides with the start of measurable dilatation[9]; this phenomenon has been referred to as "dilatation failure." It is being suggested, on the basis of the observations presented in Figs. 3 and 4, that the quasi-stationary viscoelastic creep that proceeds at small or moderate strain rates before the stage of measurable dilatation and rapid creep is attained, reflects the predewetting stage of gradual deterioration of filler-matrix interaction rather than a genuine viscoelastic deformation of the matrix. It is not unreasonable to expect that such a process involving molecular phenomenon be governed by reaction rate theory, although the physical constants will necessarily differ in magnitude from those governing true viscoelastic deformation.

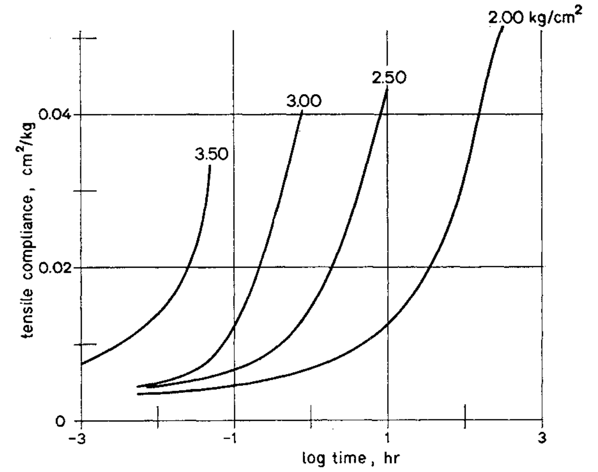

Fig. 5 Tensile creep compliance of polyurethane rubber filled with 50 volumes percent of sodium chloride particles of size 210–300 µm under different applied stress levels.[5]

The deterioration of filler-matrix interaction resulting from uniaxial straining can, in first approximation, be related to a reduction, with increasing strain, of the "effective" volume concentration c of the filler that produces the composite modulus, without attempting to specify the momentary physical nature of the gradually changing breakdown process. Thus, the change with tensile strain ϵ of the initial relaxation modulus $E[c(\epsilon),t]$ from $E_o(t) = E(c_o,t)$, where $c = c_o$ at $\epsilon = 0$, to E at $\epsilon \rightarrow \infty$, $c \rightarrow 0$ can be expressed in the form

$$\partial E/\partial \epsilon = (\partial E/\partial c)\cdot dc/d\epsilon \qquad (2.1)$$

The function $E(c)$ can be identified with one of the established equations for the effect of high filler concentration on the elastic moduli of the unstrained medium, so that the change of "effective" filler concentration with strain is associated with reduction of filler particle "effectiveness" by interface stress relaxation or microvacuole formation.

Using an equation of the form[10]

$$E = E_\infty(1 - \alpha c)^{-n} \qquad (2.2)$$

where α and n are experimental constants, for the determination of $\partial E/\partial c \sim (dE/dc)$ the relation is obtained

$$dE/dc = n\alpha(1 - \alpha c)^{-(n+1)}E_\infty \qquad (2.3)$$

The decrease with strain of the effective volume concentration of filler particles is the decrease of the volume fraction of particles not affected by the breakdown process, if it is assumed that the particles are roughly of uniform size. Intro-

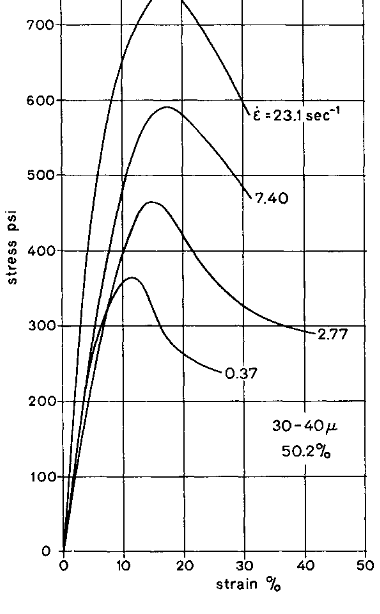

Fig. 6 Stress strain relations at different constant strain rates of polyurethane rubber filled with 50 volume percent of sodium chloride particles of size 30–40 µm.[6]

