

A Relaxation Model for Property Changes During the Cure Reaction of Filled and Unfilled Silicone Elastomers

H. S.-Y. HSICH, L. C. YANYO, and R. J. AMBROSE, *Lord Corporation, Mechanical Products Group, Material Process/Research and Development, Erie, Pennsylvania 16512*

Synopsis

A generalized kinetic model of cure, which is described by a distribution relaxation function, is used to predict physical and mechanical properties of silicone elastomers during isothermal and nonisothermal cure reactions. The model can also predict the effect of filler and cure behavior of filled elastomers. The structural relaxation times of the molecular state of uncured and cured elastomers is also discussed.

INTRODUCTION

It is well known that the properties of elastomeric and thermosetting materials depend on their cure history. Recently, Gillham and his colleagues¹⁻³ gave a detailed discussion on the structure/property changes of epoxy materials based on the cure history. Although the properties of curable materials are controlled by the condition of cure, in the molding operation, rarely is any model of cure used for controlling the properties and optimizing cure conditions. Instead rules of thumb are widely used in the industry for setting cure conditions. The difficulty in optimizing cure conditions may be due to the lack of an adequate model of cure kinetics to predict physical or mechanical properties during the cure cycle. Therefore, modelling cure kinetics is of practical importance both in molding process control and mechanical property optimization of elastomeric materials. Precise control of the dynamic mechanical properties is the key to good end-product performance, particularly for elastomers used as engineering materials.

Based on the need to control mechanical properties of engineering materials, we will propose and discuss a kinetic model of cure which can better predict physical or mechanical properties of elastomers with varied base polymer, curative, and filler system.

MODEL OF CURE KINETICS AND PROPERTY PREDICTION

The chemistry of cure reactions in elastomers has been discussed extensively by Bateman et al.,⁴ Morrell,⁵ and Coran.⁶ Cure reactions are quite complex and, in general, are multiple chemical reactions. Therefore, it would not be expected that a single first-order chemical reaction could explain cure kinetics during a complete cure cycle, particularly for elastomers with various curative and filler loadings. Although Roller,⁷ Graig,⁸

and Musatti and Macosko⁹ have given models to predict the viscosity or modulus during cure reactions, these models cannot predict the changes of properties of elastomers during a complete cure cycle. These models also do not include the effect of filler on cure for elastomers with various filler loadings.

In order to account for the effect of filler, a distribution relaxation function has been proposed by Hsich and co-workers,^{10,11} to explain the cure kinetics of isothermal and nonisothermal cure reactions. The model for predicting the physical or mechanical properties during an isothermal cure reaction can be written as:

$$P(t) = P_0 + (P_\infty - P_0) \{1 - \text{EXP}[-(t/\tau)^\beta]\} \quad (1)$$

where $P(t)$ is the physical or mechanical property at time t and P_0 and P_∞ are the minimum and final values of the property. β is a parameter which describes the width of the relaxation spectrum, and τ is the relaxation time which is a function of temperature T and activation energy H of cure. τ can be defined using an Arrhenius function:

$$\tau = \tau_0 \exp(H/RT) \quad (2)$$

where τ_0 is a constant which represents the relaxation time as temperature approaches infinity and R is the universal gas constant.

The values of the relaxation time τ and the width of the relaxation spectrum, β , will depend on what property is measured. That is, different physical or mechanical properties measured during a cure cycle may have different values of τ and β . If the property studied is the shear modulus or viscosity, then eq. (1) can be modified as:

$$G(t) = G_0 + (G_\infty - G_0) (1 - \exp\{-[(t - t_0)/\tau]^\beta\}) \quad (3)$$

or

$$\eta(t) = \eta_0 + (\eta_\infty - \eta_0) (1 - \exp\{-[(t - t_0)/\tau]^\beta\}) \quad (4)$$

where $G(t)$ and $\eta(t)$ are the shear modulus and viscosity, respectively, at cure time t . The subscripts 0 and ∞ denote the minimum and maximum values of the measured property during the cure cycle. The induction time t_0 is the heating time until the onset of cure.

Since nonisothermal cure is of practical importance, the cure model has been extended to include nonisothermal cure kinetics. The modification can be expressed as follows:

$$P(t) = P_e \exp\left[\frac{E}{RT(t)}\right] + \left[P_\infty - P_e \exp\left(\frac{E}{RT_c}\right)\right] \left\{1 - \exp\left[-\left(\int_{t_0}^{t_f} \frac{d(t - t_0)}{\tau}\right)^\beta\right]\right\} \quad (5)$$

and

$$T(t) = \int_0^t \frac{dT}{dt} dt + T(0) \quad (6)$$

where P_e represents the value of the property at temperatures approaching infinity. E is the activation energy of viscous flow and it is ascribed to intermolecular forces. T_c is the equilibrium or final cure temperature, and t_f is the final cure time. Under isothermal cure conditions, τ is a function of temperature only. However, under nonisothermal conditions, τ is a function of temperature which in turn is a function of time as shown in eq. (6). In eq. (5), $P_e \exp[E/RT(t)]$ describes the effect of temperature on the property of concern in the absence of cure. The remaining part of eq. (5) describes the effect of the curing reaction on the property. If the property being investigated is modulus or viscosity, then eq. (5) is modified as:

$$G(t) = G_e \exp\left[\frac{E}{RT(t)}\right] + \left[G_\infty - G_e \exp\left(\frac{E}{RT_c}\right)\right] \times \left\{ 1 - \exp\left[-\left(\int_{t_0}^{t_f} \frac{d(t-t_0)}{\tau}\right)^\beta\right] \right\} \quad (7)$$

or

$$\eta(t) = \eta_e \exp\left[\frac{E}{RT(t)}\right] + \left[\eta_\infty - \eta_e \exp\left(\frac{E}{RT_c}\right)\right] \times \left\{ 1 - \exp\left[-\left(\int_{t_0}^{t_f} \frac{d(t-t_0)}{\tau}\right)^\beta\right] \right\} \quad (8)$$

where $G(t)$ is the modulus and $\eta(t)$ is the viscosity at cure time t .

