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Rheology of Carbon-Black Filled Rubber During Cure

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Rheology of Carbon-Black Filled Rubber During Cure

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Abstract

Our previous experimental data indicated that a KBKZ constitutive law could adequately represent the rheological behavior of green carbon black-filled rubber. In this manuscript, we follow the evolution of nonlinear viscoelasticity as the rubber cures. By first focussing on the fully-cured filled rubber, we find that a KBKZ formalism, with the green rubber damping function but a different spectrum of relaxation times, applies equally well. Differential scanning calorimetry allow us to monitor the extent of reaction and, thereby, correlate the change in relaxation spectrum to rubber chemistry. A complete constitutive equation is presented that allows calculation of stresses in filled rubbers through cure.

I. INTRODUCTION

In order to model the tire shaping process, a constitutive law for the filled rubber is required which will predict the change in viscoelasticity with cure and properly accumulate stresses during simultaneous deformation and cure. Since rubber temperatures in processing are neither uniform in time nor space, we cannot simply isothermally measure changes in rubber viscoelasticity with time during cure, but are forced to develop structure/property relations that correlate rubber rheology to chemistry. In this manner, we can calculate temperature and extent of reaction profiles within a tire which then uniquely determine the rubber's instantaneous response at each point. Stresses then accumulate through competition between nonlinear viscoelastic relaxation, stiffening by additional reaction, and applied deformations.

Our previous investigations on the rheology of green carbon black-filled rubber[1] employed an 18 vol.% carbon black filled natural rubber. This same rubber was used in the present study with added sulfur. All compounds were prepared at Goodyear Technical Center, Akron, Ohio. Vulcanization was complete within roughly twenty minutes at 150°C, and significant degradation in apparent modulus resulted at much longer cure times.

In this paper, we present, in Section II, the linear and nonlinear viscoelasticity of fully-cured filled and unfilled natural rubbers. In Section III, the evolution of linear viscoelasticity during cure is discussed. Section IV contains our investigations of extent of reaction from differential scanning calorimetry. We present a complete formalism for calculating stresses during rubber cure in Section V and discuss how to obtain the required material parameters in Section VI.

II. VISCOELASTICITY OF CURED RUBBER

Linear Viscoelasticity

Linear viscoelasticity was probed with a Rheometric RDS-2 in oscillatory shear. At temperatures above $30^{o}C$, 25mm diameter, 8^{o} cone-and-plates were used, while at lower temperatures, torsional rectangular geometry was employed with nominal sample dimensions of 0.125 x 0.5 x 2". Samples were prepared by pressing the productive green rubber between heated plattens ($150^{o}C$) to form sheets for torsion rectangular geometry or directly onto the cone and plates. These samples were then held in the heated plattens for 20 minutes to complete the cure. To remain in the linear regime, strains were typically kept below 0.1%. All samples were annealed at $120^{o}C$ for 10 minutes prior to data acquisition to erase all previous strain history.

Figures 1 and 2 portray the linear viscoelastic behavior of unfilled and filled cured rubber. We see from Figure 1 that the in-phase component of the unfilled rubber modulus attains its equilibrium value of roughly 2×10^{6} dynes/cm^{2} at temperatures greater than $60^{o}C$ within our experimental frequency window. The out-of-phase component, which is proportional to the spectrum of relaxation times, displays a power-law decay with a slope of roughly -0.18. The green unfilled rubber WLF parameters found previously[1] apply equally well to the unfilled cured rubber implying that the relatively low crosslink density does not significantly affect mobility. At a reference temperature of $25^{o}C$, these WLF parameters are $C_1=6.6$ and $C_2=150^{o}C$ in agreement with literature values.[2]

In Figure 2, the entire relaxation spectrum of fully-cured, carbon black-filled natural rubber is displayed at a reference temperature of $-70^{o}C$ (the glass transition temperature). Shown for comparison is the corresponding spectrum for the green, filled rubber.[1] As expected,[2] crosslinking does not appreciably affect the

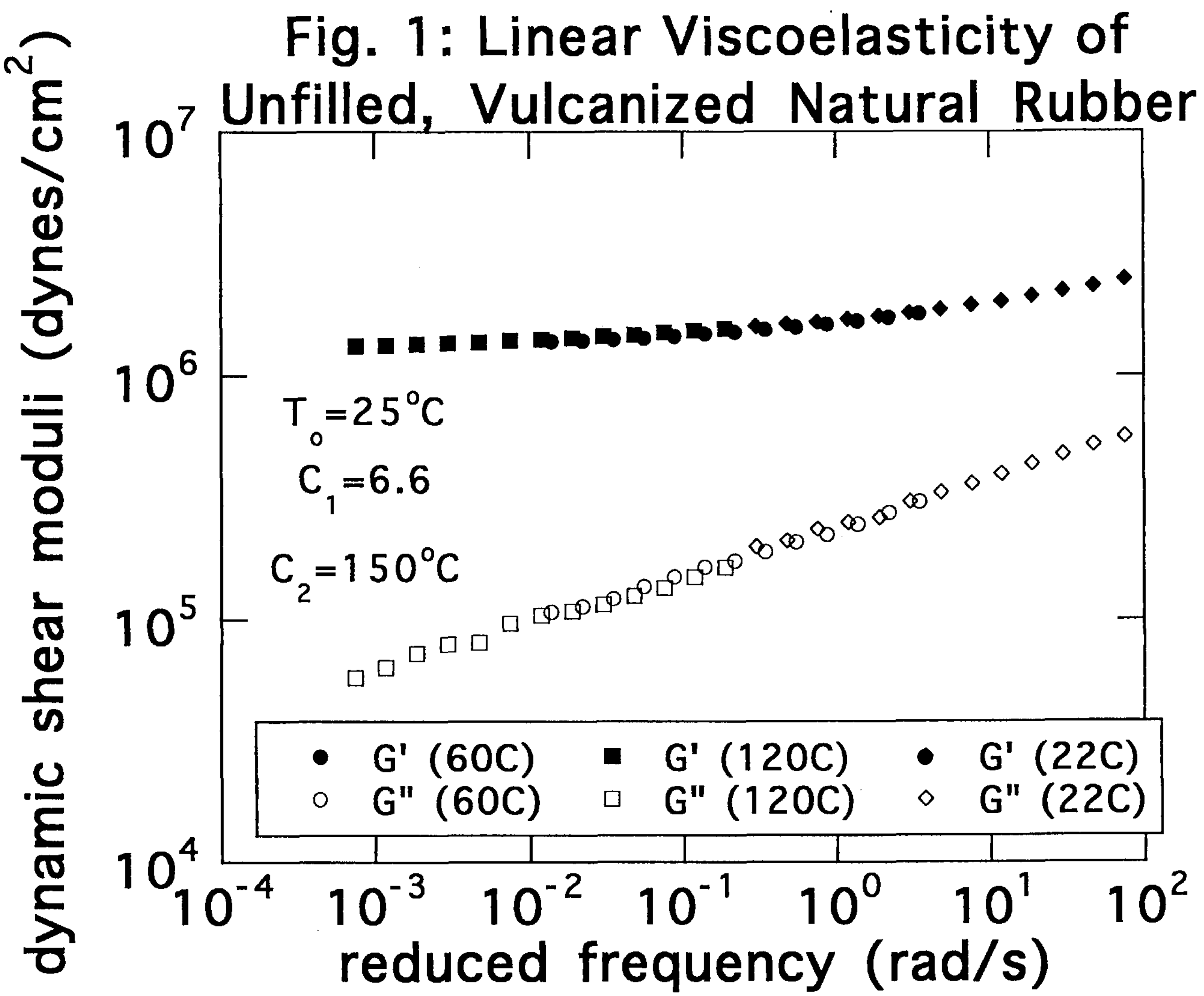
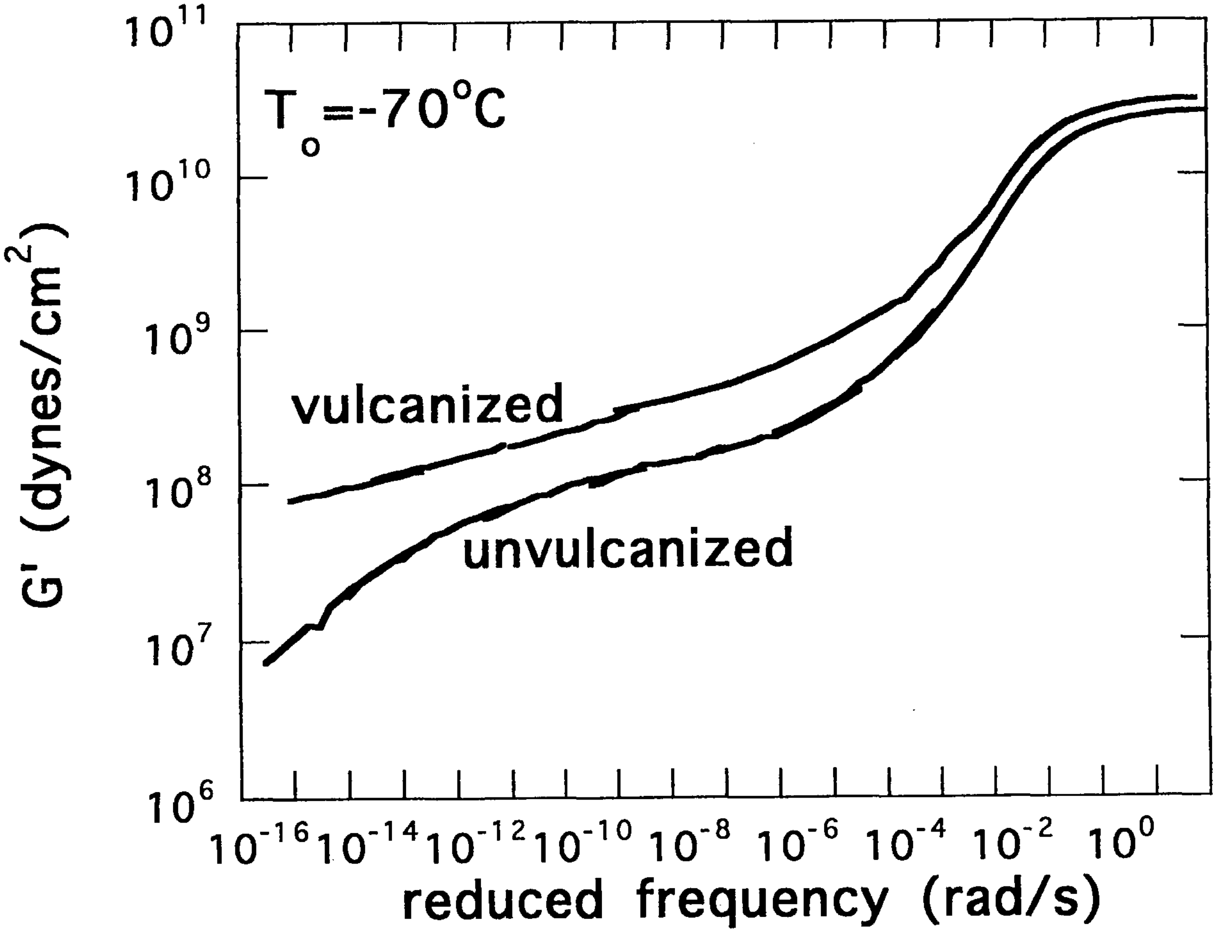