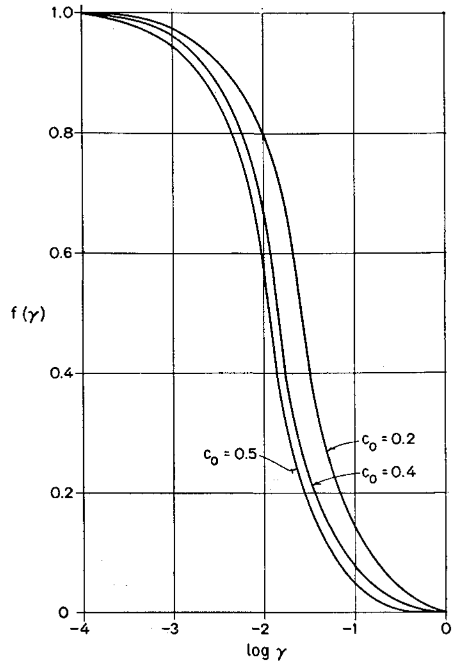

Fig. 7 **Function $f(\gamma)$ expressing reduction of shear modulus with strain for different filler contents according to Eq. (2.11).**

ducing the simple rate process assumption according to which the rate of decrease with strain of the effective filler concentration is roughly proportional to the volume fraction of "effective" particles

$$-dc/d\epsilon = kc \tag{2.4}$$

it follows that

$$c = c_o e^{-k\epsilon} \tag{2.5}$$

where k is an empirical constant. Hence

$$d\epsilon/dt = (\partial\epsilon/\partial c)(dc/dt) = -(1/k)(d/dt)\ \ln c \tag{2.6}$$

which relates the rate of decrease of "effective" filler concentration to the creep rate.

Substituting Eqs. (2.3) and (2.4) into Eq. (2.1) produces

$$dE/d\epsilon = -[n\alpha k c_o E_\infty/(1 - \alpha c_o e^{-k\epsilon})^{(n+1)}]e^{-k\epsilon} \tag{2.7}$$

while from Eq. (2.2)

$$E(\epsilon) = E_\infty(1 - \alpha c_o e^{-k\epsilon})^{-n} \tag{2.8}$$

and, therefore

$$E(\epsilon) = E_o[(1 - \alpha c_o)/(1 - \alpha c_o e^{-k\epsilon})]^n \tag{2.9}$$

The parameters $\alpha = 1.2$ and $n = 2.5$ have been found to reproduce fairly well experimental results for sodium chloride filled polyurethane with c between $0 < c < 0.50$.[10] The parameter k cannot be directly evaluated since experimental functions $E(\epsilon)$ for filled polyurethanes are not available. Using observations on carbon-black filled rubbers from which it can be deduced that at a strain of 0.01 the modulus for a highly filled rubber is reduced to about $E = 0.5E_o$ it follows from Eq. (2.8) that $k \sim 15$ would represent a realistic value for such materials and, thus, probably a low estimate of k for nonactive fillers of larger particles size like sodium chloride.

The location ϵ' of the inflection point of $E(\epsilon)$ is obtained from Eq. (2.7) by setting $d^2E/d\epsilon^2 = 0$

$$(n + 2)\alpha c_o e^{-k\epsilon'} = 1 \text{ or } \epsilon' = (1/k)\ \ln[(n + 2)\alpha c_o] \tag{2.10}$$

Using in first approximation equations of similar form for the strain dependence of the shear modulus G the normalized ratio is

$$(G - G_\infty)/(G_o - G_\infty) = [(1 - \alpha c_o e^{-k\gamma})^{-n} - 1]/ [(1 - \alpha c_o)^{-n} - 1] = f(\gamma) \tag{2.11}$$

and has been plotted in Fig. 7 for $\alpha = 1.2$, $n = 2.5$ and $k = 15$ and various filler fractions c_o.

The function $f(\gamma)$ can be empirically approximated by the simpler form

$$f(\gamma) \sim f_1(\gamma) = \exp[-(\gamma/\gamma_o)^\beta] \tag{2.12}$$

with filler dependent parameters $\gamma_o(c_o)$ and $\beta(c_o)$. The dependence of these parameters on filler concentration is shown in Fig. 8. Therefore

$$\ln[-\ln f_1(\gamma)] = \beta \ln(\gamma/\gamma_o) \tag{2.12a}$$

which implies that a characteristic form of probability function (distribution of smallest extremes) describes the change of modulus with strain from G_o to G_∞ fairly well, an implication that is reasonable since the process of decrease of effective concentration of filler with strain is a statistical process in which the probability of encountering "effective" filler particles decreases with strain. Loss of "effective" filler particles with strain expressed by a reduction of modulus represents a loss of stored strain energy in the part of the matrix surrounding those particles; it will, therefore, appear as a "damping" under cyclic strain, with a maximum at the strain amplitude at which the modulus reduction is largest.