The above equations were used for studying the cure kinetics of natural rubber with sulfur type curatives at various carbon black filler loadings.^{10,11} The results of the study not only showed that the model can predict physical and mechanical properties of elastomers, but also can give physical insight into the effect of filler upon cure kinetics. The main conclusions from the natural rubber study were:

Carbon black filler in natural rubber tends to accelerate the cure reaction and, therefore, reduces scorch time and cure time (τ_0 and t_0 decrease with increasing filler loading).

The activation energy of viscous flow will be decreased by an increase in filler loading. This is not surprising, because the presence of filler tends to reduce the intermolecular forces between polymer chains, and, therefore, the flow behavior and mechanical properties of a polymer system become less temperature-dependent. On the other hand, filler loading has little effect on the activation energy of the cure reaction.

Increasing filler loading broadens the relaxation spectrum of the cure reaction. Broadening of the "structural" relaxation spectrum by filler has also been found in viscosity data of uncured rubber¹² and in dynamic mechanical properties of cured rubber.¹³

In this study, we have investigated the cure kinetics of silicone elastomers.

EXPERIMENTAL RESULTS AND DISCUSSION

Kinetic Considerations

The base polymer used in this study is silicone rubber gum cured with 0.3 phr (parts per hundred rubber) of *t*-butyl perbenzoate and 0.8 phr of *t*-butyl peroctoate. Samples were prepared with 0, 20, 40, and 60 phr of powdered silica filler.

Isothermal cure curves, at 110°C, 130°C, and 150°C, were measured on a Rheometrics Mechanical Spectrometer (RMS) operating at 3% strain and at an angular frequency of 1 rad/s. The results of dynamic storage shear modulus and complex viscosity data vs. cure time are shown in Figures 1-6.

The nonisothermal cure curves were also obtained from the RMS at the same frequency and strain with a preprogrammed heating rate of 12°C/min from room temperature to final cure temperature. However, due to the slow heat transfer common in rubber, the actual temperature rise in the polymer was monitored with a thermocouple probe, and this temper-

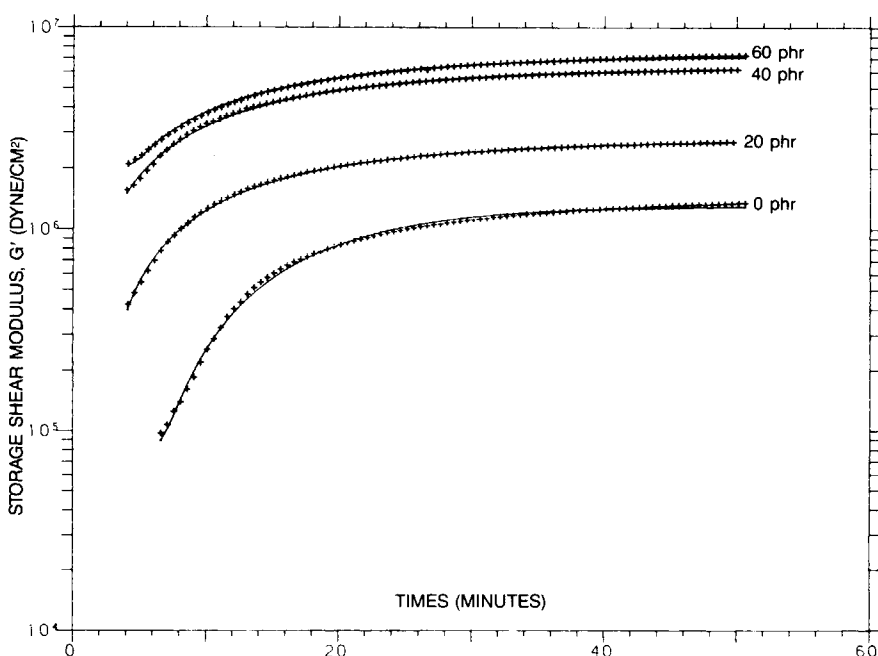


Fig. 1. Shear storage modulus vs. cure time at isothermal cure temperature of 110°C: (—) theoretical calculation; (+) experimental data.