Fig. 1: Linear Viscoelasticity of Unfilled, Vulcanized Natural Rubber

Fig. 2: Linear Viscoelasticity of 18 vol% Carbon Black Filled Natural Rubber

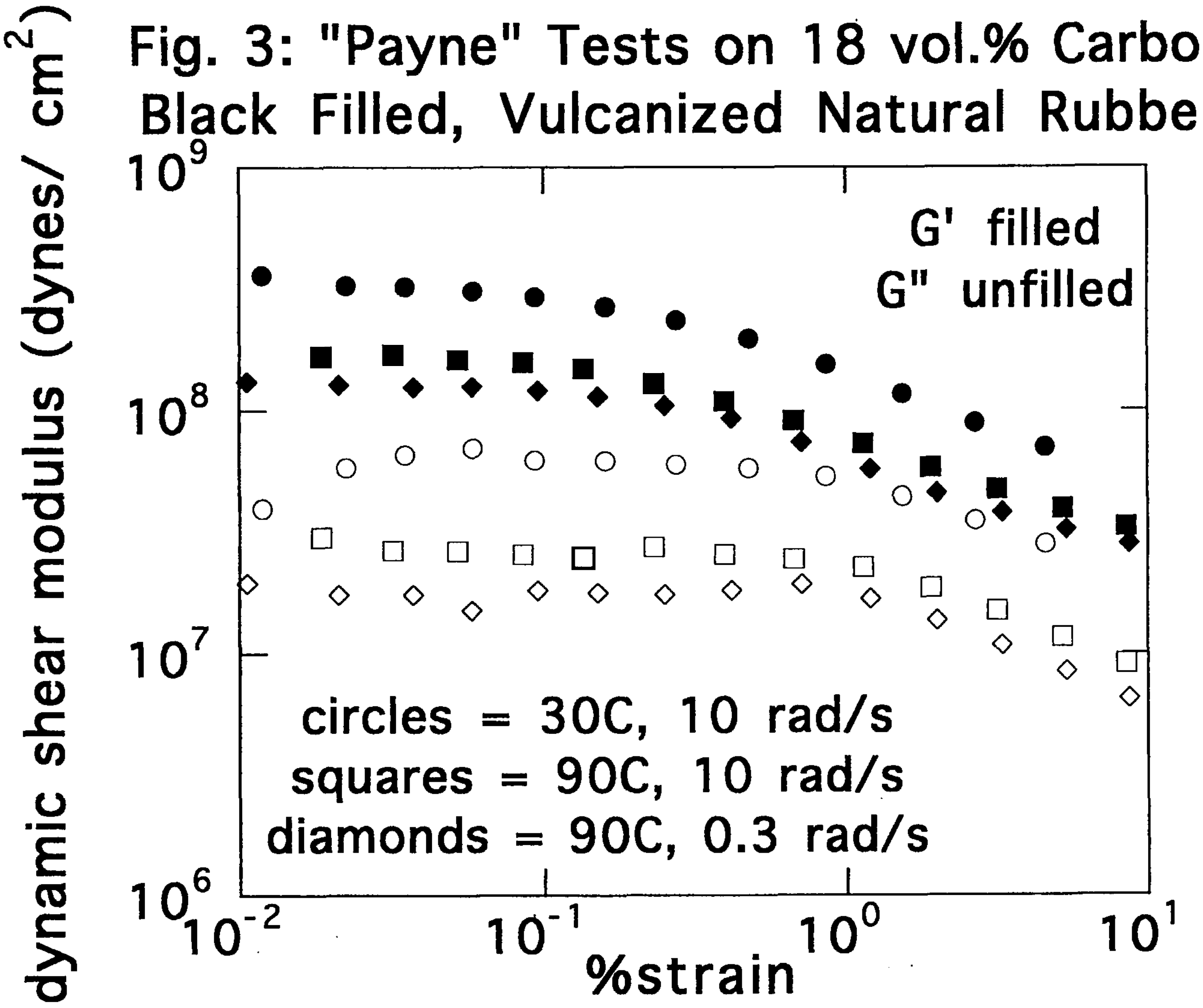


glassy modulus (~3×10^9 dynes/cm^2), the glass transition temperature, nor the initial Rouse-like decay. The cured, filled rubber does not exhibit an entanglement plateau as does the green rubber but, rather, displays a sluggish, power-law decay, $G' \sim \omega^{1/10}$, at low frequencies. The cured, filled rubber master curve was constructed using the same WLF parameters as for the unfilled, cured rubber above. While this procedure is unambiguous in the transition regime, the observed power-law behavior in the terminal regime makes the time-temperature shifting procedure somewhat arbitrary. Therefore, while use of the unfilled WLF parameters for the long-time, high temperature response of the cured, filled rubber is consistent with the data, it is not unique. We default to Occam's razor and choose to use these parameters throughout the spectrum with the belief that it is simpler to invoke a single relaxation mechanism.

Nonlinear Viscoelasticity

We previously determined that a separable KBKZ constitutive law accurately predicted the observed nonlinearities in green, carbon black-filled natural rubber.[1] In this formalism, the apparent modulus of the rubber decreases with increasing strain in the nonlinear regime. The onset of nonlinearities is defined by a critical strain, and the magnitude of the softening by the "damping function". In Figure 3, we show the results of a series of oscillatory shear tests on fully-cured, filled rubber in which the frequency is held constant within the test but the strain magnitude is increased. Three such tests were performed in which we examined the effect of temperature and strain frequency. Cone-and-plate geometry was employed and the samples were prepared and cured as above. From Figure 3, we can conclude that the onset of nonlinearity is governed solely by strain

Fig. 3: "Payne" Tests on 18 vol.% Carbon Black Filled, Vulcanized Natural Rubber



magnitude and is independent of temperature and strain frequency, which is consistent with the KBKZ formalism.

In Figure 4, we show the results of a series of step strain, stress relaxation experiments of increasing strain magnitude for the fully-cured, filled rubber. Again, cone-and-plate geometry, sample preparation, and cure history followed that described previously. The separable KBKZ constitutive law predicts that the shape of the modulus in these step strain tests is independent of applied strain, and experiments at 90°C bear this out for strains ranging from 0.5 to 7%. All moduli exhibit the same slow power-law decay, $G \sim t^{-1/10}$, observed in the linear regime. The depression of the nonlinear modulus from its linear value, $h(\gamma)=G(t,\gamma)/G(t)$, defines the damping function. The damping function for cured, filled rubber is shown in Figure 5 along with the damping functions for two linear filled green rubbers investigated previously.[1] It is apparent that the damping function is unaffected by crosslinking, consistent with the interpretation that nonlinearities arise from a carbon black aggregate network. Moreover, the normalized in-phase oscillatory modulus from Figure 3 tracks the damping function as explained in reference 1. The invariance of the damping function with crosslink density will be shown to greatly simplify calculation of stresses during cure.

Bulk Modulus

To complete the characterization of the green or cured rubber viscoelasticity, we require the bulk modulus which is typically difficult to measure. Fortunately, Sandia owns a presssure dilatometer in which we can measure the volume of a sample as pressure is increased as a function of temperature. A $1cm^3$ sample of the 18vol.% green carbon black filled natural rubber studied previously was placed in the dilatometer at room temperature

Fig. 4: Nonlinear Response to Step Strains

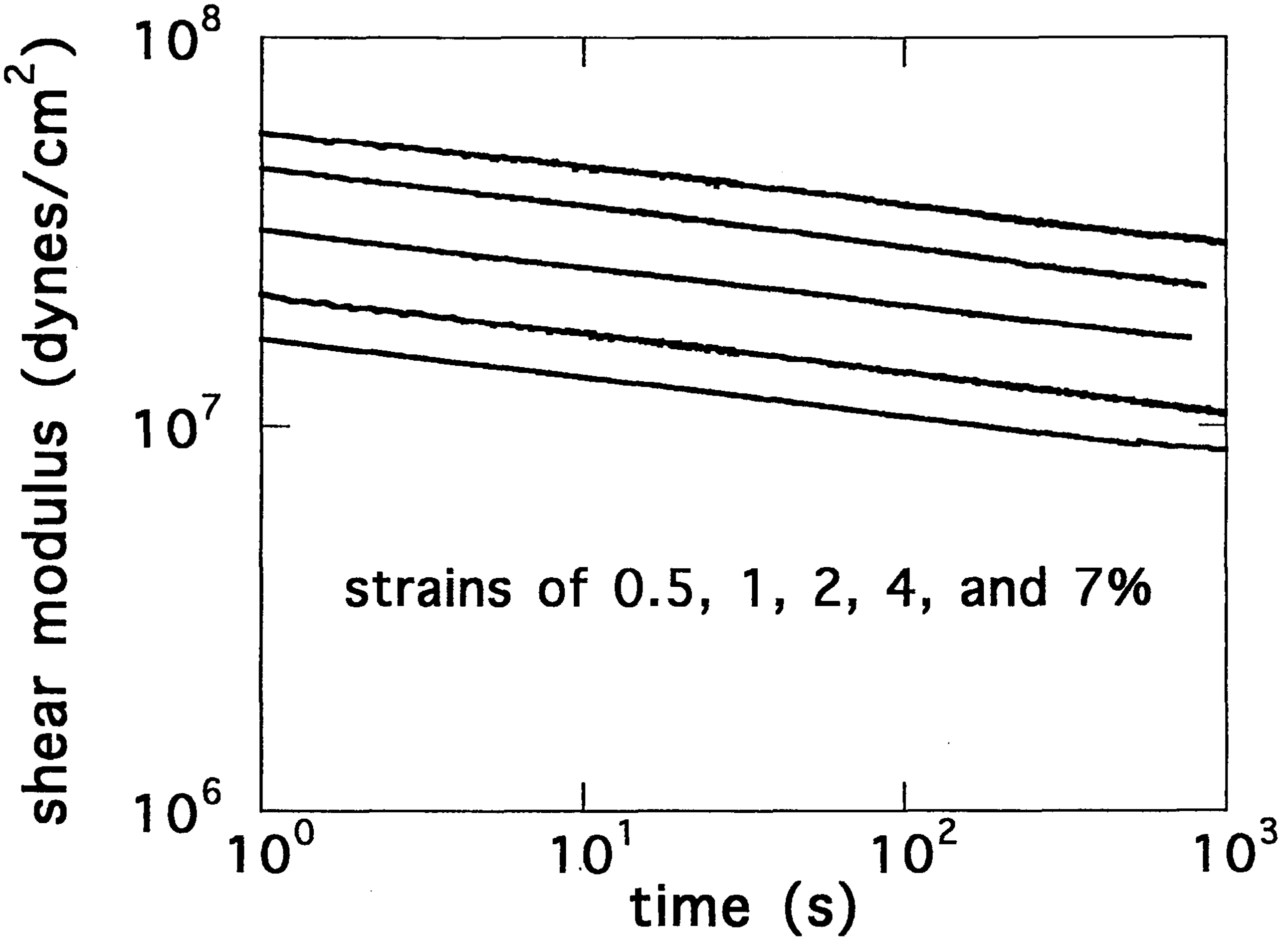
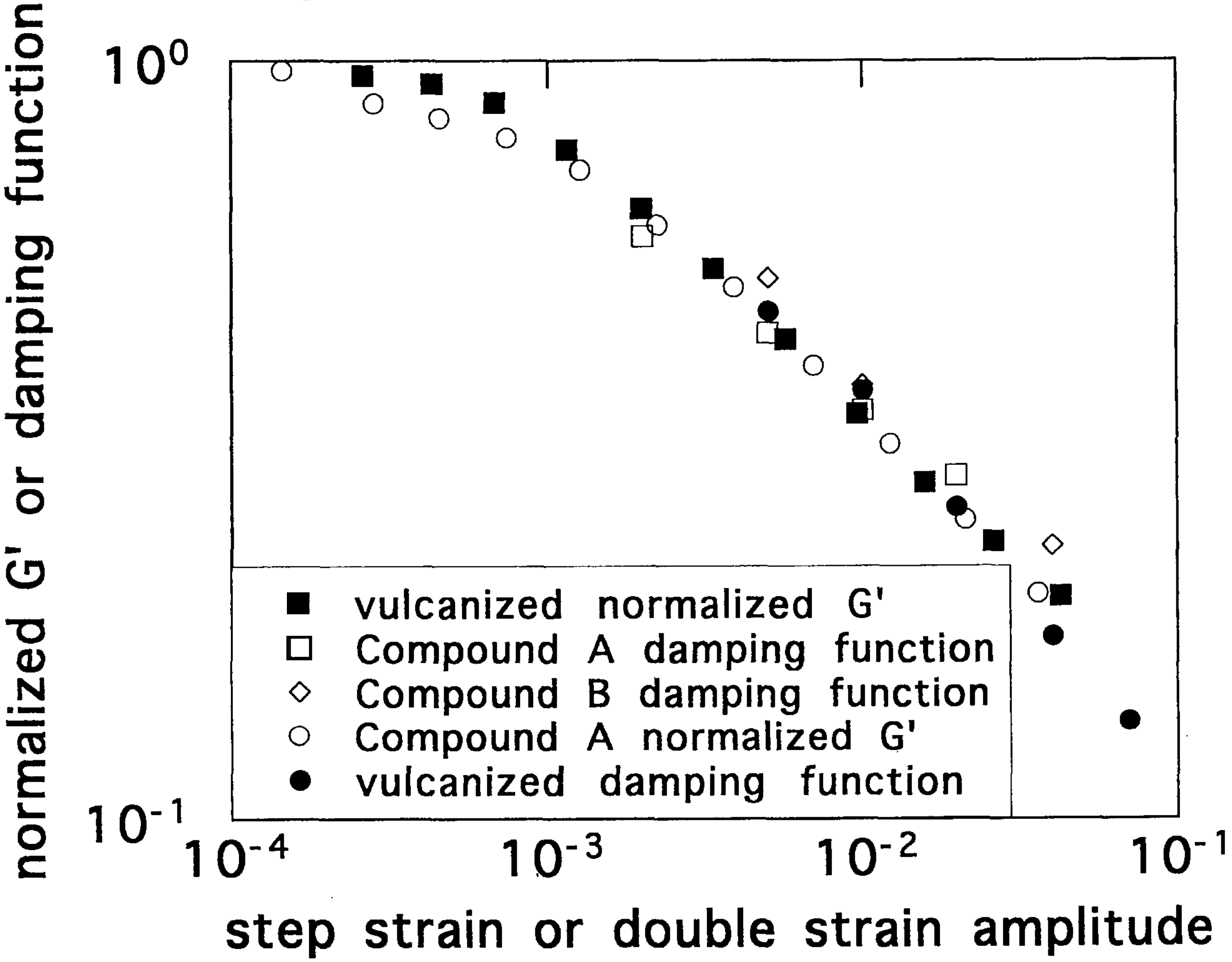