Combining the strain dependent elastic modulus

$$G = G_\infty + (G_o - G_\infty)f_1(\gamma) \tag{2.13}$$

associated with a certain experimental time scale with various types of viscous response, differential equations for strain sensitive viscoelastic behavior can be obtained. At zero strain $f_1(\gamma) = 1$ and therefore $G = G_o$, at infinite strain $G = G_\infty$, both of which are functions of time or of frequency.

The response of an elastic material of shear modulus given by Eq. (2.13) under the assumption of small strain is of the form

$$\tau = \gamma G(\gamma) = \gamma G_\infty + (G_o - G_\infty)\gamma f_1(\gamma) \tag{2.14}$$

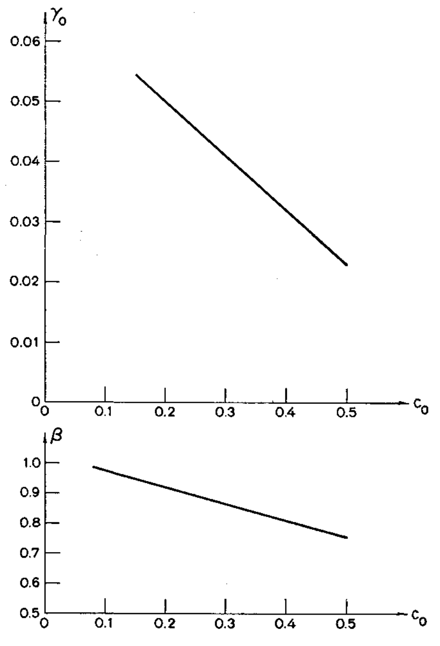

Fig. 8 **Dependence on filler content of parameter γ_o and β in Eq. (2.12).**

or with $f_1(\gamma)$ according to Eq. (2.12)

$$\tau = \gamma G_\infty + (G_o - G_\infty)\gamma \cdot \exp[-(\gamma/\gamma_o)^\beta] \qquad (2.15)$$

Under the assumption that $G_\infty \ll G_o$

$$\tau \doteq G_o\gamma \exp[-(\gamma/\gamma_o)^\beta] \qquad (2.16)$$

This stress strain relation has a maximum at

$$\gamma = \gamma_o(1/\beta)^{1/\beta} > \gamma_o \qquad (2.17)$$

which for $\beta = 0.75$, is roughly at $1.45\gamma_o$, from where it decreases asymptotically towards zero. The form of Eq. (2.16) shown in Fig. 9 is characteristic of those observed for filled elastomers; the parameters β and γ_o might therefore be estimated from the observed strain at peak stress and the magnitude of the stress, since from Eq. (2.16) the peak stress is related to β and γ by the expression

$$\tau_{\max}/G_o\gamma = \exp(-1/\beta) \qquad (2.18)$$

Thus, for instance, γ at $\tau_{\max}$ is about 0.10 to 0.15 and $\alpha \sim 0.75$; the ratio $(\tau_{\max}/G_o\gamma) \sim 0.027$ to 0.04 which is fairly close to observed values.

The order of magnitude of the correction of Eqs. (2.16) to (2.18) for finite strain is obtained by assuming the uniaxial traction strain relation associated with the simple incompressible elastic strain energy potential $W = \frac{1}{2}G(I_1 - 3)$

$$t = G(\lambda)(\lambda - \lambda^{-2}) \qquad (2.19)$$

where $G(\lambda) = \frac{1}{3}E(\lambda)$ is introduced in the approximate form of

$$t = E_o \exp[-(\lambda^2 - 1)/(\lambda_o^2 - 1)\ ](\lambda - \lambda^{-2}) \qquad (2.20)$$

the stress on the deformed section $\sigma = \lambda t$. The strain at which either t or σ attain a maximum can be obtained by solving the equation $dt/d\lambda = 0$ (or $d\sigma/d\lambda = 0$) by trial and error, for different values of λ_o and β

$$(d/d\lambda)[(\lambda^2 - 1)/(\lambda_o^2 - 1)]^\beta = (\lambda^3 + 2)/(\lambda^2 - 1) \qquad (2.21)$$

Experimental evidence for the determination of the combined strain and time-dependent viscoelastic response is not available. One approximate assumption may be that of separability of the time and the strain dependence; it is equivalent to disregarding the effect of strain on the difference between the relaxed and unrelaxed modulus. Therefore, in the model of a standard solid only the quasi static elastic modulus may be considered as a function of strain, whereas the other parameters are strain insensitive.