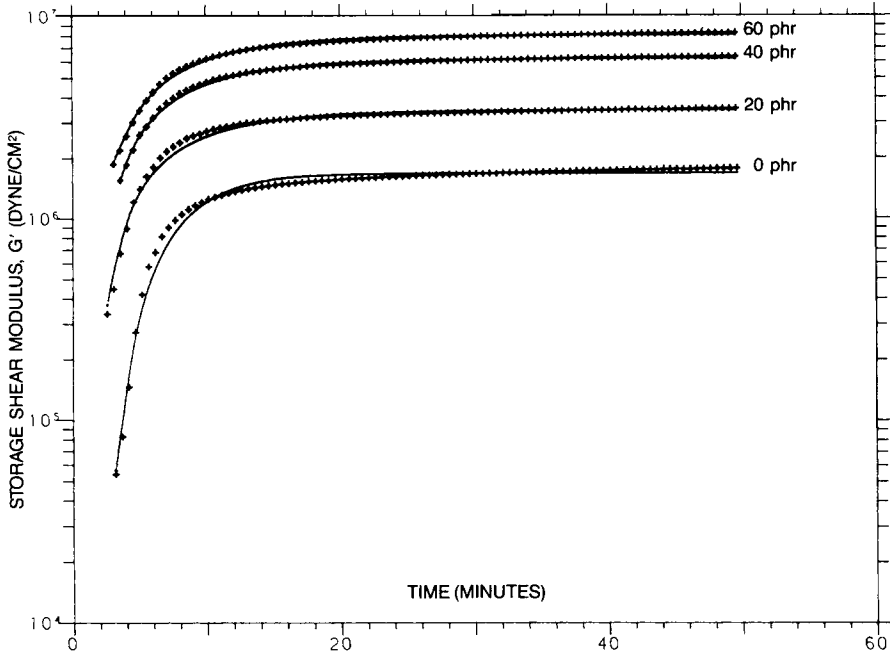


Fig. 2. Shear storage modulus vs. cure time at isothermal cure temperature of 130°C: (—) theoretical calculation; (+) experimental data.

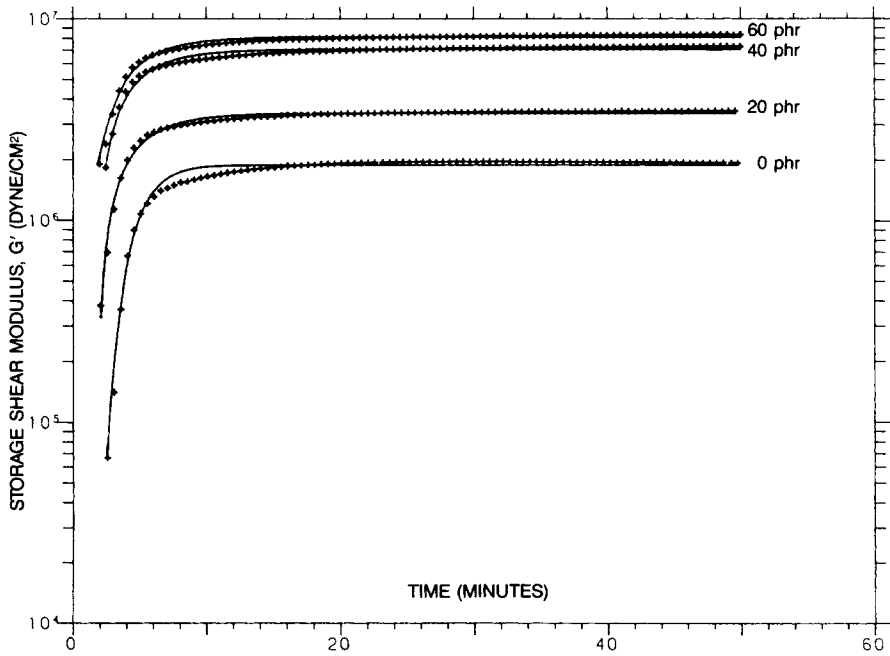


Fig. 3. Shear storage modulus vs. cure time at isothermal cure temperature of 150°C: (—) theoretical calculation; (+) experimental data.

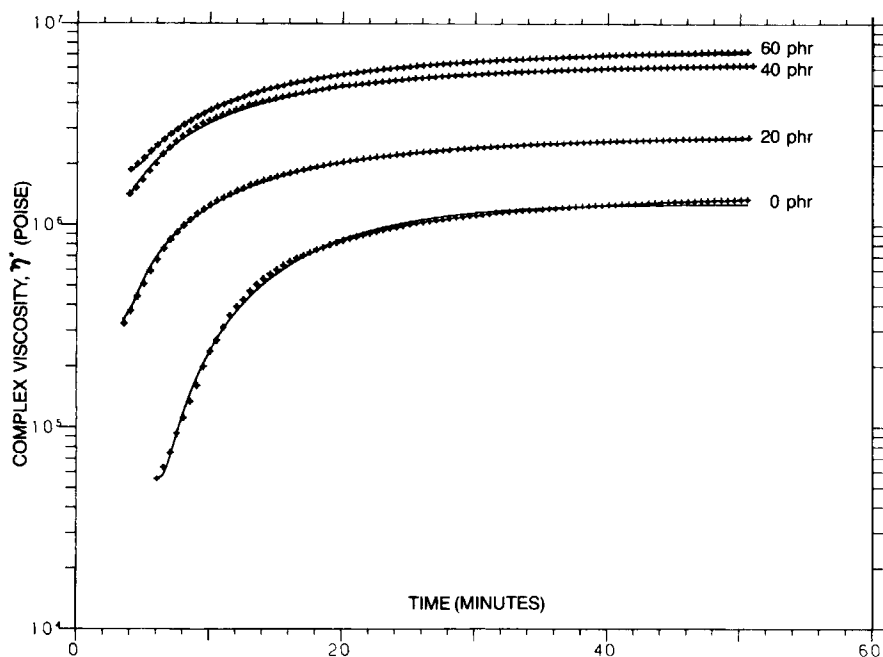


Fig. 4. Complex viscosity vs. cure time at isothermal cure temperature of 110°C: (—) theoretical calculation; (+) experimental data.