Fig. 5: KBKZ Damping Function



(22°C), and the specific volume was recorded as the pressure increased from atmospheric to 10 MPa. The results are shown in Figure 6. From this, we find a bulk modulus of 3.22×10^{10} dynes/cm^2. If we assume that the underlying equilibrium shear modulus of the filled, cured rubber is within a factor of two of the unfilled cured rubber,[3] then Poisson's ratio for the equilibrium solid is roughly 0.49995 - quite an incompressible material.

III. EVOLUTION OF LINEAR VISCOELASTICITY DURING CURE

Unfilled Natural Rubber

In a simple procedure to monitor the change in viscoelasticity with cure, we performed sequential oscillatory frequency scans as the rubber cured between the cone-and-plate. We, therefore, obtained "snapshots" of the viscoelasticity during cure with minimal variations due to sample and fixturing differences or uncertainties in cure time and temperature history. Samples were prepared by pressing the rubber between plattens heated at 120°C. Heating times and temperatures were kept as low as possible to minimize cure during preparation. The cone-and-plate was then fixtured to the rheometer and heated to 150°C. Frequency scans spanned from 1 to 100 rad/s taking 3 points per decade. With these parameters, a single scan lasted only 20 seconds, during which little reaction occurred.

Figure 7 shows the changes in the in-phase modulus of unfilled natural rubber as it cured at 150°C. From 0 to 15 minutes, the magnitude of the modulus increased and its frequency dependence lessened. By 15 minutes, the sample was nominally fully-cured and the equilibrium modulus was roughly 3×10^6 dynes/cm^2 (note that the absolute temperature dependence of the equilibrium modulus accounts for the difference in measured values at 150°C here and 22°C in section II). As the sample was heated for longer times at

Fig. 6: Bulk Modulus of 18 vol% Carbon Black Filled Unvulcanized Natural Rubber

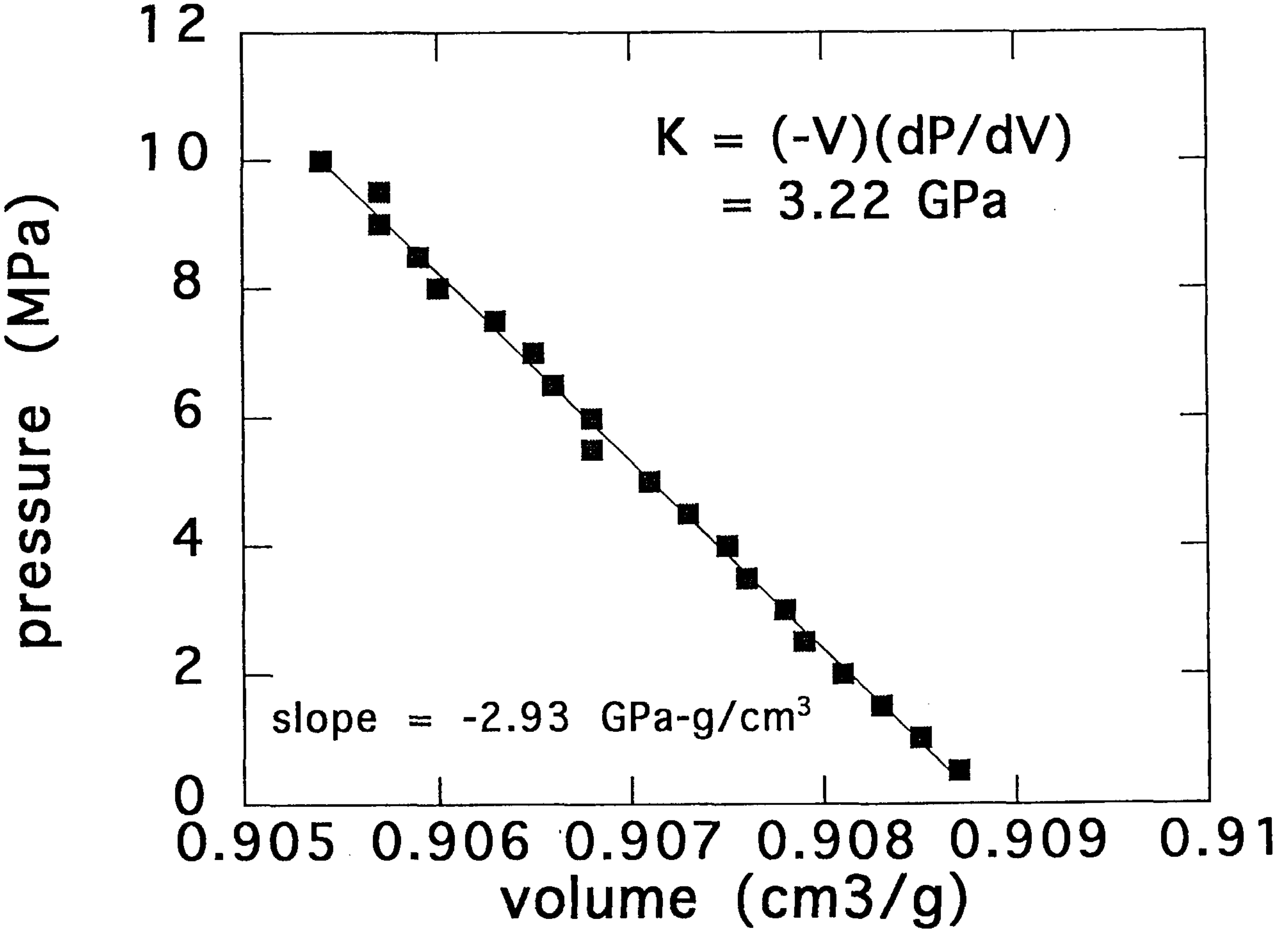
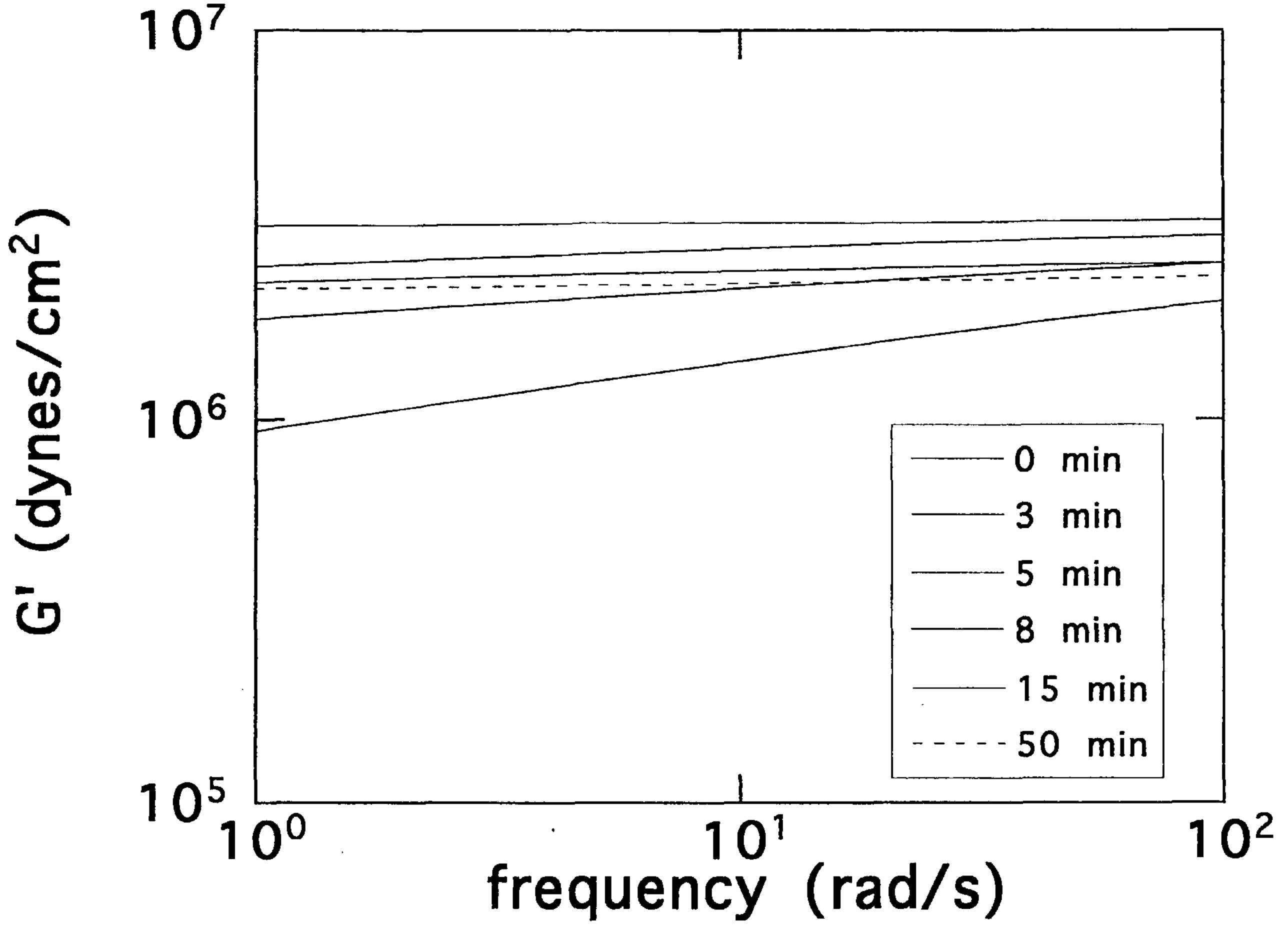