A modified Voigt body is obtained by adding a velocity term with strain independent parameter to Eq. (2.16)

$$\tau \doteq G_o\gamma \exp[-(\gamma/\gamma_o)^\beta] + \lambda\dot{\gamma} \qquad (2.22)$$

which for τ = const produces the differential equation for the creep rate

$$\theta\dot{\gamma} = k - \gamma \exp[-(\gamma/\gamma_o)^\beta] \qquad (2.23)$$

where $k = \tau/G_o$. The "creep rate" decreases more slowly than in the case of the strain independent Voigt body and does not approach zero but a constant value determined by the applied stress and the coefficient of viscosity. This trend is confirmed by Fig. 5.

III. The Standard Solid

The differential equation of the Standard Solid is obtained in the conventional manner with $G(\gamma)$ according to Eq. (2.12) representing the quasi static modulus of the spring, G_2 and η_2 specifying the parameters of the strain insensitive Maxwell element which are coupled is parallel. Hence

$$\dot{\gamma}_1 = \dot{\tau}_1/G(\gamma); \quad \dot{\gamma}_2 = \dot{\tau}_2/G_2 + \tau_2/\eta_2 \qquad (3.1)$$

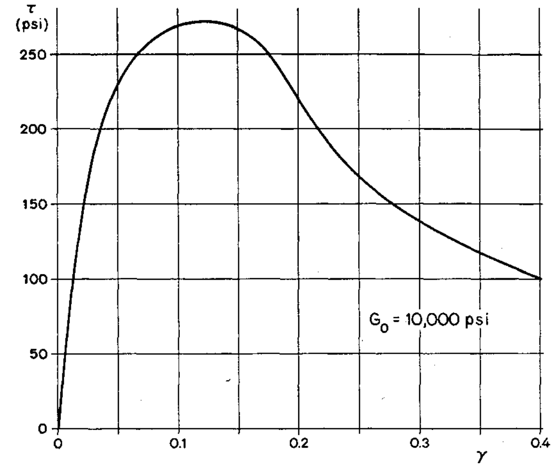

Fig. 9 Stress strain relation of elastic material with strain dependent shear modulus according to Eq. (2.14).

where

$$\dot{\gamma}_1 = \gamma_2 = \dot{\gamma} \text{ and } \tau_1 + \tau_2 = \tau \text{ or } \tau_2 = \tau - \tau_1 \qquad (3.2)$$

and, therefore

$$\dot{\tau}_1 G^{-1}(\gamma) = G_2^{-1}(\dot{\tau} - \dot{\tau}_1) + \eta_2^{-1}(\tau - \tau_1) \qquad (3.3)$$

or

$$\dot{\tau}_1[G^{-1}(\gamma) + G_2^{-1}] + \tau_1\eta_2^{-1} = G_2^{-1}\dot{\tau} + \eta_2^{-1}\tau \qquad (3.4)$$

Introducing the first Eq. (3.1) into Eq. (3.4) produces the differential equation of the Standard Solid with strain dependent parameters

$$\tau + \theta_2\dot{\tau} = G(\gamma)[\gamma + \dot{\gamma}\theta(\gamma)] \qquad (3.5)$$

where

$$\theta(\gamma) = \theta_2[1 + G_2/G(\gamma)] > \theta_2 \qquad (3.6)$$

and, therefore

$$\theta_2/\theta(\gamma) = G(\gamma)/[G(\gamma) + G_2] = G_R(\gamma)/G_U(\gamma) \text{ since } G_2 = G_U - G_R \qquad (3.7)$$

since $G_2 = G_U - G_R$ where G_R and G_U denote, respectively, the relaxed and the unrelaxed shear modulus at a specified strain γ.