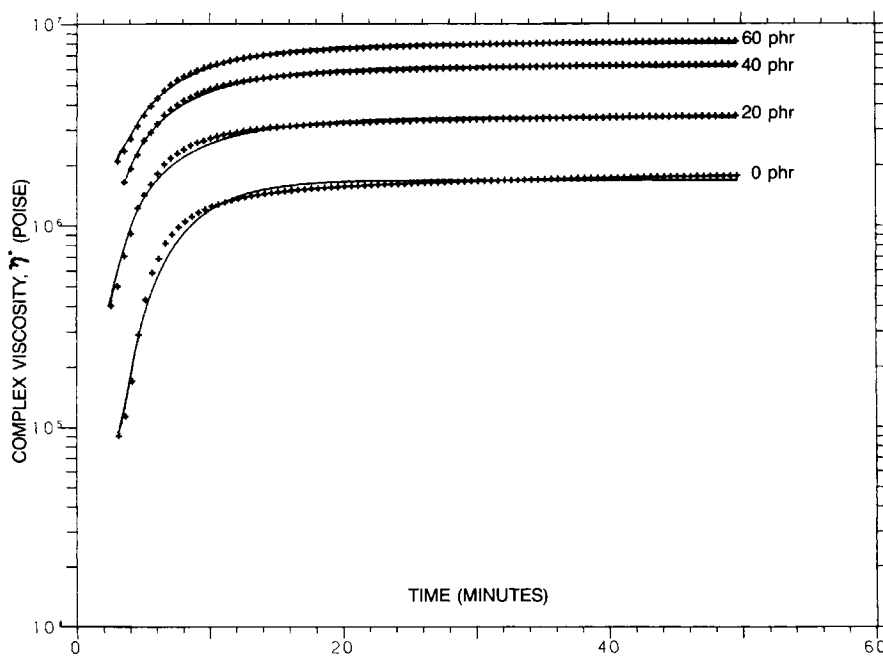


Fig. 5. Complex viscosity vs. cure time at isothermal cure temperature of 130°C: (—) theoretical calculation; (+) experimental data.

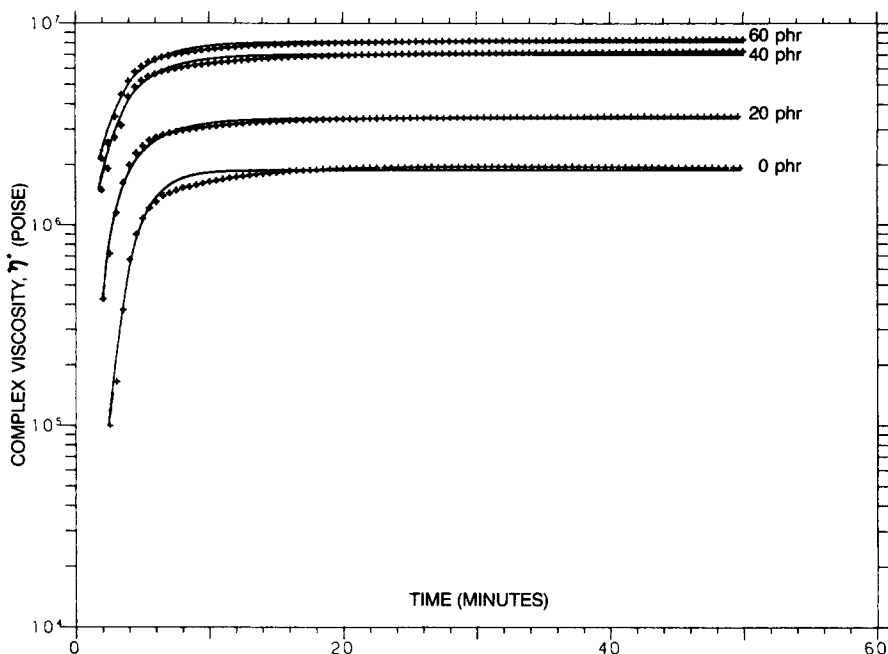


Fig. 6. Complex viscosity vs. cure time at isothermal cure temperature of 150°C: (—) theoretical calculation; (+) experimental data.

ature profile was used in calculations. The nonisothermal results of dynamic storage shear modulus and complex viscosity data versus cure time are shown in Figures 7–10.

The best fit of the theoretical data to the experimental points was determined using the reduced χ^2 criterion. Reduced χ^2 was minimized using a computerized nonlinear minimization technique based on the Davidon algorithm.^{14,15} For the isothermal cures, originally all five parameters (t_0 , τ , β , P_∞ , and P_0) in eq. (1) were adjusted to obtain the best fit values. From these results, the activation energy H , from values of τ , was determined to be approximately constant and equal to 12.7×10^3 cal/mol \cdot °K with $\tau_0 = 7.6 \times 10^{-7}$ min. Values for P_0 were chosen based on the minimum property values before the onset of cure, exhibited by the data. Ideally, the initial shear modulus or viscosity should be temperature-dependent, as will be discussed in the nonisothermal cure. However, for silicone rubber, the change in the property value over a 40°K temperature difference is small so a constant value for P_0 was assumed. The value of β was seen to be affected by the presence of filler and unaffected by cure temperature. Once the values for τ , P_0 , and β were set, computer minimization was used again to fit t_0 and P_∞ . The final values for the parameters, used in eqs. (3) and (4) to generate the plots in Figures 1–6, are listed in Tables IA and IB. The theoretical curves show excellent agreement with the experimental data.