Fig. 7: Change in Linear Viscoelasticity with Cure in Unfilled Natural Rubber at 150°C



150^{o}C, degradation occurred, and at 50 minutes, the equilibrium modulus measured 2x10^{6} dynes/cm^{2}. If one could track the increase in equilibrium modulus with time during cure, we would have a reasonably direct measurement of extent of reaction, since theory relates reaction to network topology to equilibrium modulus. However, even at 8 minutes when the reaction has progressed considerably, significant viscoelastic relaxation clouds our ability to determine the true equilibrium modulus, and we must revert to other means of monitoring extent of reaction. (For the best, and only, complete description of the evolution of viscoelasticity in unfilled curing rubbers, see reference 4.)

Filled Natural Rubber

We followed the same procedure to monitor the evolution of viscoelasticity in our filled natural rubber, except that the curing temperature was lowered to 120^{o}C to allow us time to follow more completely the changes in the relaxation spectrum. These scans, obtained from 0 to 70 minutes, are shown in Figure 8. Again, the apparent modulus increases with time, the slope lessens, and no equilibrium modulus is observed. Within our experimental frequency window at 120^{o}C, the in-phase modulus seems to be obey a power-law frequency relation, $G' \sim \omega^{\Delta}$, with the slope Δ decreasing from the green value of roughly 0.3 to the fully-cured value of 0.1 as cure progresses. In the next section, we will relate the exponent Δ to the extent of reaction.

In Figure 9, we replot Figure 2, in which the in-phase dynamic moduli for green and fully-cured filled rubber were shown at a reference temperature of -70^{o}C, and add two viscoelastic "snapshots" during cure from Figure 8 (appropriately shifted to -70^{o}C). We can now see more clearly the effect of cure on the linear viscoelastic behavior of filled rubber.The transition regime (from 10^{-4}

Fig. 8: Changes in Linear Viscoelasticity with Cure in Carbon Black Filled Natural Rubber at 120°C

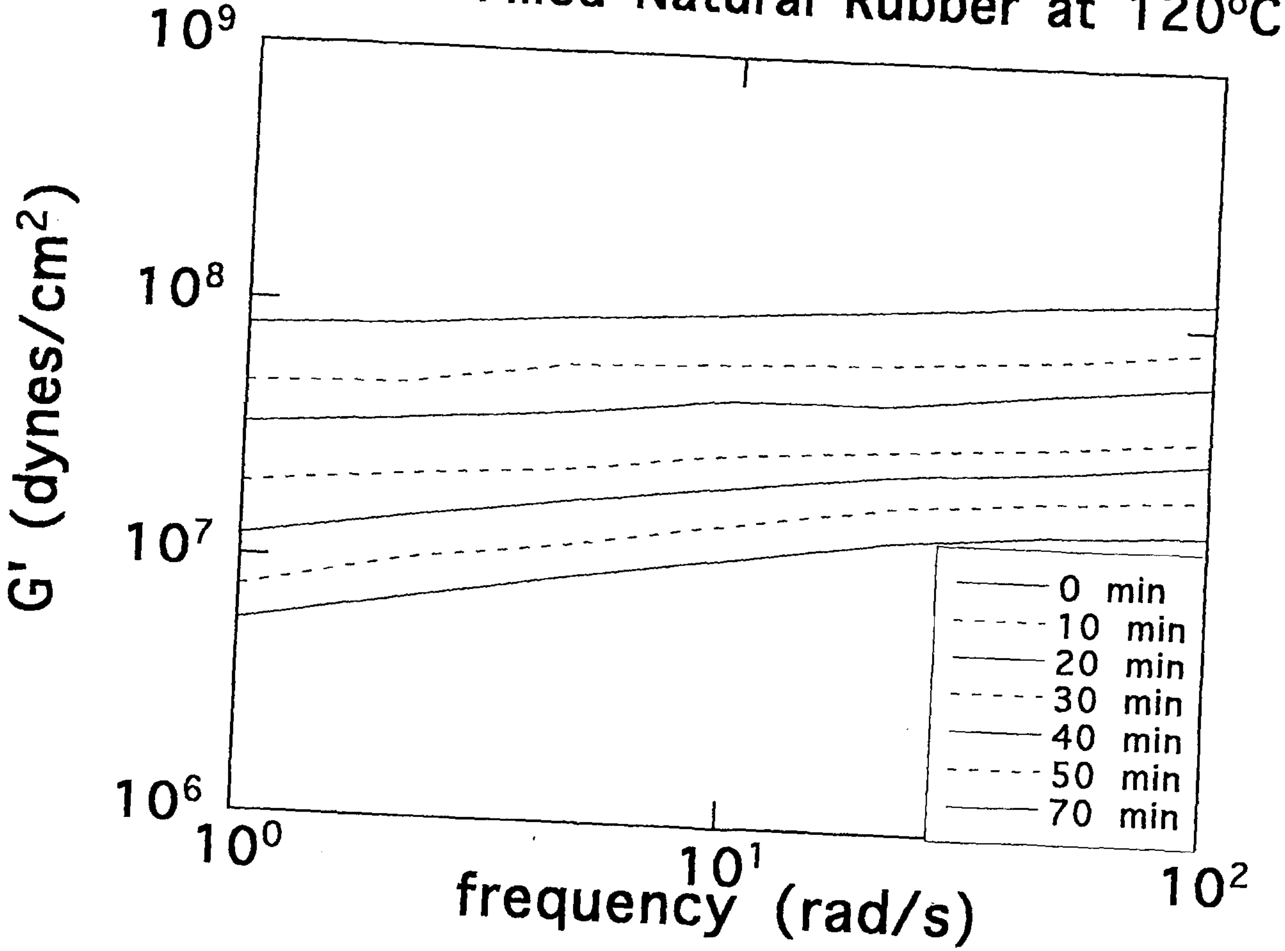
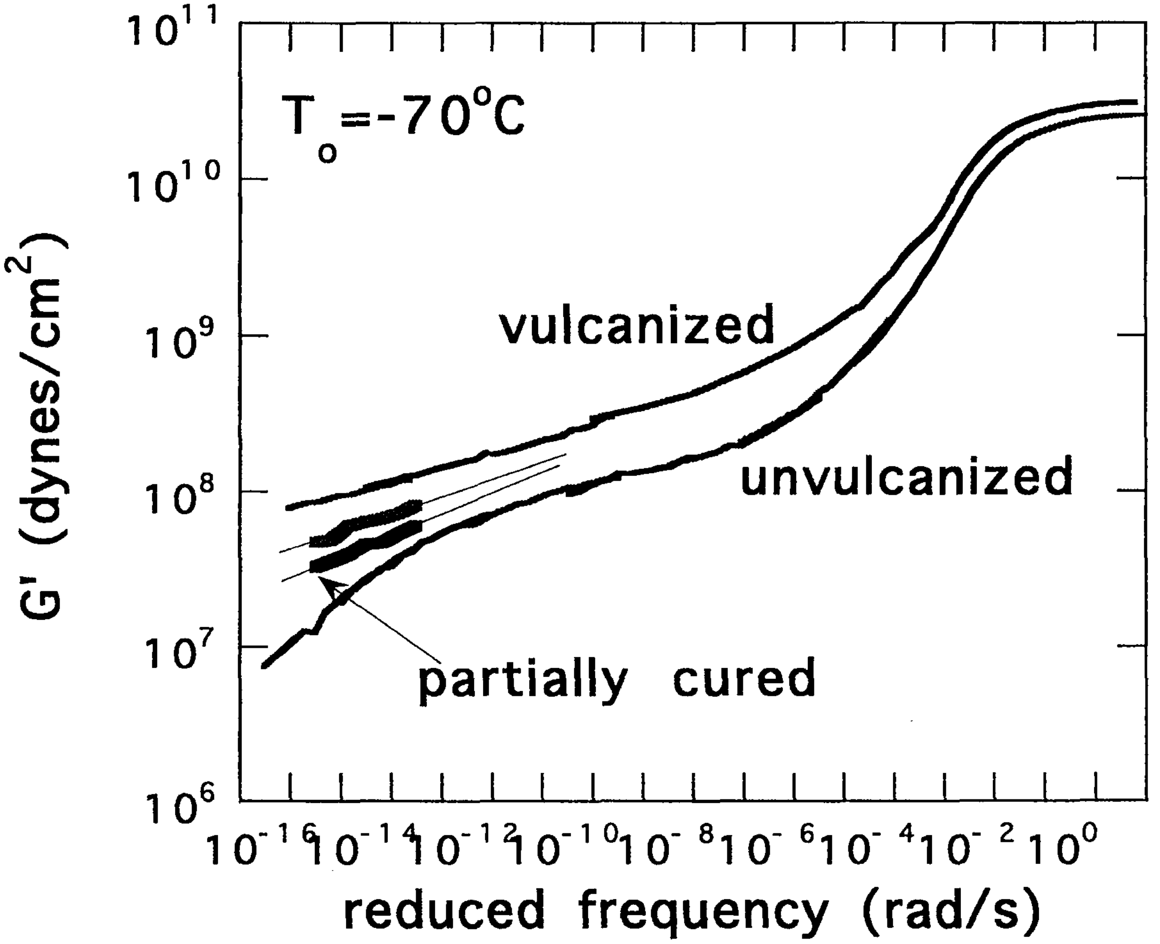


Fig. 9: Changes in Linear Viscoelasticity with Cure in 18 vol.% Carbon Black Filled Natural Rubber



to 10 rad/s) is affected only slightly by cure. However, to calculate accurately stress evolution during cure, it is imperative to capture the change in the spectrum of relaxation times with cure at long-times.

IV. MEASUREMENT OF EXTENT OF REACTION

Differential Scanning Calorimetry

As stated before, our goal is to develop structure/property relationships for curing filled rubber so that the local viscoelastic response can be related to a molecular property calculable from a knowledge of thermal history alone. Therefore, we need to measure the extent of reaction. Perhaps the easiest method to follow a reaction is by differential scanning calorimetry (DSC) where the evolution of heat is monitored as the reaction progresses. Here, we will assume that the major source of heat comes from the actual crosslinking reaction. The instantaneous reaction rate is then found by normalizing the DSC signal by the integrated total heat released (the heat of reaction). Isothermal DSC traces (reaction rates) for filled and unfilled productive natural rubber cured at 150°C are shown in Figure 10. Both curves exhibit autocatalytic behavior, and the unfilled system reacts a bit slower than the filled.