The linear differential equation of stress-relaxation obtained by setting in Eq. (3.5) the initial strain $\gamma = \gamma_i$ at $t > 0$ and, therefore $\dot{\gamma} = 0$ is for any value γ_o identical with that of the conventional standard solid

$$\tau + \theta_2\dot{\tau} = G(\gamma_i)\gamma_i \qquad (3.8)$$

since for a specified strain γ_i the right side is a constant and θ_2 is strain independent. The form of Eq. (3.8) suggests the time-and-strain dependent relaxation modulus $G(\gamma,t)$ schematically presented by the surface shown in Fig. 10.

The differential equation of "strain retardation" or "creep," however, obtained from Eq. (3.5) by imposing the constant stress τ_o at $t \geqq 0$

$$G(\gamma)\ [\gamma + \dot{\gamma}\theta(\gamma)] = \tau_o \qquad (3.9)$$

is highly nonlinear with initial condition $\gamma_o = \tau_o G_{OU}^{-1}$, where $G_{OU} = G_{OR} + G_2$ is the unrelaxed modulus at zero strain. Assuming, in first approximation that in Eq. (2.13) $G_\infty \ll G_o$ then roughly

$$G(\gamma) \sim G_{OR}f_1(\gamma) \text{ and } \theta(\gamma)G(\gamma) \sim \theta_2[G_U - G_R + G_{OR}f_1(\gamma)] \qquad (3.10)$$

where $G_U - G_R = G_2$ has been assumed to be independent of

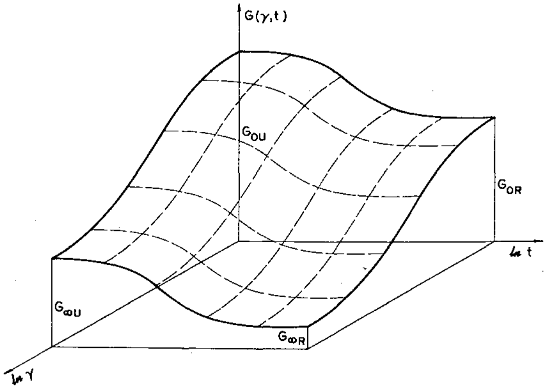

Fig. 10 Schematic representation of relaxation modulus of Standard Solid with strain dependent parameters.

strain. Hence, Eq. (3.9) becomes

$$G_{OR}f_1(\gamma)\{\gamma + \dot{\gamma}\theta_2[G_2 + G_{OR}f_1(\gamma)]\} = \tau_o \qquad (3.11)$$

Writing this equation in the form

$$\theta_2\dot{\gamma} = k\exp[(\gamma/\gamma_i)^\beta] - \gamma[G_2 + G_{OR}\exp[-(\gamma/\gamma_o)^\beta]^{-1} \qquad (3.12)$$

the observed sharp increase of creep rate with creep is clearly implied without the necessity of going to a numerical solution.

The dynamic response of the standard solid might be obtained by evaluating the moduli $G_1(\gamma,\omega)$ and $G_2(\gamma,\omega)$ from Eq. (3.5) under the assumptions $\tau = \tau_o e^{i\omega t}$ and $\gamma = \gamma_o e^{i\omega t}$. Such separation of the real and imaginary parameters is, however, not possible in the strain-dependent medium. The assumed shape of the $G^*(\gamma,\omega)$ relation is, schematically shown in Fig. 11.

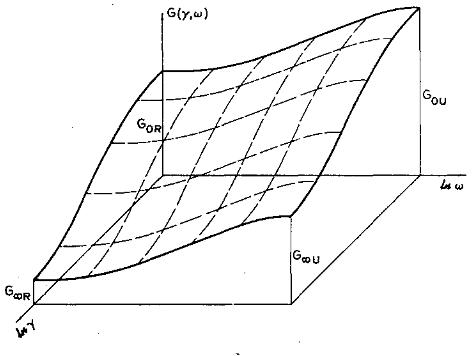

Fig. 11 Schematic representation of in phase dynamic modulus of Standard Solid with strain amplitude dependent parameters.

IV. Conclusions

The analysis of solid-propellant grains on the basis of viscoelastic constitutive equations in which the strain dependence of the parameters is considered obviously leads to equations that can be solved, even approximately, only by very time consuming numerical methods. However, so far not even the constitutive equations have been formulated for two- or three-dimensional states of stress. If the analysis of the grain is to be more than an exercise in conventional viscoelastic computation only vaguely related to its real behavior, a systematic investigation of strain dependence in the response of filled elastomers, both experimental and analytical, is required urgently.

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