From Tables IA and IB, it is seen that β changes initially upon addition of filler but is not affected by the amount of filler present. A change is expected because the presence of filler broadens the relaxation spectrum; however, this is different behavior than that of natural rubber. In natural

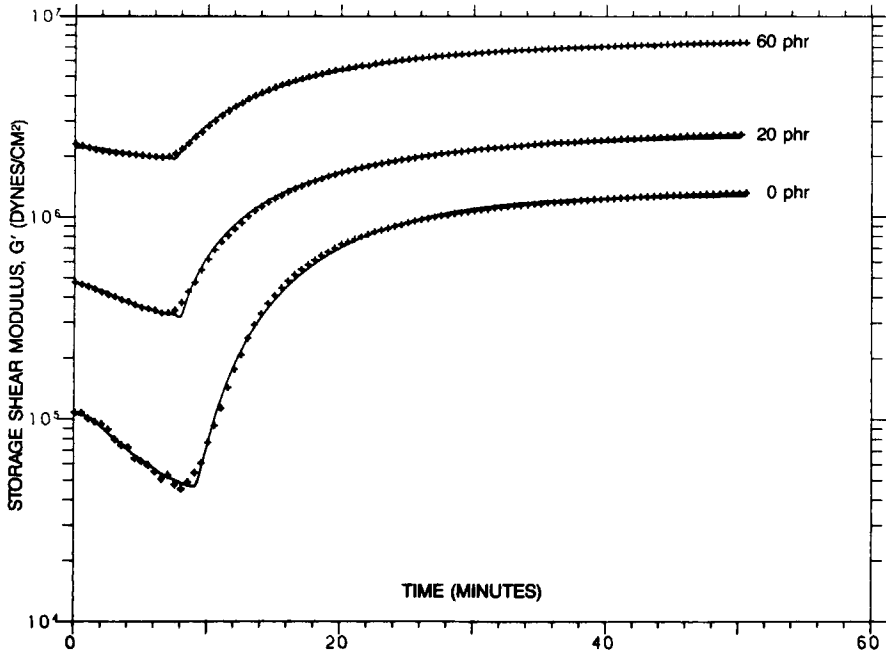


Fig. 7. Shear storage modulus vs. cure time for nonisothermal cure with final temperature of 110°C: (—) theoretical calculation; (+) experimental data.

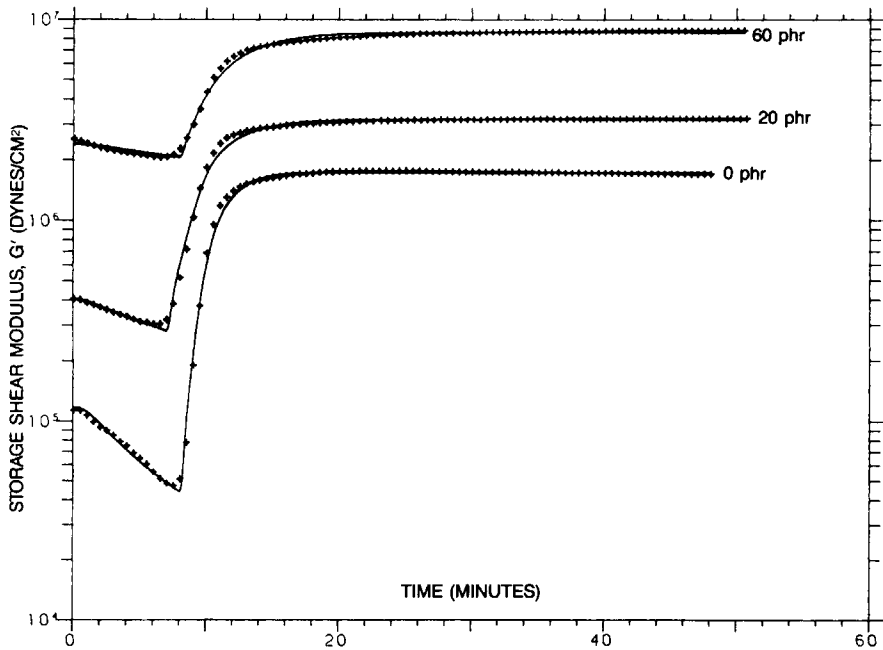


Fig. 8. Shear storage modulus vs. cure time for nonisothermal cure with final temperature of 150°C: (—) theoretical calculation; (+) experimental data.