The integrated extents of reaction for filled rubber at 120 and 150°C are shown in Figure 11. The DSC results are in agreement with our viscoelastic experience in that the reaction is complete in roughly 20 minutes at 150°C. Curves for extent of reaction or reaction rate versus time at different temperatures (from 120 to 160°C) can be superposed by simply scaling time, which implies that a single reaction mechanism is operative over this range. The time for which the reaction rate is greatest (the peak time) is plotted against the reciprocal reaction temperature in Figure 12. The

Fig. 10: DSC Reaction Rate at 150°C

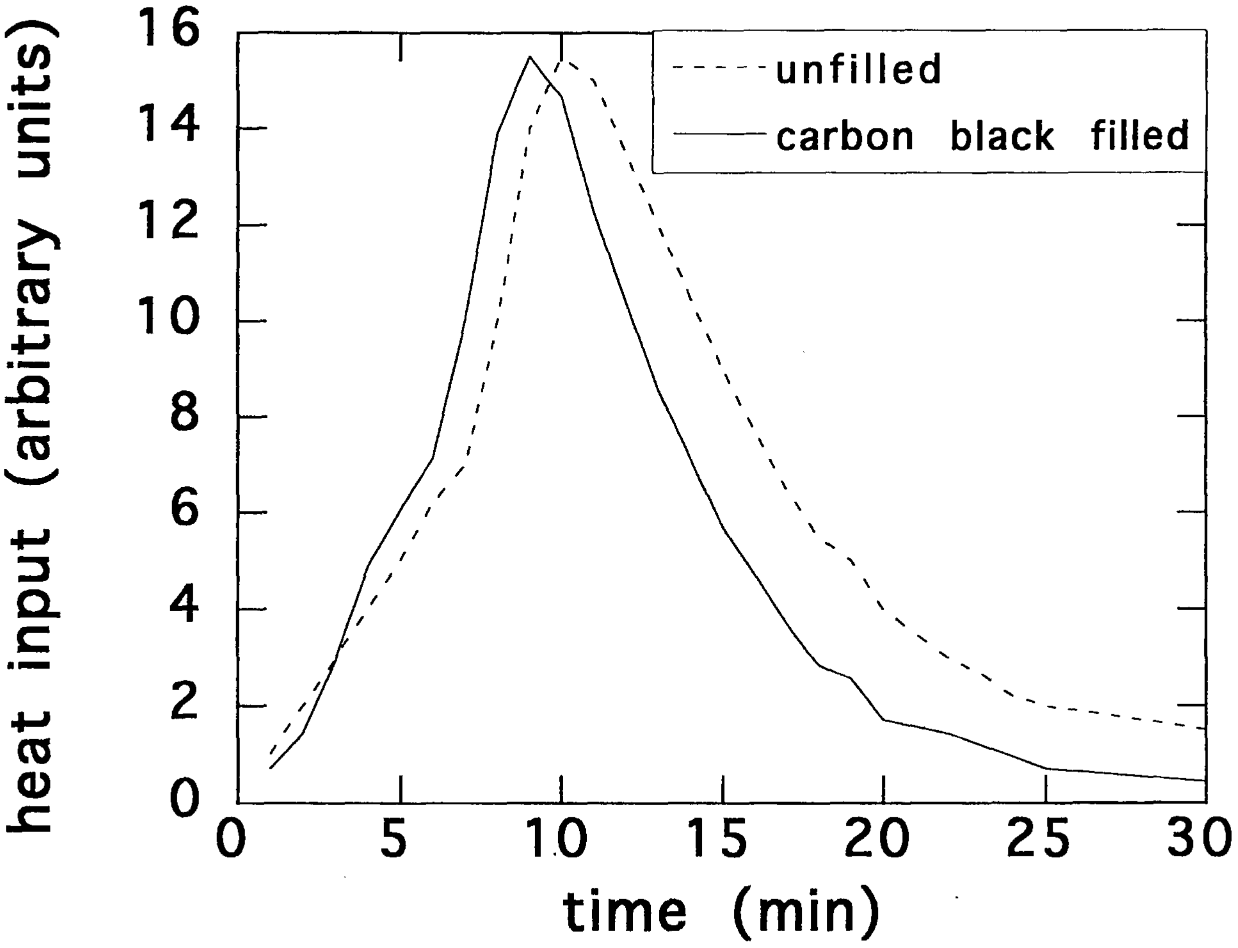


Fig. 11: Reaction Kinetics for 18 vol.% Carbon Black Filled Natural Rubber

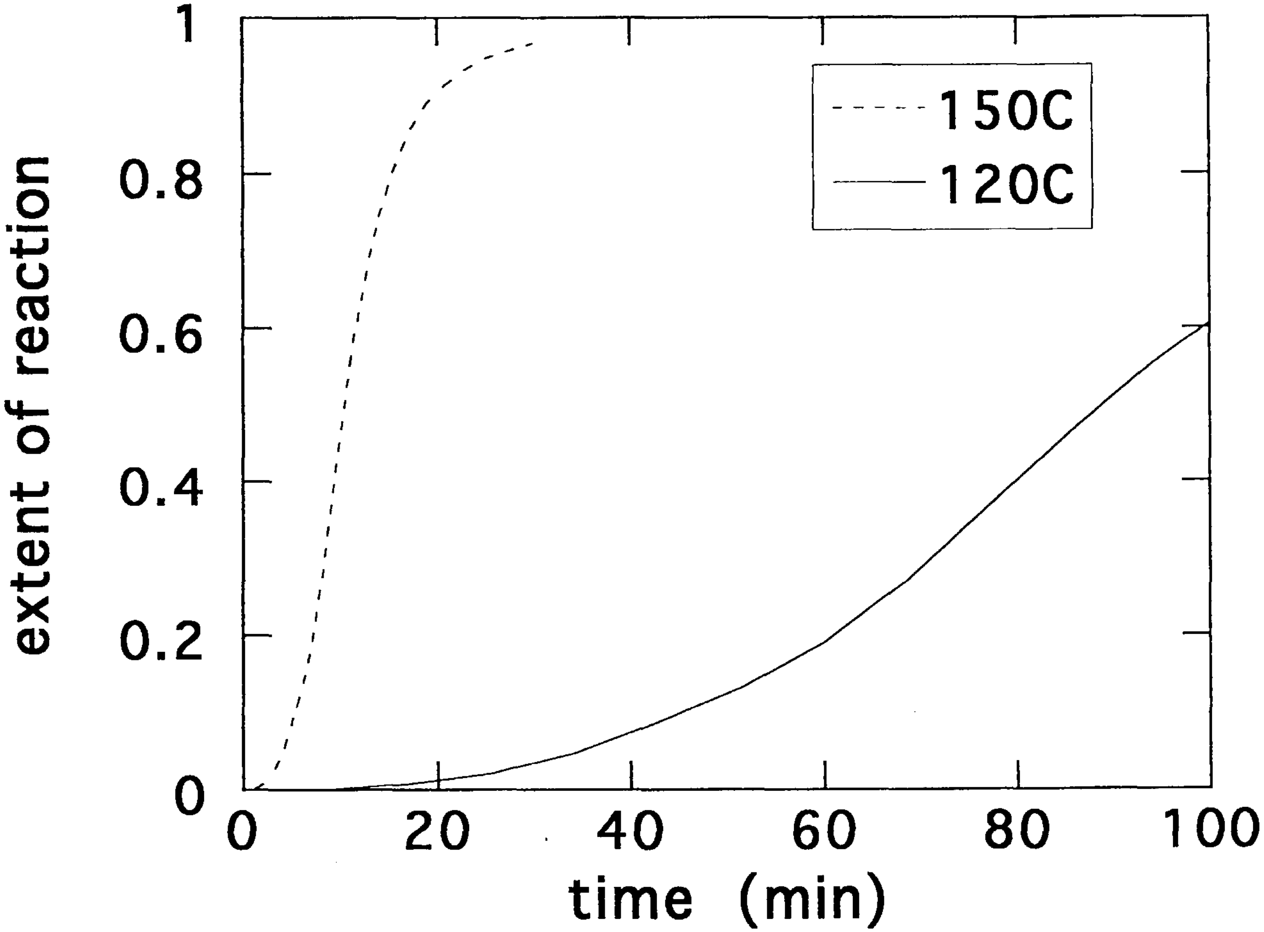
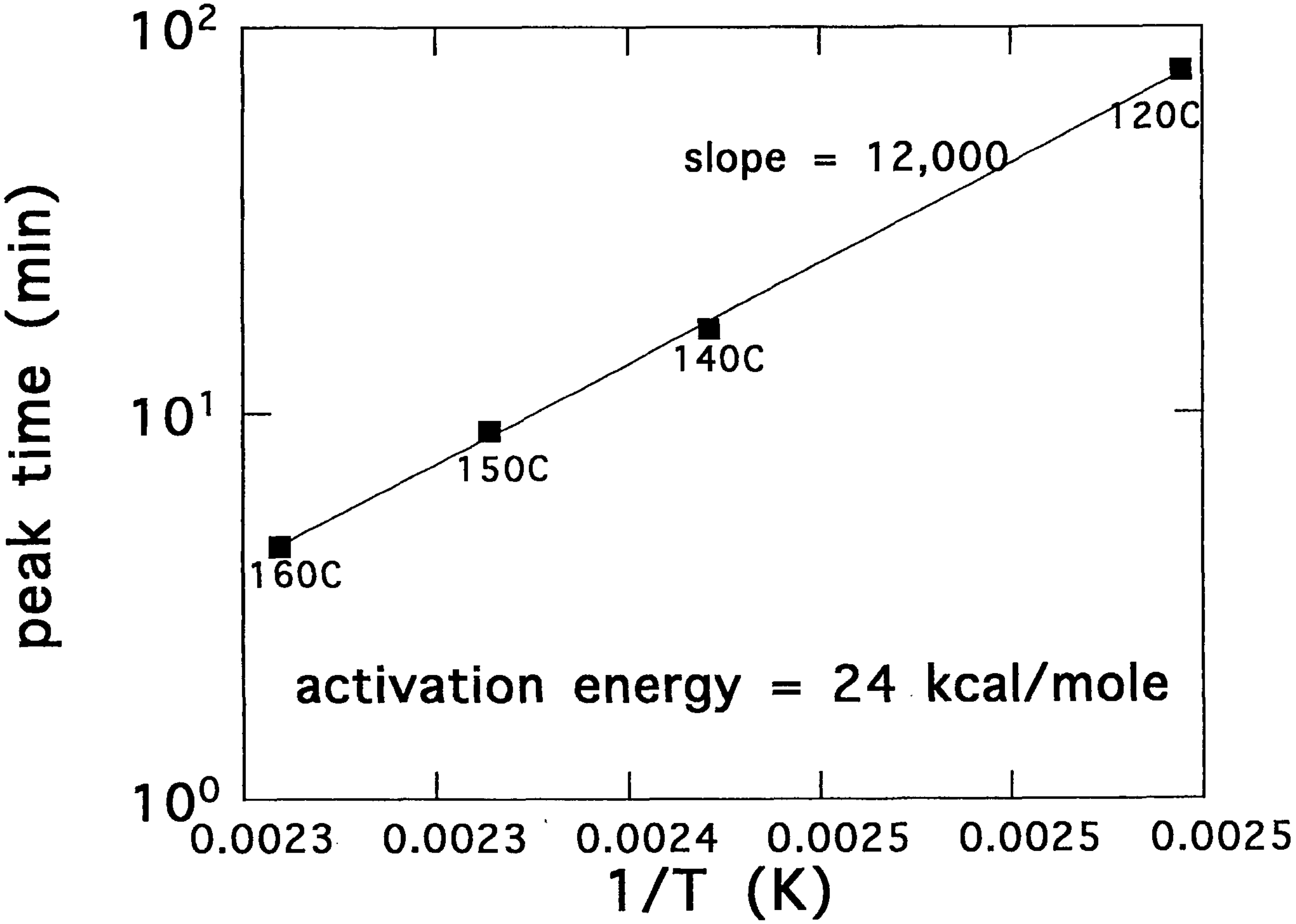


Fig. 12: Arrhenius Plot for 18 vol.% Carbon Black Filled Natural Rubber



reaction does follow an Arrhenius relation (rate~$e^{-E/RT}$) and our observed activation energy is 24 kcal/mole for which the reaction rate roughly doubles every 10°C.