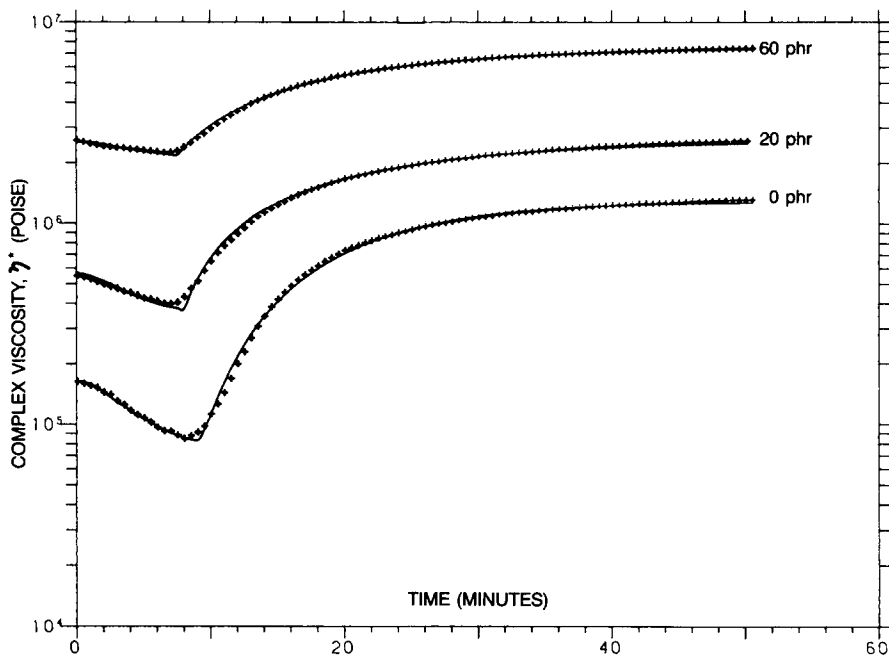


Fig. 9. Complex viscosity vs. cure time for nonisothermal cure with final temperature of 110°C: (—) theoretical calculation; (+) experimental data.

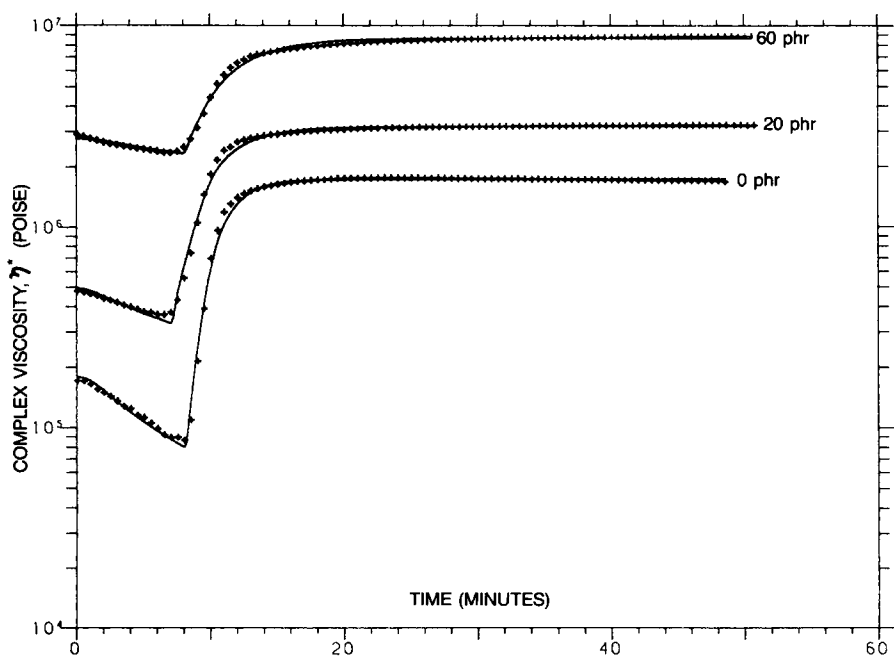


Fig. 10. Complex viscosity vs. cure time for nonisothermal cure with final temperature of 150°C: (—) theoretical calculation; (+) experimental data.

TABLE IA
 Shear Modulus Data for Isothermal Cures

Loading (phr)	Cure temp (°C)	t_0 (min)	β	G_∞ (dyn/cm ² × 10 ⁻⁶)	G_0 (dyn/cm ²)
0	110	6.41	1.42	1.29	5.4×10^4
	130	3.27		1.69	
	150	2.72		1.90	
20	110	3.79	1.00	2.80	3.1×10^5
	130	2.72		3.50	
	150	2.08		3.44	
40	110	3.99	1.00	6.42	1.4×10^6
	130	3.41		6.25	
	150	2.55		7.13	
60	110	4.32	1.00	7.39	1.8×10^6
	130	3.20		8.12	
	150	2.11		8.19	

rubber β decreased continually with the addition of carbon black filler. The value of β is also notable. When β equals unity, the distribution relaxation function reduces to a single relaxation function. Thus the cure reaction of silicone rubber behaves as a simple first-order chemical reaction.

Increasing amounts of filler increase the initial shear modulus or complex viscosity, G_0 or η_0 , as well as the final modulus or viscosity, G_∞ or η_∞ . This is expected since the modulus and viscosity of a mixture such as rubber are determined by the moduli or viscosities of the components in the mixture. The filler has a higher modulus than the base polymer; thus, increasing the proportion of filler increases the modulus of the rubber.^{12,13}

The induction time t_0 decreases with increasing cure temperature. That is, the higher the temperature of cure, the more quickly cure begins. Also the induction time is unaffected by the amount of filler. This is in contrast to natural rubber where increasing amounts of carbon black filler decreased the induction time.^{10,11} In natural rubber, carbon black accelerates the cure

 TABLE IB
 Complex Viscosity Data for Isothermal Cures

Loading (phr)	Cure temp (°C)	t_0 (min)	β	η_∞ (P × 10 ⁻⁶)	η_0 (P)
0	110	6.62	1.39	1.31	9.1×10^4
	130	3.30		1.70	
	150	2.74		1.91	
20	110	3.96	1.00	2.81	3.8×10^5
	130	2.74		3.50	
	150	2.17		3.46	
40	110	3.94	1.00	6.44	1.5×10^6
	130	3.40		6.27	
	150	2.14		7.11	
60	110	4.56	1.00	7.42	2.1×10^6
	130	3.27		8.13	
	150	2.13		8.21	

reaction and shortens the induction time. On the other hand, silicone filler has little effect on the cure rate.

For the nonisothermal cures, the values for β and H used were those found by the isothermal cures. After an initial fit of P_∞ , P_e , E , and t_0 , E was found to be affected by filler content while t_0 was little affected by filler. Equation (5) was then fitted again setting values for E and t_0 as above and adjusting P_∞ and P_e . The values of the parameters used in eqs. (7) and (8) to generate the curves in Figures 7–10 are listed in Tables IIA and IIB. The results show excellent agreement between the theoretical calculation and the experimental data.

The activation energy of viscous flow, E , decreases with increasing amounts of filler. The filler tends to reduce the intermolecular forces between polymer chains, and thus the flow behavior of the system becomes less temperature-dependent. The value of the activation energy for viscous flow for silicone rubber is also much less than that of natural rubber.

In contrast to the isothermal cures, the induction time depends less on the cure temperature because heat history determines the induction time. Since the temperature increase per unit time was used for all samples, all had the same heat history; hence all had cure onset at the same time.

Structural Considerations

During the cure of an elastomer, changes in molecular structure take place. The changes in structure lead to changes in the "structural" relaxation time τ_R . The structural relaxation time is the time it takes for molecules to recover their equilibrium state after an applied force is released. The "chemical" relaxation time τ , used in the model of cure kinetics, does not change with cure time. The chemical relaxation time describes how rapidly the reaction takes place and is proportional to the reciprocal of the rate constant for the reaction.

It should be noted that the shape of the structural relaxation spectrum depends on the temperature and frequency at which the relaxation spectrum is measured. At constant temperature, the relaxation time can be defined as the inverse of the angular frequency at the peak value of the imaginary component of the property measured. Conversely, at constant frequency, the structural relaxation time can be observed only at that temperature where the imaginary part of the modulus (or other measured property) peaks. These relaxation "peaks" can only occur when the experimental frequency and temperature are chosen in the correct range.^{16,17}

TABLE IIA
Shear Modulus Data for Nonisothermal Cures

Loading (phr)	Cure temp (°C)	G_∞ (dyn/cm ² × 10 ⁻⁶)	t_0 (min)	G_e (dyn/cm ²)	E (cal/mol)
0	110	1.29	9.5	1.99×10^3	2400
	150	1.75	8.5	2.17×10^3	
20	110	2.62	8.5	8.22×10^4	1050
	150	3.20	7.5	7.19×10^4	
60	110	7.67	8.0	1.18×10^6	385
	150	8.72	8.5	1.27×10^6	

TABLE IIB
Complex Viscosity Data for Nonisothermal Cures

Loading (phr)	Cure temp (°C)	η_{∞} ($P \times 10^{-6}$)	t_0 (min)	η_c (P)	E (cal/mol)
0	110	1.29	9.5	6.37×10^3	1960
	150	1.95	8.5	6.87×10^3	
20	110	2.63	8.5	8.25×10^4	1160
	150	3.21	7.5	7.29×10^4	
60	110	7.67	8.0	1.22×10^6	450
	150	8.73	8.5	1.33×10^6	

In an isothermal cure study, we measured properties such as modulus and viscosity at both constant temperature and frequency. These properties change throughout the cure cycle. Therefore, we can conclude that both the structural state of the polymer and the structural relaxation time change throughout the cure cycle. These changes in structural relaxation time during the cure cycle can be spotted as changes in the mechanical spectra measured at different frequencies, as shown in Figure 11. It can be seen that there are relaxation peaks or maxima, as indicated by arrows, for the G'' plots measured at two different frequencies. These peaks occur at 8 min and 10 min for the frequencies of 10 and 1 rad/s, respectively. There is no relaxation peak or maxima for the G'' data measured at 100 rad/s.

The structural relaxation time of the silicone molecules increases as the cure proceeds. We expect a relaxation peak or maxima when the reciprocal

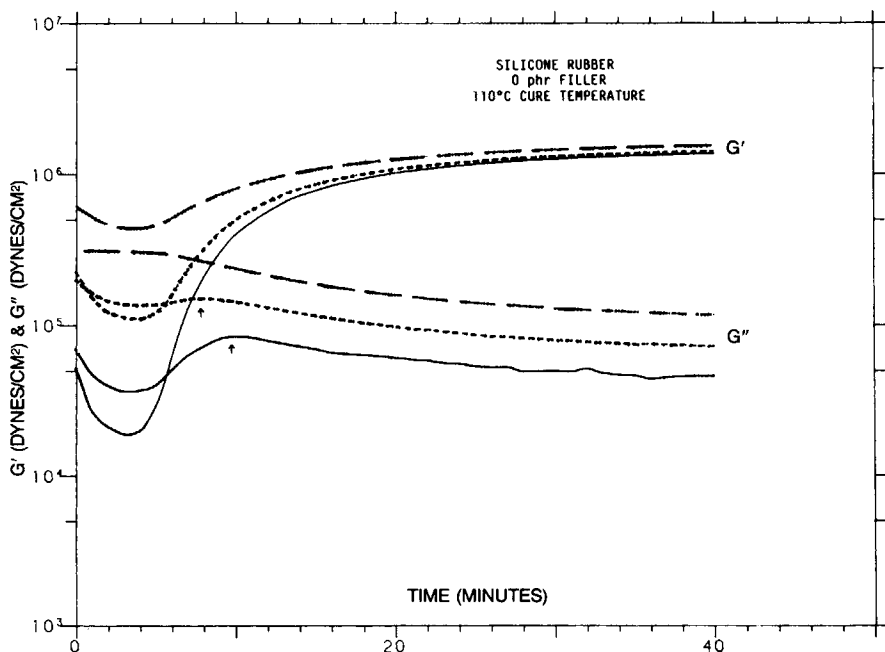


Fig. 11. Silicone rubber: shear moduli vs. cure time at various experimental frequencies: (—) 100 rad/s; (---) 10 rad/s; (· · ·) 1 rad/s.

of the experimental frequency is equal to the molecular structural relaxation time, i.e., when $\tau_R = 1/\omega_p$. From Figure 11, the structural relaxation time is 0.1 s at 8 min into the cure cycle measured at 10 rad/s and 110°C ($\tau_R = 1/10$). The relaxation time increases to 1 s at 10 min into the cure cycle measured at 1 rad/s and 110°C ($\tau_R = 1/1$).