Now that we can measure the extent of reaction, we are in a position to develop structure/property relations. Specifically, we could fit the spectrum of relaxation times at a given time during cure to a series of exponentials and relate the change in series prefactors and relaxation times to the extent of reaction at that time. Since we observed in Figure 8 that the terminal relaxations can be described by a single exponent Δ, it is more convenient here to plot this single parameter against extent of reaction (Figure 13). Interestingly, the decay exponent quickly decreases to the fully-cured value of 0.1 when the reaction is only 20% complete.

Cure Shrinkage

For completeness sake, we also attempted to measure the volume shrinkage due to cure in our dilatometer. In this experiment, the green, productive, unfilled rubber was placed in the dilatometer, and the temperature was raised from room temperature to 90°C. Since the dilatometer requires massive walls for pressure tests, the thermal response is quite slow; it took roughly two hours to reach steady state. We chose a relatively low cure temperature of 90°C so that minimal cure would occur during this initial transient. Over a one day period, no volume change was observed even though the reaction progressed to roughly 70% (Figure 14). We, therefore, conclude that cure shrinkage is unimportant for stress calculations.

Fig. 13: Change in Relaxation Spectrum with Vulcanization

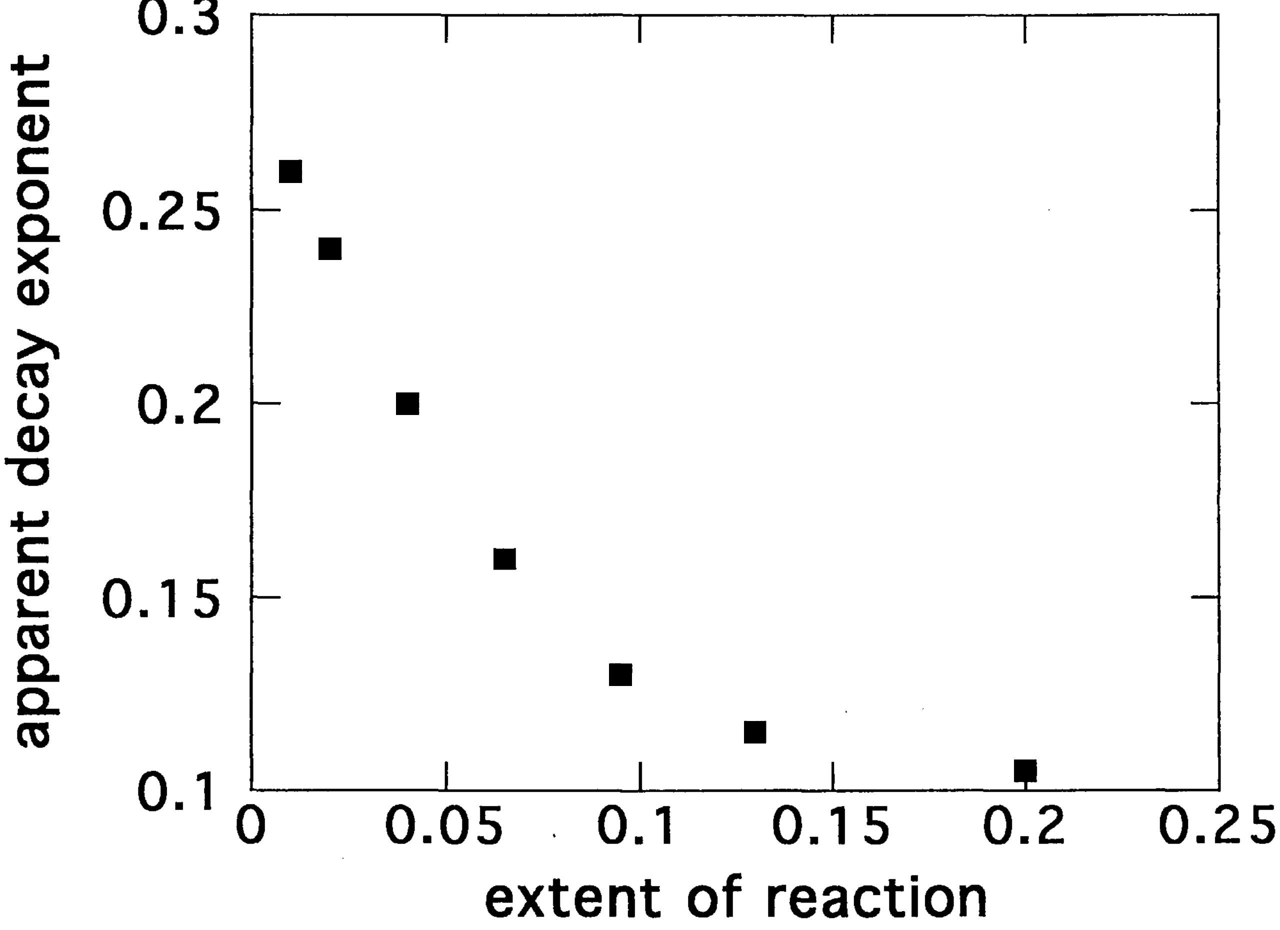
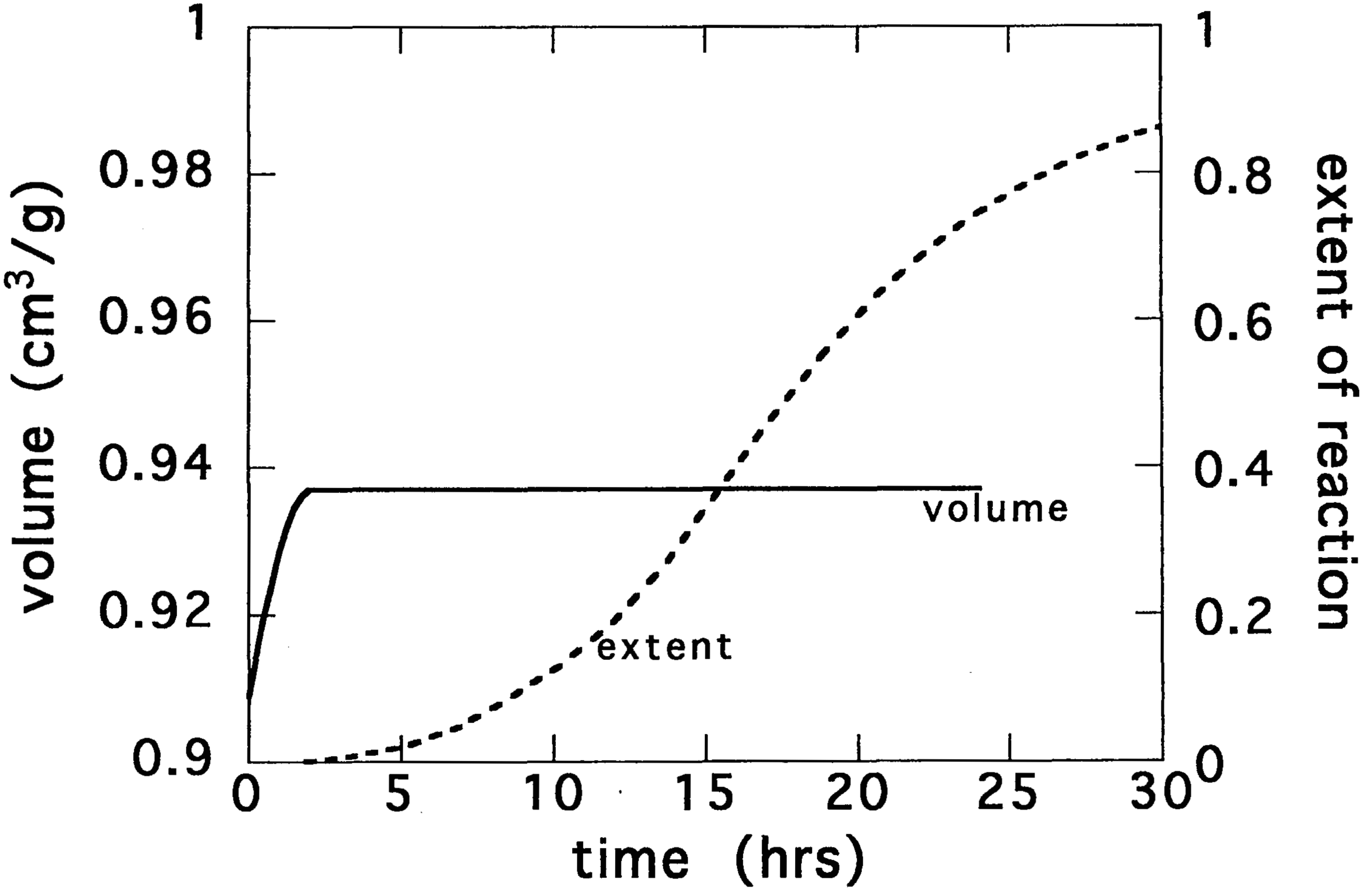


Fig. 14: Investigation of Cure Shrinkage at 90°C for 18 vol.% Carbon Black Unfilled Natural Rubber



V. FORMALISM FOR CALCULATING STRESSES DURING RUBBER CURE

Computational Considerations

Stress calculations during cure are greatly simplified if the thermal problem can be solved independently prior to the actual stress calculations. In this case, one could first determine the temperature history for each point in the rubber and then, since the extent of reaction is dependent only upon temperature history, calculate the extent of reaction time profile at each point. This information could then be passed to the stress calculations in which material properties at a given time are related to extent of reaction.

Unfortunately, the tire shaping process may not lend itself to such a decoupling. For instance, the tire temperature at the instant of steam inflation is room temperature. Initial inflation is so fast that no appreciable thermal transport occurs by conduction through the tire. Therefore, we conjecture that the tire temperature rises significantly only when it first meets the heated mold. If our goal is to model the relatively slow tread filling, then the thermal and stress problems do not seem to decouple. However, we may have less difficult goals, such as predicting cord deformation within the tire, which may be less sensitive to this surface phenomema.

For simplicity, let's assume that the thermal and stress codes do decouple. (The coupled problem can be handled in essentially the same fashion but in an iterative process.) We would first calculate the thermal and extent of reaction profiles at each point in the rubber. This information would then be passed to the stress codes which require a proper constitutive law for rubber rheology that we discuss now.