Since there is no relaxation peak in the cure curve measured at 100 rad/s and 110°C, we conclude that the structural relaxation time of uncured silicone rubber at all levels of cure is greater than 0.01 s ($\tau_R = 1/100$).

We can compare these results with the results from a previous study on natural rubber.¹¹ The isothermal cure curves of natural rubber for three different frequencies, 10, 1, and 0.2 rad/s, at a cure temperature of 140°C were replotted from Ref. 11 and are shown in Figure 12. There is no relaxation peak at a frequency of 10 rad/s and 1 rad/s, but there is a relaxation peak at 0.2 rad/s frequency. Therefore, the structural relaxation time of the molecular state of uncured natural rubber is longer than 1 s but shorter than 5 s. In this study, the structural relaxation time of silicone rubber is shorter than 0.1 s and longer than 0.01 s. These findings are not surprising, since silicone rubber has a more flexible chain structure than that of natural rubber. It is expected that the structural relaxation time of the molecular state of uncured silicone rubber will be shorter than that of natural rubber.

CONCLUSIONS

A generalized kinetic model of cure has been developed from the aspect of relaxation phenomenon. The equations model the isothermal and non-isothermal cure curves of storage shear modulus and complex viscosity data

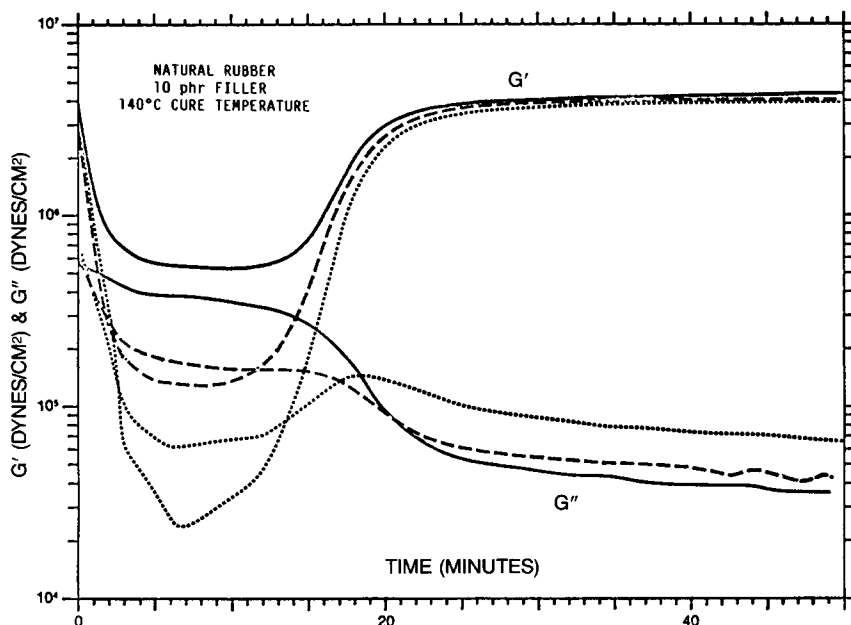


Fig. 12. Natural rubber: shear moduli vs. cure time at various experimental frequencies: (—) 10 rad/s; (---) 1 rad/s; (· · ·) 0.2 rad/s.

and also account for the effect of filler and cure temperature. The prediction of viscosity and modulus values during the cure cycle allows for preprogramming of cures to improve material processing and end-product performance. The conclusions of this study are as follows.

1. The activation energy of viscous flow is decreased by an increase in silica filler loading in silicone rubber. This is behavior similar to that found in carbon black filled natural rubber. Therefore, the viscosity and modulus of filled polymer systems are less temperature-dependent than unfilled polymer systems. On the other hand, filler loading has little effect on the activation energy of cure.

2. Silica filler in silicone rubber, like carbon black in natural rubber, increases the uncured and cured modulus and viscosity values of the rubber. Contrary to carbon black, increasing the silica loading does not accelerate the cure reaction.

3. The presence of filler broadens the relaxation spectrum. However, unlike natural rubber with carbon black, increasing amounts of filler do not further broaden the relaxation spectrum of silicone rubber. This may be due to a different polymer-filler interaction in silicone rubber.

4. The cure reaction of filled silicone rubber behaves as a simple first-order chemical reaction. That is, the distribution relaxation function reduces to a single relaxation function; $\beta = 1$.

5. During the cure reaction, the structural relaxation time of the polymer molecular state continues to increase until the cure reaction is completed. The structural relaxation time of uncured silicone rubber is longer than 0.01 s but shorter than 0.1 s. The structural relaxation time of uncured natural rubber is longer than 0.1 s. This finding is expected because silicone rubber molecules are more flexible than natural rubber.

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