Green and Cured Constitutive Law

From our studies on green and fully-cured carbon black-filled natural rubber we conclude that a separable KBKZ formalism accurately predicts the observed shear nonlinearities. Moreover, the damping function seems to be independent of extent of cure. As seen in Section III, however, the spectrum of relaxation times does change with cure. For a small simple shear strain, the separable KBKZ shear stress prediction for green or cured filled rubber is

$$\sigma = \int_{-\infty}^{t} ds\, m(t-s)\ \{h[\gamma(t)-\gamma(s)]\}\ [\gamma(t)-\gamma(s)] + G_{\infty}\gamma(t) \quad (1)$$

where $h(\gamma)$ is the damping function and $m(t)=-dG/dt$ ($G_{\infty}=0$ for green rubber).

An integral equation such as Eq. 1, however, does not lend itself to iterative solution as well as a differential version. Therefore, Dan Segalman[5,6] has developed a differential constitutive equation which mimics the separable BKZ equation in a step strain experiment. For small strains, his model gives (in the limit as $\beta=1, \varepsilon_o=0$, and $\lambda_D=\lambda_k=\lambda_i=\lambda$)

$$\frac{d\underline{\underline{\sigma}}_i}{dt} + \frac{\underline{\underline{\sigma}}_i}{\tau_i} = G_i\, g(D)\, \frac{d\underline{\underline{\varepsilon}}}{dt} \quad \text{with} \quad \frac{dD}{dt} + \frac{D}{\lambda} = R \qquad (2)$$

where the total stress $\underline{\sigma} = \Sigma\underline{\sigma}_i + G_{\infty}\gamma$, $\underline{\varepsilon}$ is the infinitesimal strain tensor, D is the "damage" which decays with a characteristic time, λ, and R is the rate of damage accumulation that follows its own evolution law.

$$\text{if } D = \left|\underline{\underline{\varepsilon}} - \underline{\underline{\varepsilon}}_k\right| \text{ and } E = \frac{d\underline{\underline{\varepsilon}}}{dt} \bullet \frac{\left(\underline{\underline{\varepsilon}} - \underline{\underline{\varepsilon}}_k\right)}{\left|\underline{\underline{\varepsilon}} - \underline{\underline{\varepsilon}}_k\right|} > 0,$$

$$\text{then } R = E;\ \text{otherwise } R = 0 \tag{3}$$

$$\text{where } \frac{d\underline{\underline{\varepsilon}}_k}{dt} + \frac{\underline{\underline{\varepsilon}}_k}{\lambda} = \frac{\underline{\underline{\varepsilon}}}{\lambda}$$

The shear stress, σ, in response to a fast (in the sense that negligible damage healing or viscoelastic relaxation occurs), monitonically rising shear strain of magnitude, γ, can be calculated.

sin ce

$$\sigma_i(t) = G_i e^{-t/\tau_i} \int_0^{\bar{t}} ds\, e^{s/\tau_i}\, g(D(s))\, \frac{d\varepsilon}{dt}(s)$$

$$\approx G_i e^{-t/\tau_i} \int_0^{\bar{t}} ds\, g(\varepsilon(s))\, \frac{d\varepsilon}{dt}(s) \; = G_i e^{-t/\tau_i} \int_0^{\gamma} d\gamma'\; g(\gamma') \tag{4}$$

then

$$\sigma(t) = \gamma\left[\sum G_i\; e^{-t/\tau_i} + G_\infty\right]\left[\frac{\int_0^{\gamma} d\gamma'\; g(\gamma')}{\gamma}\right] = \gamma G(t)\, h(\gamma)$$

From this, we can relate g(D) to the KBKZ damping function, h(γ), by differentiating the integral to obtain, $g(\gamma) = h(\gamma) + \gamma\;\; dh/d\gamma$, or in general, $g(D) = h(D) + D\;\; dh/d\gamma$.

From thermorheological simplicity, the τ_i's and λ must obey a single WLF law.

$$\log\left(\frac{\lambda(T)}{\lambda(T_r)}\right) = \log\left(\frac{\tau_i(T)}{\tau_i(T_r)}\right) = \log(a_T) = \frac{-C_1(T - T_r)}{C_2 + T - T_r} \tag{5}$$

For nonisothermal operation, Eq. 2 now becomes

$$\begin{aligned}
&\frac{d\underline{\underline{\sigma}}_i}{dt}+\frac{\underline{\underline{\sigma}}_i}{a_T\tau_i}=G_i\,g(D)\,\frac{d\underline{\underline{\varepsilon}}}{dt}\\
&\frac{dD}{dt}+\frac{D}{a_T\lambda}=R,\ \text{and}\\
&\frac{d\underline{\underline{\varepsilon}}_k}{dt}+\frac{\underline{\underline{\varepsilon}}_k}{a_T\lambda}=\frac{\underline{\underline{\varepsilon}}}{a_T\lambda}
\end{aligned}\tag{6}$$

and, for a step strain experiment in which temperature may vary during the test, the result analogous to Eq. 4 is

$$\begin{aligned}
\sigma(t)&=\gamma\left[\sum G_i\exp\left(-\int_0^t\frac{du}{a_T[T(u)]\,\tau_i(T_r)}\right)+G_\infty\right]\left[\frac{\int_0^\gamma d\gamma'\,g(\gamma')}{\gamma}\right]\\
&=\gamma\left[\sum G_i\,e^{-\xi_i(t)}+G_\infty\right]h(\gamma)=\gamma\,G[\xi(t)]\,h(\gamma)
\end{aligned}\tag{7}$$

from which a natural "reduced" time, $\xi(t)$, is defined.

From our studies on green and fully-cured rubbers, we also know that λ and $g(D)$ are independent of cure. Unfortunately, the spectrum of relaxation times does change with cure as does the equilibrium modulus. Now we must incorporate these changes into the constitutive law and determine how to evaluate the required parameters.

Constitutive Law Through Cure

Let's first consider the effect of an increase in equilibrium shear modulus with cure. From theory,[7] the equilibrium modulus of vulcanizates is proportional to the crosslink density, which we will assume is in turn proportional to the extent of reaction as measured by DSC. That is, $G_\infty \sim (p - p_{gel})$ where p_{gel} is the extent of reaction at the gel point. However, p_{gel} is vanishingly small due to the high molecular weight of the green rubber chains (~300k), such that $G_\infty \approx G_\infty^f\, p$ where G_∞^f is the equilibrium shear modulus of the fully-cured network. Now, we will also assume that new crosslinks are attached to the existing network in an unstrained state. This is not quite correct, in general, (see references 8 and 9 for a complete theory) but is quite adequate for the current problem. Therefore, the residual stresses at long times accumulate in the rubber according to the following equation

$$\underline{\underline{\sigma}}(t \to \infty) = \int_{-\infty}^{t} ds \frac{d\underline{\underline{\varepsilon}}}{dt}(s)\, G_\infty(s) \qquad (8)$$

We now turn to the change in the stress relaxation modulus with cure as seen in Figure 8. Examining Eq. 2, we could conceivably imbed this cure dependence in either the relaxation times, τ_i, or the mode weightings, G_i. To determine the appropriate path, let's consider the following thought experiment. A step strain is imposed initially on green rubber. Immediately following this, the rubber is magically fully cured. Our expectation is that the time dependence of the stress response will be indistinguishable from the response for step strain on a *fully-cured* rubber. However, the two choices presented above for describing the cure dependence lead to two distinct stress predictions. If we only use cure dependent weightings and constant relaxation times, we get

$$\sigma(t) = \gamma h(\gamma) \left[\sum G_i(0) e^{-t/\tau_i}\right] = \gamma h(\gamma)\, G(t, p=0) \qquad (9)$$

which is inconsistent with our expectation in that the predicted shape of the response mimics that of the green rubber rather than that of the cured rubber. If we use only cure dependent relaxation times and constant weightings, we get

$$\sigma(t) = \gamma h(\gamma) \left[\sum G_i \exp\left(-\int_0^t \frac{du}{\tau_i[p(u)]} \right) \right] \tag{10}$$
$$= \gamma h(\gamma) \left[\sum G_i \, e^{-t/\tau_i(p=1)} \right] = \gamma h(\gamma) \, G(t, p=1)$$

which is the anticipated result. Therefore, we conclude that the change in linear viscoelastic properties with cure (as seen in Figure 8) should be expressed as cure dependent relaxation times solely.

Now we need to determine how the relaxation times change with cure. Returning to theories of linear viscoelasticity,[2] we remember that the "relaxation spectrum", $H(\tau)$, is defined as

$$G(t) - G_\infty = \int_{-\infty}^{\infty} d\log\tau \; H(\tau) \; e^{-t/\tau} \tag{11}$$

Since we will be working with a discrete spectrum of relaxation times (a Prony series), Eq. 11 reduces to

$$G(t) - G_\infty = \sum_{i=0}^{N} H(\tau_i) \left[\log\tau_{i+1} - \log\tau_i \right] e^{-t/\tau_i} = \sum_{i=0}^{N} G_i e^{-t/\tau_i} \tag{12}$$

which defines G_i in terms of $H(\tau_i)$. We argued above that we needed to imbed all the cure dependence into the relaxation times and none in the weightings. In other words, the G_i's must not depend upon cure. However, from Eq. 11, $H(\tau)$ does depend upon cure since $G(t)$ changes with cure. This implies that the term, $[\log\tau_{i+1} - \log\tau_i]$, in Eq. 12 which defines the spacing between our discrete relaxation times, must exactly balance any changes in $H(\tau_i)$. While this may sound like a problem, it actually allows us to calculate the cure dependence of the relaxation times.

If we require $G_i(p_j)=G_i(p_{j+1})$, then from Eq. 12 we must satisfy the following equation for a change in cure from state p_j to p_{j+1}

$$\log \tau_{i+1}(p_{j+1}) = \log \tau_i (p_{j+1}) + \frac{H[\tau_i(p_j)]}{H[\tau_i(p_{j+1})]} \log \frac{\tau_{i+1}(p_j)}{\tau_i(p_j)} \quad (13)$$

which is simply a recursion formula for the new relaxation times given our knowledge of the green rubber (p=0) discrete relaxation times and the change in $H(\tau)$ with cure. The green rubber discrete spectrum is discretionary (whatever fits works!), and the theory of linear viscoelasticity[2] gives us simple algebraic approximations for $H(\tau)$. For example, $H(\tau)$ can be related to the stress relaxation modulus by

$$H(\tau) = -G(t)\left[\frac{d\log G(t)}{d\log t} - \left(\frac{d\log G(t)}{d\log t}\right)^2 - \frac{d^2 \log G(t)}{d(\log t)^2}\right]\Bigg|_{t=2\tau} \quad (14)$$

so that changes in $G(t)$ are translated into changes in $H(\tau)$.

We now have a complete formalism to describe the evolution of stress during the cure of carbon black-filled rubber.

$$\begin{gathered}
\underline{\underline{\sigma}} = \sum_{i=0}^{N} \underline{\underline{\sigma}}_i + \int_{-\infty}^{t} ds \frac{d\underline{\underline{\varepsilon}}}{dt}(s)\, G_\infty(s) \\
\frac{d\underline{\underline{\sigma}}_i}{dt} + \frac{\underline{\underline{\sigma}}_i}{a_T a_{p_i} \tau_i} = G_i\, g(D)\, \frac{d\underline{\underline{\varepsilon}}}{dt} \quad \text{with} \quad \frac{dD}{dt} + \frac{D}{a_T \lambda} = R \\
\text{if } D = \left| \underline{\underline{\varepsilon}} - \underline{\underline{\varepsilon}}_k \right| \text{ and } E = \frac{d\underline{\underline{\varepsilon}}}{dt} \bullet \frac{\left(\underline{\underline{\varepsilon}} - \underline{\underline{\varepsilon}}_k\right)}{\left|\underline{\underline{\varepsilon}} - \underline{\underline{\varepsilon}}_k\right|} > 0, \\
\text{then } R = E;\ \text{otherwise } R = 0 \\
\text{where} \quad \frac{d\underline{\underline{\varepsilon}}_k}{dt} + \frac{\underline{\underline{\varepsilon}}_k}{a_T \lambda} = \frac{\underline{\underline{\varepsilon}}}{a_T \lambda} \quad \text{and} \quad \log(a_T) = \frac{-C_1 (T - T_r)}{C_2 + T - T_r}
\end{gathered} \tag{15}$$

These equations with Eq. 13 and 14 fully characterize our system.

VI. DETERMINATION OF MATERIAL PROPERTIES

Let's now assume that the above approach will be adopted for modelling curing rubbers. We are now faced with the task of gathering the required parameters for the model on a series of new rubber compounds. It would behoove us to determine the minimal suite of experiments. As a first step, we will list the required parameters.

the WLF parameters: C_1, C_2, and T_r
the damping function parameters: $h(\gamma)$ or λ and $g(D)$
the linear viscoelastic parameters: G_i, $\tau_i(p)$

We first must characterize the linear viscoelasticity of the green rubber. The simplest approach is to employ cone-and-plate geometry (angle<10^o) and measure the oscillatory moduli at various temperatures at extremely small strains (<0.5%). As explained in Reference 1, it is important to anneal these samples carefully to erase the strain history of sample preparation and fixturing such that one obtains a true representation of the linear viscoelastic modulus. The WLF parameters (C_1, C_2, and T_r) can be determined from the superposition shifts and G(t) is directly related^2 to G' and G".

$$\text{for example,}\quad G(t) = G'(\omega) - 0.4G''(0.40\omega) + 0.014G''(10\omega)\big|_{\omega=1/\tau} \qquad (16)$$

The relaxation spectrum, $H(\tau)$, could be calculated from Eq. 14 or directly from G' or G". The relaxation time spacing for the green rubber is discretionary, so that, using Eq. 12, we can determine the corresponding G_i's for the green rubber.

While the rubber is between the cone-and-plate, we can characterize the nonlinearities in a series of straightforward tests, single step shear strains in which the strain magnitude is increased from the linear regime ($\sim 10^{-4}$) to processing strains of interest. It is imperative to anneal the sample between tests. The vertical shifts are identically the KBKZ damping function, $h(\gamma)$, and can be related to the differential damage function, $g(D)=h(D) + D\, dh/d\gamma$.

The damage model requires the additional parameter λ which describes the rate of damage healing. This requires examination of our sample at various intervals after damage has been created. At the completion of the final step shear strain test described above, we have created damage equal to the strain amplitude. If we leave the sample in the rheometer, we can monitor the damage healing by periodically measuring the apparent linear oscillatory moduli (which creates no additional damage), and, since damage heals slowly, the damage during each of these measurements will be constant. From Eq. 2, the ratio of the apparent linear G' at a time t after the original step strain test to the virgin linear G' (when there was no damage) equals g(D). Damage itself will healing as $D = \gamma(1-e^{-t/\lambda})$. We can use our measured KBKZ damping function to calculate g(D) for various values of λ and compare to our measured g(D).

$$g_{\mathrm{exptl}}(D) = \frac{G'_{\mathrm{linear}}(t)}{G'_{\mathrm{linear}}(0)} \tag{17}$$

$$g_{\mathrm{th}}(D) = h\left(\gamma[1-e^{-t/\lambda}]\right) + \gamma[1-e^{-t/\lambda}]\,\frac{dh}{d\gamma}\left(\gamma[1-e^{-t/\lambda}]\right)$$

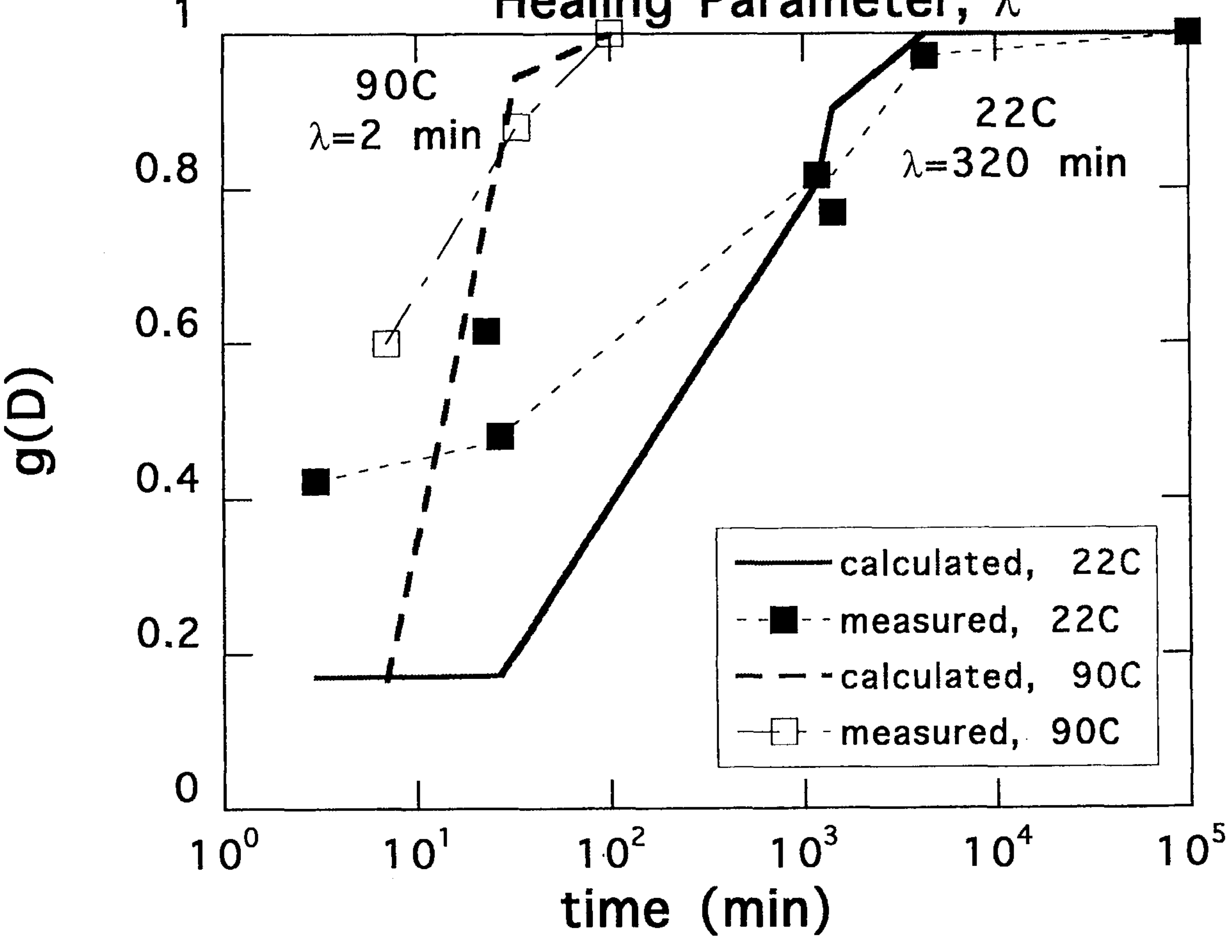
For comparison, the KBKZ formalism would predict that the reduction in G'_{linear} in these experiments arises from the fading memory of the step strain history rather than from "damage", and anneals with the only available spectrum of relaxation times, G(t).

$$\frac{G'_{\mathrm{linear}}(t)}{G'_{\mathrm{linear}}(0)} = 1 - \frac{G(t)}{G'_{\mathrm{linear}}(0)}[1-h(\gamma)] \tag{18}$$

Using Eq. 17, we can compare experimental data with theoretical predictions for green carbon black-filled rubber to determine the best value for λ. In Fig. 15, we see that λ=320 and 2 minutes fit the data at 22°C and 90°C respectively (this corresponds to the predicted WLF shift from 22 to 90°C). While it is encouraging that the fits are reasonable and that λ does follow the WLF prediction, both sets of data suggest that a spectrum of damage healing times (i.e. many λ_i's) would be more appropriate as predicted by a KBKZ formalism (Eq. 18).

We now require a knowledge of how the relaxation times depend upon cure. The simplest method for determining extent of reaction relies on differential scanning calorimetry, as discussed in Section IV. Frequency scans, as described in Section III, can then be run during cure at various temperatures to gather snapshots of linear viscoelasticity. Psuedo-time-temperature master curves at constant extent of reaction can be constructed by piecing iso-cure snapshots together from these scans at differing temperatures. Of course, the fully-cured rubber is amenable to a more conventional,

Fig. 15: Determination of Damage Healing Parameter, λ



rigorous investigation of G' and G" as undertaken for the green rubber and true time-temperature master curves can be constructed. From these data, we can construct $H(\tau)$ as cure progresses using Eq. 14, and can then determine the cure dependence of the discrete relaxation times using Eq. 13.

Finally, we need to determine the increase in equilibrium modulus with cure. As strange as its may sound, the calculated stresses for many problems will not depend strongly on the equilibrium modulus - that is, the rubber really doesn't know it is a solid. This apparent oxymoron is true due to the extremely slow relaxations in filled rubbers and the fact that the majority of cure will occur under no large applied deformations.

Consider the tire shaping process once again. The largest deformation by far occurs at the start when the rubber is unvulcanized. Here, the equilibrium modulus is rigorously unimportant. Only in the latter stages of filling when the temperature rises sharply and cure begins will the equilibrium modulus enter. However, since the incremental strains are small at this point and the relaxation times exceedingly long, the apparent modulus governing the stress evolution will not reflect the equilibrium modulus but rather some higher value associated with the relaxing rubber. For example, in Figure 4, the linear modulus has only decreased by a factor of two in 10^3 seconds. Since the decay slope is roughly -1/10, the modulus will have only decreased by a factor of three even in an additional 5 years (10^8 seconds). However, we must decay yet another decade to observe the underlying equilibrium modulus, so we see how unimportant the true solid-like behavior really is. Even the softening effect of the KBKZ formalism does not help since, from Figure 5, we see that a strain of 10% only decreases the modulus by an order of magnitude, which still leaves us far from the equilibrium modulus. The important role of cure is not to increase the equilibrium modulus but to change the relaxation spectrum which gives the appearance of "solid-like" behavior.

The true equilibrium modulus does become more important for less highly filled rubbers since they display less of the obscuring nonlinear viscoelastic character, and it may be possible to measure the underlying equilibrium modulus directly by oscillatory or step strain experiments at large strains and high temperatures. For the highly filled rubbers, extremely high strains will be required (e.g. 300% modulus).

VII. CONCLUSIONS

The equations presented here enable calculation of stresses in carbon black filled rubber through cure. We have tried to minimize the pain of implementing these equations by chosing differential versions of the constitutive model for computational efficiency and by presenting a minimal suite of experiments to characterize new materials.

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